WORKSHOP ON
PARENT-BODY AND NEBULAR MODIFICATION
OF CHONDRITIC MATERIALS

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M. E. Zolensky, A. N. Krot, and E. R. D. Scott

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Cover: Olivine with amorphous olivine rims in a primitive (?) clast in the Ningqiang chondrite.
View measures 1 μm across.

Preface

This volume contains abstracts that have been accepted for presentation at the Workshop on Parent-Body and Nebular Modification of Chondritic Materials, July 17–19, 1997, in Maui, Hawai'i. The workshop was organized by co-conveners M. E. Zolensky (*NASA Johnson Space Center*), A. N. Krot (*University of Hawai'i*), and E. R. D. Scott (*University of Hawai'i*). Members of the Scientific Organizing Committee were A. Bischoff (*Institut für Planetologie, Münster*), P. Cassen (*NASA Ames Research Center*), B. Fegley Jr. (*Washington University*), K. Keil (*University of Hawai'i*), J. Kerridge (*University of California–San Diego*), H. Nagahara (*University of Tokyo*), H. Palme (*Universität zu Köln*), S. Russell (*Smithsonian Institution*), and K. Tomeoka (*Kobe University*).

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Contents

Abstracts

THERMALLY METAMORPHOSED ANTARCTIC CM AND CI CARBONACEOUS CHONDRITES IN JAPANESE COLLECTIONS, AND TRANSFORMATION PROCESSES OF PHYLLOSILICATES.

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Since the first discovery of thermal metamorphism of CM and CI chondrites [1,2] a lot of interest has been focused on these materials and some data have been accumulated [1–10]. Thermal metamorphism is very characteristic of CM and CI chondrites, in contrast to non-Antarctic carbonaceous chondrites. In the metamorphism, phyllosilicates change to olivine, through some intermediate structures [4,5,7–9]. The cause of this metamorphism has also been variously estimated [11–14]. Some shock effect experiments have been carried out to ascertain this possibility [15]. However, the possibility of heating by shock events was considered less likely. Hiroi et al. [13,14] suggested possible thermal metamorphism in many of the C-, G-, B-, and F-type asteroids. They interpreted it as due to thermal metamorphism after extensive aqueous alteration in the parent body. The different degrees of thermal metamorphism may depend partly on the different water content and depth. More data are necessary to ascertain the validity of these scenarios or suggest others. The ratio of thermally metamorphosed carbonaceous chondrites/unheated carbonaceous chondrites may become the fundamental datum.

The objectives of this study are (1) Using as many Antarctic CM and CI carbonaceous chondrite specimens as possible, we want to obtain the ratio in Antarctic meteorites. In this study we searched for the mineralogical evidence of metamorphism in the constituent minerals. (2) We further describe constituent minerals by TEM. (3) Summarizing previous data also, the authors will describe the thermal transformation process of phyllosilicates.

The following 14 Antarctic carbonaceous chondrite specimens were examined (carbonaceous chondrites that have been examined

Fig. 1. (a) TEM lattice image of patchy structure in serpentine minerals found in Y 793595. (b) Corresponding ED pattern suggesting 14-Å diffraction maxima.

by the author are also included): CI1: Y 82162; CI2: Y 86720, B 7904; CM2: Y 74662, Y 791198, Y 793321, Y 793595, Y 82042, Y 82054, Y 82098, Y 86695, A 881334, A 881458, and A 881955.

These specimens can be grouped as follows, based on the degree of thermal metamorphism, although some have not been fully examined yet. Estimated temperatures are also shown for some specimens. Intensely metamorphosed specimens include Y 86720 (700°–850°C), Y 82162 (600°–800°C), B 7904 (750°–900°C), Y 82054, Y 82098, Y 86695, and A 881334. Weakly or very weakly metamorphosed

Fig. 2. Schematic transformation process of serpentine during thermal metamorphism.

specimens include Y 793321 (300°–500°C), Y 793595 (<250°C?), A 881458 (<250°C?), and Y 82042 (slightly to unmetamorphosed?). Unheated specimens include Y 74662, Y 791198, and A 881955.

These data indicate that thermally metamorphosed Antarctic CM and CI carbonaceous chondrites dominate compared to non-Antarctic chondrites. These characteristics correspond to the past flux of meteorite falls to the Earth. In this study, very weak metamorphism was suggested in several specimens (Y 793595, A 881458, etc.). More detailed examinations may be necessary in some cases to detect very weak metamorphism on other specimens that have been previously reported as unheated. Thus, degrees of metamorphism from very weak to intense are expected, assuming inner heating processes in the parent body.

Recent investigation of Y 793595 indicated that it contained polygonal serpentine, which is rarely found in terrestrial environments. The other characteristics of phyllosilicates and related layer-lattice minerals are similar to those in non-Antarctic carbonaceous chondrites: tochilinite, and regularly mixed layer minerals of tochilinite and serpentine structures, etc., were found for these unheated or very weakly metamorphosed CM2 specimens.

In Y 793595 and A 881458, which may have experienced very weak metamorphism, characteristic streaks with 14-Å diffraction maxima from patchy structures were associated with main 7-Å spots (Fig. 1). This may correspond to an initial stage of decomposition of 7-Å serpentine structure. Summarizing these data, the decompositional sequence (stages) of serpentine minerals during thermal metamorphism were estimated: Ordered 7-Å serpentine → patchy textures with broad 14-Å diffraction spots → decomposed intermediate transitional structure with halo diffraction → domain formation of olivine structure with broad olivine diffraction spots → ordered olivine structure (with or without void structures [16]). Sometimes two or more stages are contained in the same grains. These mineralogical processes can be schematically summarized (Fig. 2).

References: [1] Akai J. (1984) *9th Symp. Antarct. Meteorites,* 59–61. [2] Kojima H. et al. (1984) *Mem. Natl. Inst. Polar Res. Spec. Issue, 35,* 184–199. [3] Akai J. and Kanno J. (1986) *Mem. Natl. Inst. Polar Res. Spec. Issue, 41,* 259–275. [4] Akai J. (1988) *GCA, 52,* 1539–1599. [5] Akai J. (1990) *Proc. NIPR Symp. Antarct. Meteorites, 3,* 55–68. [6] Akai J. (1992) *Proc. NIPR Symp. Antarct. Meteorites, 5,* 120–135 [7] Tomeoka K. et al. (1989) *Proc. NIPR Symp. Antarct. Meteorites, 2,* 36–54. [8] Tomeoka K. et al. (1989) *Proc. NIPR Symp. Antarct. Meteorites, 2,* 55–74. [9] Zolensky M. E. et al. (1989) *14th Symp. Antarct. Meteorites; Natl. Inst. Polar Res.,* 24–26. [10] Ikeda Y. (1991) *Proc. NIPR Symp. Antarct. Meteorites, 4,* 187–225. [11] Miyamoto M. (1991) *Meteoritics, 26,* 111–115. [12] Kimura M. and Ikeda Y. (1992) *Proc. NIPR Symp. Antarct. Meteorites, 5,* 74–119. [13] Hiroi (1993) *Science, 261,* 1016. [14] Hiroi (1996) *LPS XXVII,* 611. [15] Akai J. and Sekine T. (1994) *Proc. NIPR Symp. Antarct. Meteorites, 7,* 101–109. [16] Akai J. (1994) *Proc. NIPR Symp. Antarct. Meteorites, 7,* 94–100.

AQUEOUS ALTERATION OF CARBONACEOUS CHONDRITES: EVIDENCE FOR PREACCRETIONARY ALTERATION.

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Carbonaceous chondrites are very complex rocks that carry important information about processes in the early solar system, including nebular and parent-body processes. The study of minerals altered and formed by aqueous processes before accretion or within the meteorite parent body(ies) is of fundamental importance considering various aspects in the evolution of solid matter in the early solar system. Below, evidence for preaccretionary aqueous alteration of carbonaceous chondrites will be discussed in detail.

The following remarks have to be made in advance:

1. Concerning the topic of this contribution two very important questions have to be considered: When do nebular processes end and planetary (parent-body) processes start? Should we use the term "nebular" or "preaccretionary" to characterize processes that happend before accretion of the final (CI, CM, CR, etc.) parent body? Here, the term "preaccretionary" will be used, because this term would allow processes that occurred in small precursor planetesimals (see below; [1,2]).

2. This abstract will summarize evidence for preaccretionary aqueous alteration. Describing and discussing preaccretionary features resulting from aqueous alteration does not mean that the author rules out any kind of aqueous alteration on the meteorite parent bodies as an important process in the evolution of several groups of carbonaceous chondrites. Many aqueous alteration features in CM and (perhaps all) in CI chondrites certainly result from parent-body processes [e.g., 3–8].

Observations in C Chondrites: In CI chondrites no indications for preaccretionary aqueous alteration are found. Any preaccretionary signature has been erased by (1) severe aqueous alteration processes certainly due to the presence of liquid water (e.g., early formation of carbonate veins [7,9]) and (2) impact brecciation (individual clasts usually <1 mm (e.g., [7]).

For CM chondrites the situation is quite different. Clear evidence for both parent-body and preaccretionary alteration exists. Lee [6] describes a calcium sulfate vein that certainly results from aqueous activities on the meteorite parent body. Hanowski and Brearley [8] discuss the parent-body alteration of large metal inclusions. Also, Metzler et al. [1] do not exclude parent-body processes to explain certain mineral associations as a result of aqueous alteration of the meteorite parent body. To explain the occurrence of phyllosilicates parent-body alteration processes have been widely proposed (e.g., [4,10–13]. Clear evidence for preaccretionary (nebular) aqueous alteration is given [1]. To date, no convincing arguments have been made to explain (besides other observations) the mineral paragenses shown in Figs. 20 and 21 of [1] as a result of parent-body processes. Preaccretionary aqueous alteration has also been proposed [2,14–16].

CR and CH chondrites contain hydrous phases within various components (e.g., matrix, accretionary rims, chondrules, dark inclusions [e.g., 17–20]). Weisberg et al. [20] provide convincing arguments in favor of a prelithification hydration in these and related chondrites. Based on chemically different types of phyllosilicates in adjacent, but different, components of the CR chondrite Y 8449 Ichiwaka and Ikeda [21] suggest nebular formation of chondrule phyllosilicates prior to the formation of the parent body.

For the CO and CV chondrites the situation is less clear. Only very few occurrences of hydrous minerals have been reported in CO chondrites [e.g., 22,23]. Keller and Buseck [23] found micas in Ca,Al-rich inclusions and ameboid olivine aggregates in Allende and Kaba (CV chondrites). For the formation of these hydrous phases preaccretionary (nebular) processes were proposed [23,24].

Discussion: The importance of phases altered and formed due to the presence of water in the nebula or/and within meteorite parent

bodies for the evolution of early solar system materials has been summarized by Kerridge et al. [25]. These authors state that evidence either for nebular or planetary aqueous alteration processes would have fundamental implications for ideas concerning nebular dynamics, gas-solid interactions in the nebula, and accretionary processes.

Considering various phases and paragenesis in carbonaceous chondrites affected by aqueous alteration, it is in many cases difficult to distinguish between nebular and parent-body effects. However, based on mineralogical evidence [1] and Tomeoka et al. [2] provide clear evidence that phyllosilicates in rims formed prior to the formation of the parent body. Due to the paragenesis in the rims and sizes of the rims, a parent-body origin can be ruled out (compare, e.g., Figs. 10c and 11 of [1] and discussions of [1,2]). Also, based on chemical studies, evidence has been found that certain phyllosilicates probably formed in the nebula [15]. Schirmeyer et al. [15] found that phyllosilicates within several Ca,Al-rich inclusions of CM chondrites contain Li, whereas mineralogically very similar phyllosilicates in the accretionary rims of the CAI (10 μm apart from the Li-bearing grains) do not. A nebular origin for certain phyllosilicates in CAIs is supported by the finding of hydrous phases within CAIs of CV chondrites [23,24]. On the other hand, some observations such as the formation of calcite [25] are difficult to explain by nebular gas-solid interactions.

Certainly, parent-body aqueous alteration of CM and CI chondrites exists. The degree of parent-body alteration varies among the chondrites. It is also certain that some aqueous alteration took place before accretion of the final CM parent body(ies). It may, however, be difficult to explain all observations by gas-solid reactions in the nebula (e.g., calcite formation). Therefore, an alternative model should certainly be considered. If aqueous alteration occurred in relatively small and uncompacted precursor planetesimals that were subsequently destroyed and dispersed by collisions prior to the accretion of the dust mantles and the meteorite parent body(ies), most, if not all, of the observations discussed above can convincingly be explained (compare [1]).

In summary, preaccretionary aqueous alteration is a fundamental process in the evolution of primitive chondritic materials. The formational history of CM (and probably other C) chondrites is certainly more complex than thought a decade ago. Figures 20 and 21 of [1] provide clear evidence for preaccretionary aqueous alteration. Everyone who opposes the model of preaccretionary aqueous alteration should first convincingly explain the features within these figures; this will be very difficult.

References: [1] Metzler K. et al. (1992) *GCA, 56,* 2873. [2] Tomeoka K. et al. (1991) *16th Symp. Antarct. Meteorites,* 37. [3] Kerridge J. F. and Bunch T. E. (1979) in *Asteroids* (T. Gehrels, ed.), p. 745, Univ. of Arizona, Tucson. [4] Tomeoka K. and Buseck P. R. (1988) *GCA, 52,* 1627. [5] Grimm R. E. and McSween H. Y. Jr. (1989) *Icarus, 82,* 244. [6] Lee M. R. (1993) *Meteoritics, 28,* 53. [7] Endress M. and Bischoff A. (1996) *GCA, 60,* 489. [8] Hanowski N. P. and Brearley A. J. (1997) *LPS XXVIII,* 503. [9] Endress M. et al. (1996) *Nature, 379,* 701. [10] Bunch T. E. and Chang S. (1980) *GCA, 44,* 1543. [11] Brearley A. J. and Geiger T. (1993) *Meteoritics, 28,* 328. [12] Browning L. B. et al. (1995) *LPS XXVI,* 182. [13] Browning L. B. and Keil K. (1997) *LPS XXVIII,* 163. [14] Nakamura T. et al. (1991) *16th Symp. Antarct. Meteorites,* 40. [15] Schirmeyer S. et al. (1997) *LPS XXVIII,* 1253. [16] Ikeda Y. and Prinz M. (1993) *GCA, 57,* 439. [17] Bischoff A. et al. (1993) *GCA, 57,* 1587. [18] Bischoff A. et al. (1993) *GCA, 57,* 2631. [19] Endress M. et al. (1994) *Meteoritics, 29,* 26. [20] Weisberg M. K. et al. (1995) *Proc. NIPR Symp. Antarct. Meteorites, 8,* 11. [21] Ichikawa O. and Ikeda Y. (1995) *Proc. NIPR Symp. Antarct. Meteorites, 8,* 63. [22] Brearley A. J. (1993) *GCA, 57,* 1521. [23] Keller L. P. and Buseck P. R. (1990) *LPS XXI,* 619. [24] Hashimoto A. and Grossman L. (1987) *GCA, 51,* 1685. [25] Kerridge J. F. et al. (1994) *Meteoritics, 29,* 481.

MAGNETITE IN VIGARANO: AN IRON-57 MÖSSBAUER SPECTROSCOPY STUDY.

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Introduction: CV chondrites are subdivided into two main subgroups based on their apparent state of oxidation. The distinction between "oxidized" and "reduced" meteorites is defined petrographically in the relative proportions of metal vs. magnetite (determined by point counting) and in the Ni content of sulfides [1]. While this approach has been of use in interpreting aspects of the evolution of the CV chondrites, point counting has a serious limitation as a quantitative tool for deriving modal analyses, particularly in meteorites with a large volume of matrix: the resolving power of the microscope. Although Mössbauer spectroscopy only detects Fe-containing phases, it has the significant advantage of detecting any Fe nuclei bound in a lattice. The intensity of an individual absorption in a Mössbauer spectra is directly related to the proportion of the total Fe at that site in a lattice (and often the proportion of the total Fe in an individual phase). Thus, given an accurate determination of weight percent Fe [e.g., 2] in the sample, a Mössbauer analysis may be recalculated to give weight percent of Fe-containing phases. Given the density of the meteorite, and relevant mineral phases, we can convert weight percent values to an approximate volume percent.

In this study we compare Mössbauer spectra of Vigarano, recorded before and after a hydrous heating experiment, to constrain the abundance of Fe-containing phases in the sample and to observe how phases respond to (artificial) "aqueous alteration."

Methodology: Hydrous heating of Vigarano was accomplished by loading 1.8 g of the powdered meteorite into a stainless steel insert (T316, 1-ml i.v.) with 0.4 ml high-purity degassed water (water/rock ratio = 0.22). The insert was purged with N_2 gas and placed in a high-pressure reactor (4740, Parr Inst. Co; 71-ml i.v.) with 20 ml water to minimize pressure differentials across the insert wall. This arrangement was then heated to 320°C for 72 hr. Before and after heating the sample was analyzed by Mössbauer spectroscopy. Spectra were recorded at 298 K with a microprocessor-controlled Mössbauer spectrometer using a [57]Co/Rh source. Drive velocity was calibrated with the same source and a metallic Fe foil. Spectra were fitted with a constrained nonlinear least-squares fitting program of Lorentzian functions.

While it's unlikely that these heating conditions reproduce aqueous alteration on the parent body, the mineral transformations produced may bear some relation to those produced by natural aqueous events.

Results and Discussion: Mössbauer spectrum recorded before hydrous heating of Vigarano is shown in Fig. 1. The percentage area of the spectra [before (A) and after heating (B)] assigned to olivine, pyroxene, troilite, magnetite (fitted to two sextets), and paramagnetic Fe^{3+} is shown in the table. Also shown are the data from both spectra recalculated for weight percent based on a total Fe content for the bulk meteorite of 24.71 wt% [2]. Volume percent is calculated based on specific gravity of minerals (see Table 1), and a density for Vigarano of 3.0. Doublets associated with olivine and pyroxene are treated as a single absorption for the purposes of this paper, as peaks are not well separated. The Mössbauer parameters of the paramagnetic Fe^{3+} absorption (isomer shift 0.47, quadrupole splitting 0.66) are typical of a number of oxides and oxyhydroxides (e.g., ferrihydrite, small-particle goethite, lepidocrocite). Low-temperature work would be required to unambiguously resolve this phase.

Iron-57 Mössbauer spectra of magnetite typically show two sextets (six-line absorptions) at 298 K: one (at approximately 49T) arising from Fe^{3+} in tetrahedral "A" sites in the spinel structure, the other (at 45–46T) from mixed Fe^{2+}/Fe^{3+} in octahedral "B" sites. Because of electron hopping, the latter Fe^{2+}/Fe^{3+} gives an averaged subspectrum. "B" sites contain equal numbers of Fe^{2+} and Fe^{3+} ions, so ideally we expect a 2:1 ratio in the spectral area of the 45T sextet to the 49T sextet. Although Mössbauer spectroscopy is not always a

precise tool for mineral identification, no other common oxide or oxyhydroxide shows a sextet absorption at 45–46T at 298 K. The association of a smaller sextet at 49T allows us to be reasonably confident in our assignment. Thus, in our 298 K spectra of Vigarano, we assign the two broad sextets (45.8T and 49.1T; ratio 2.1:1) to magnetite.

What is apparent from our analysis is that we find substantially more magnetite in Vigarano than has previously been reported (2.5 vol% compared to 0.3 vol% in the earlier study of McSween [1]). One possible explanation for this discrepancy is that much of the magnetite in this meteorite exists as a fine-grained matrix phase. In a detailed study of the Vigarano matrix, Lee et al. [3] found interstitial to matrix silicates, spinels, Fe-sulfides, and Fe-Ni alloys, areas ≤2 µm^2 in size filled by intergrowths of a finely crystalline fibrous material. These authors used selected-area electron diffraction to identify this material as ferrihydrite; however, as noted by [3] and [4], d spacings for ferrihydrite and magnetite are very similar. We propose that much of this interstitial matrix phase is actually magnetite. If the paramagnetic Fe^{3+} phase that we identify in our first Mössbauer spectrum is ferrihydrite, this would indicate a similar amount of ferrihydrite to magnetite in the matrix.

In our second spectrum, recorded after hydrous heating of Vigarano, we observe an increase in the relative proportion of mag-

TABLE 1.

	D	Spec. (A)	wt% (A)	vol% (A)	Spec. (B)	wt% (B)	vol% (B)
Olivine (Fa)	4.39	34.6	8.5	5.8	30.9	7.6	5.2
Pyroxene (Fs)	3.96	22.5	5.6	4.2	25.2	6.2	4.7
Troilite	4.65	12.1	3.0	1.9	8.7	2.1	1.4
Magnetite ("A" site)	5.18	5.6	4.3	2.5	9.6	6.4	3.7
Magnetite ("B" site)	*	11.7	*	*	16.3	*	*
Para. Fe^{3+} (ferrihydrite)	~3.3	13.6	3.4	3.1	9.3	2.3	2.1

* Spectral areas for both magnetite sites are given. To derive weight percent and volume percent we sum these values.
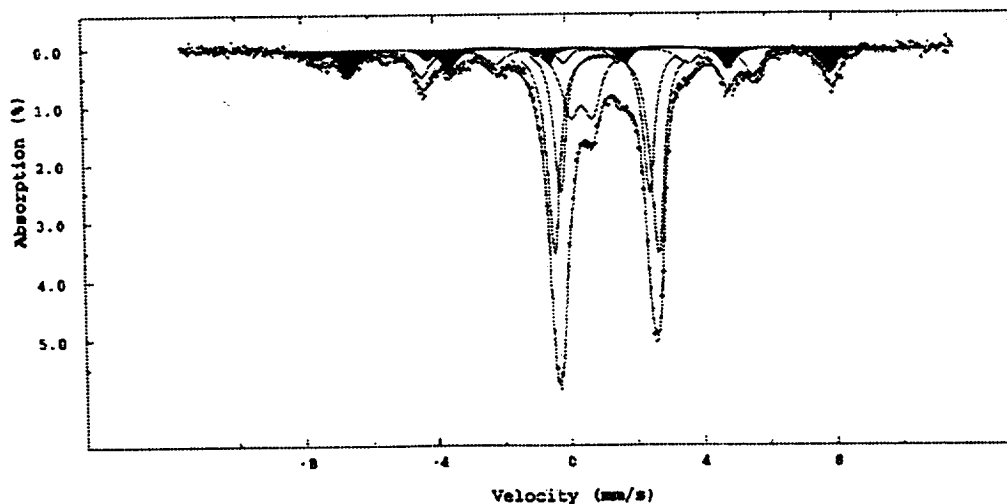
Fig. 1.

netite, predominantly at the expense of troilite and the paramagnetic Fe^{3+} phase (the combined spectral area of Fe-Mg silicates remains essentially unchanged). If ferrihydrite is being transformed to magnetite, it may indicate that magnetite in Vigarano is the product of a relatively-high-temperature aqueous event (our experiment was at 320°C, compared to estimates of <150°C for an aqueous alteration event that produced ferrihydrite and smectite in the matrix of Vigarano [3]).

Conclusions: Our work indicates that Vigarano contains 2.5 vol% magnetite, possibly as a fine-grained matrix phase. This finding raises questions as to the genetic significance of a distinction between "oxidized" and "reduced" CV chondrites, as the overall abundance of magnetite we observe in Vigarano is similar to that quoted for "oxidized" CVs. If indeed magnetite exists in two distinct morphologies in these meteorites (large grain size in oxidized CVs, small grain size in reduced), it may be this morphological difference that is significant, rather than abundance, i.e., different processes have formed magnetite in oxidized and reduced CVs. A magnetite-producing reaction (in addition to simple aqueous alteration) is "sulfurization." At 800°C olivine reacts with S to produce troilite, magnetite, and enstatite [5]. We note that in oxidized-group meteorites magnetite, and pentlandite are finely intergrown [1]. Perhaps this textural relationship is evidence of a similar, though lower-temperature, "sulfurization" reaction.

References: [1] McSween H. Y. Jr. (1977) *GCA, 41,* 1777–1790. [2] Mason B. (1963) *Space Sci. Rev., 1,* 621–646. [3] Lee M. R. et al. (1996) *Meteoritics & Planet. Sci., 31,* 477–483. [4] Barber D. J. and Hutchison R. (1991) *Meteoritics, 26,* 83–95.

[5] Kullerud G. and Yoder H. S. Jr. (1963) *Carnegie Inst. Wash. Yearb.,* 215–218.

METAMORPHIC TRANSFORMATIONS OF OPAQUE MINERALS IN CHONDRITES.

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Introduction: Transformations in silicate phases define the major petrographic divisions of chondrites [1,2]. The corresponding transformations of opaque phases throughout the metamorphic sequence have been comparatively little studied [e.g., 3] and Perron et al. [4] showed that some textural changes took place from type 3 to type 6. We here attempt to systematically describe the changes undergone by opaque minerals, and establish a metamorphic scale parallel to that based on silicates. We hope to derive (1) a better understanding of the state of opaque minerals at peak temperatures in order to better constrain cooling rate estimations and (2) an adequate way of comparing experimental metamorphic analogs with metamorphosed chondrites (since measured/estimated temperatures are insufficient due to the timescale differences involved). We have chosen to limit ourselves here to the main textural transformations, though behavior of Ni, Co, and trace elements [5] is also relevant.

Method: We have studied the textural appearance and relationship of metal and sulfides in a series of sections of ordinary chon-
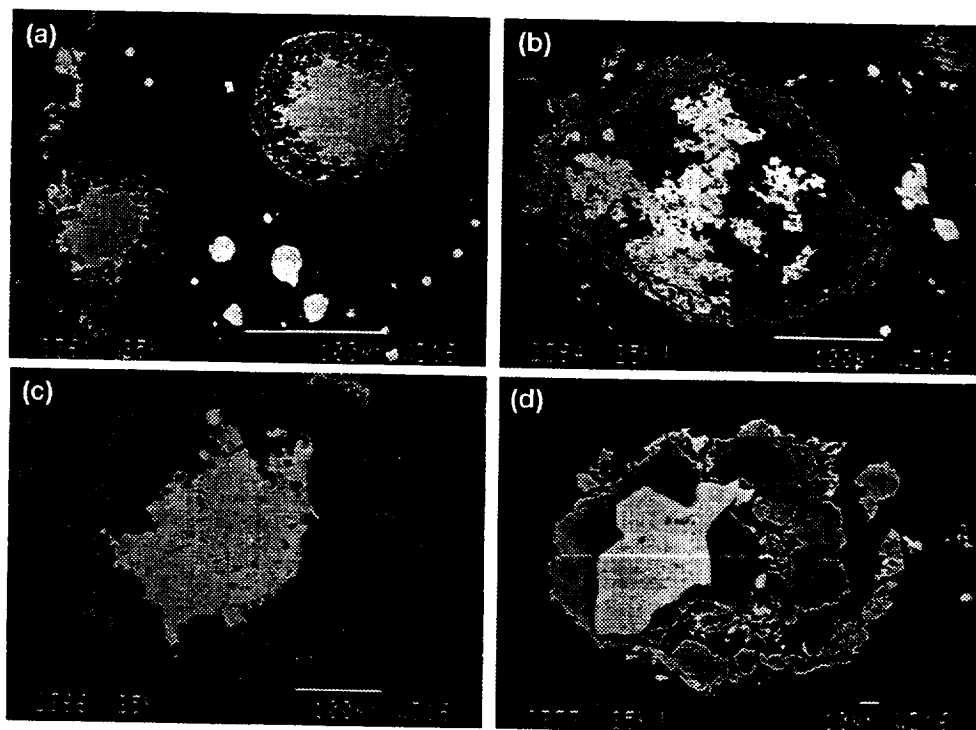
Fig. 1. BSE images of "metallic chondrules" in (a) Semarkona (LL3.0), (b) Bishunpur (LL3.1), (c) St. Mary's County (LL3.3), and (d) Chainpur (LL3.4).
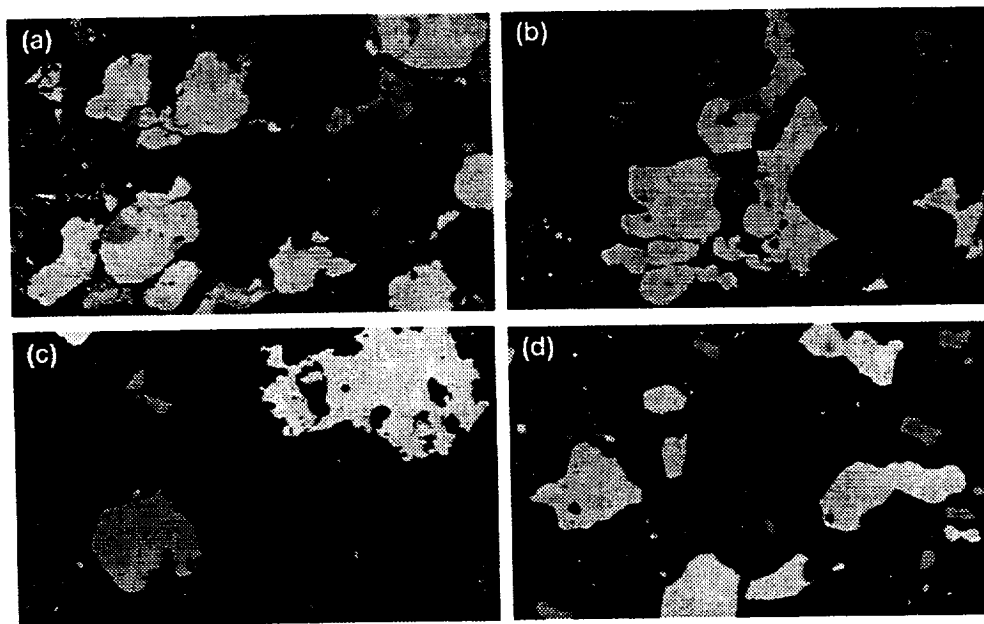
Fig. 2.   Reflected light views of **(a)** Dhajala (H3.8), **(b)** Forest-Vale (H4), **(c)** Richardton (H5), and **(d)** Estacado (H6). Field of view is 1.05 × 0.69 mm.

drites of various petrographic types. Because of the lack of H chondrites of the lowest petrographic types and of the superimposition of brecciation effects in most LLs of the highest ones, we have chosen to break our series into two overlapping parts: metamorphic effects in type 3 chondrites have been studied in L/LL chondrites of types ranging from 3.0 to 4, whereas the effects from 3.4 to 6 have been studied in H chondrites.

Results: Our results for the two metamorphic series are displayed in Figs. 1 and 2 respectively. The detailed study of opaque mineral distribution in 3.0 Semarkona indicates that, except for a few selected locations, metal and sulfide phases are constantly and intimately associated, a likely result of nebular corrosion effects of H_2S gas on kamacite partly before but mostly after chondrule formation [6]. Apart from the fine-grained matrix and a few tetrataenite grains also found in the matrix, metal grains with no associated sulfides are only found inside type I (FeO-poor) chondrules. On the other hand, sulfide grains with no metal are restricted to the interior of type II (FeO-rich) chondrules and a few isolated sulfide grains in the matrix. Figure 1a shows that the metal/sulfide contact is very highly contorted in such a material. This spatial relationship of metal and sulfide is gradually changed by metamorphism. We identify three main steps: (1) Up to 3.5 (Figs. 1b–d), metal and sulfides stay closely associated but their contact progressively changes from contorted to straight. Metal grains have a round shape both inside and outside chondrules. Sulfide appears in increasing quantities associated with the metal beads inside chondrules. (2) From 3.5 to 4 (Figs. 2a–b) metal and sulfide start separating from one another and sulfide grains tend to connect together (this effect becomes more obvious by 3.7). Opaque grains inside chondrules lose their round shape to become more angular. The first zoned taenite grains appear and metal grains start coalescing [4,7] by 3.8 (Fig. 2a). (3) From 4 to 5 (Figs. 2c–d), the separation of metal and sulfide progresses almost to completion

and adjacent metal grains between chondrules gradually coalesce. All the silicate material intially enclosed by the coalescing grains eventually gets expelled and the grains acquire a uniform clean, clear-cut aspect. No round shape survives and the shape of the opaque minerals seems to be governed by the interstices they fill between the silicates. With the disappearance of chondrules by type 6, the grains become more evenly dispersed and smaller than the large metal grains of types 4 and 5.

Interpretation: The changes from 3.0 to 3.5 seem to be mostly driven by reduction of grain boundary area as well as temperature-induced breakdown of sulfide followed by S_2 vapor migration as described in [8]. This process becomes very important by 3.7. The apparent coalescence of metal grains from 3.8 to 5 seems to be driven by grain boundary diffusion of Fe and Ni (as indicated by this process starting simultaneously with the appearance of zoned taenites), and the gradual expulsion of the enclosed silicates is related to the reduction of surface free energy. From 5 to 6, recrystallization becomes the controlling process. The size and distribution of the opaque minerals seem to be governed by the rate of nucleation rather than their initial grain size. They are still interstitial to the silicate crystals, but they look more compact because the silicates have become more polygonal.

Conclusions: Opaque phases in chondrites undergo changes with metamorphism that can be followed step by step, allowing the optical determination of a petrographic type matching that deduced from the silicate phases with a reasonable precision. In the first approximation, there is no observable difference between the opaque mineral textures observed in H and LL chondrites, which indicates that our method could potentially also be applied to metal-bearing carbonaceous chondrites.

References: [1] Van Schmus and Wood (1967) *GCA, 31*, 747. [2] Sears et al. *Nature, 287*, 791. [3] McSween et al. (1978) *Proc.*

LPSC 9th, p. 1437. [4] Perron et al. (1989) *LPS XX*, 838. [5] Zanda et al. (1994) *Science, 265*, 1846. [6] Zanda et al., this volume. [7] Spry (1969) *Metamorphic Textures*, Pergamon, 156. [8] Lauretta et al. (1997) *EPSL*, submitted.

UNRAVELING NEBULAR AND PARENT-BODY EFFECTS IN CHONDRITE MATRIXES: MINERALOGICAL AND COMPOSITIONAL CONSTRAINTS.

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Chondritic meteorites have experienced extremely complex evolutionary histories, involving formation of their different components in the nebula and subsequent processing prior to and post accretion into parent bodies. Each of these processes has imprinted its own mineralogical or chemical record on the different components of chondritic meteorites, such as chondrules, CAIs, and fine-grained matrix materials. Differentiating between the effects of nebular and parent-body processes on matrix materials has presented one of the more challenging problems in chondrite petrology, in part because of the difficulties of fully characterizing such fine-grained materials. An additional complexity is that matrixes are likely to respond in a highly sensitive fashion to parent-body processes. In essence, matrixes can be regarded as the "canary in the coal mine" of chondritic meteorites, changing rapidly during thermal metamorphism or aqueous alteration. This sensitivity can be attributed to a combination of several different chemical and physical properties of matrix materials, such as their grain size, porosity, and permeability. The high surface free energy of the micrometer to submicrometer grains in matrixes [1,2] makes them extremely reactive. For the case of aqueous alteration, high surface areas will promote rapid reaction to hydrous phases. Similarly, the high grain boundary free energy of fine-grained materials will lead to a rapid reduction in the total grain boundary area due to grain growth during metamorphism.

The high permeability and porosity of matrixes are also additional factors that make them highly susceptible to alteration by aqueous fluids. High porosities will also aid metamorphic equilibration, because mass transfer will be dominated by rapid grain boundary diffusion, with relatively minor volume diffusion over short distances within grains.

As a consequence of these characteristics few unequilibrated meteorites have matrixes that have not been affected by aqueous alteration or metamorphism. Nevertheless, several studies, discussed below, have provided clear evidence that matrixes in a few highly unequilibrated chondrites have experienced only minimal postaccretionary alteration.

Amorphous Phases: TEM studies of the matrixes of the Bishunpur (LL3.1) [3,4], ALH 77307 (CO3.0) [5], and the unique chondrite, Acfer 094 [6], show that they contain a significant component of amorphous material. In each case the amorphous material is widespread and acts as a groundmass in which other mineral phases are embedded. In Bishunpur [4], the amorphous material is rich in normative feldspar, whereas in ALH 77307 [5] and Acfer 094 [6] this component is rich in SiO_2, MgO, and FeO with minor amounts of Ni and S. These differences in composition are consistent with the much higher bulk Al_2O_3, K_2O, CaO, and Na_2O contents of unequilibrated ordinary chondrite (UOC) matrixes [4,7–9], in comparison with carbonaceous chondrite matrix material [2,5,10]. There is no consensus over the origin of this amorphous material, but derivation from chondrule mesostasis [3,4] or formation by disequilibrium condensation processes [5,6] have both been suggested. Most importantly, there does not appear to be a reasonable mechanism by which this type of material could have formed within a parent body. Amorphous materials represent a highly disordered, metastable state and will invariably recrystallize during mild annealing or alter rapidly in the presence of hydrous fluids. Thus the survival of amorphous material indicates that parent-body processing has been minimal.

Unequilibrated Mineral Compositions: Analytical electron microscope studies of the matrixes of these same chondrites show that the mineral phases present, dominantly olivine, are highly unequilibrated. Olivines with very disparate compositions can coexist within micrometers of one another [5]. In the UOCs, fine-grained matrix olivines range in composition Fa_{0-91}. This is also true of matrix olivine in ALH 77307 (CO), which has a compositional range Fa_{0-70}. In contrast, this is not the case for Acfer 094, which contains only very Fo-rich olivine. However, this meteorite is relatively highly weathered, so it is possible that FeO-rich olivines have been terrestrially altered. Alternatively, it may be even more primitive than ALH 77307. An additional and compositionally very distinct type of fine-grained olivine has also been recognized in several UOCs and carbonaceous chondrites. These so-called LIME olivines [11] are forsteritic in composition, but have very elevated MnO contents (up to 1.4 wt%). Low-Ca pyroxene compositions in matrixes are somewhat unequilibrated, but in general are restricted to relatively Mg-rich compositions (UOCs, Fs_{0-25} [4,9]; CO, $<Fs_4$).

Diverse Mineralogical Components: The only two chondrites studied to date that show clear evidence of distinct mineralogical components within their matrixes are ALH 77307 and Kakangari. In ALH 77307 several distinct textural types of olivines and pyroxenes occur that are, in most cases, compositionally distinct [5]. These include isolated, well-crystallized Mg-rich olivines and LIME olivines, fine-grained clusters of fayalitic olivine, and compositionally variable olivine that occurs within the regions of amorphous material. Distinct mineralogical aggregates of LIME olivines and pyroxenes have also been recognized in this meteorite and Mg-rich orthopyroxene fragments rather than clinopyroxene are common. In the unique carbonaceous chondrite Kakangari, the matrix is composed of distinct clusters or aggregates of crystals about 2–8 mm in size [12]. These units have distinct boundaries with one another and have clearly defined mineralogies. For example, aggregates consisting of intergrown low-Ca pyroxene and olivine are most common, but well-annealed clusters of anorthite and olivine are also present.

Discussion: These different mineralogical, textural, and compositional properties show that some matrixes are highly unequilibrated assemblages of components that experienced very different formational histories. Although there is no consensus as to the origins of each of the individual phases in matrixes, it is likely that fragments of chondrules, condensates, and certainly presolar grains, as well as organic compound formed at low temperatures, are all present, mixed on an intimate scale. Such diversity provides definitive evidence that parent-body processing has had a minimal effect on a very small group of unequilibrated chondrites.

The effects of parent-body processes on chondrite matrixes have been studied to various degrees in the different chondrite groups. Aqueous alteration is relatively well understood [e.g., 13] and has

typically obliterated or obscured evidence of nebular processes. The general effects of metamorphism are also reasonably clear, but the details are still somewhat poorly understood. Huss et al. and McSween [7,14] noted that the matrixes of the UOCs and CO chondrites become progressively more translucent with increasing petrologic type, presumably due to grain growth during metamorphism, and mineral compositions become more homogeneous. In the matrixes of UOCs the effects of parent-body metamorphism are certainly apparent by petrologic type 3.4 [4]. For example, although Bishunpur (type 3.1) matrix is dominated by amorphous material, in Sharps and Chainpur (both 3.4), the matrixes consist largely of densely packed, fine-grained, equilibrated olivine (~Fa_{50}) with minor amorphous material [4]. These observations are consistent with the behavior of matrixes in CO chondrites, except that extensive crystallization of olivine has occurred by petrologic type 3.1 rather than 3.4 [15,16]. This difference may be because the more olivine normative matrix in CO chondrites recrystallizes more readily than the feldspathic amorphous material in UOCs. These observations show that the textural and compositional effects of metamorphism manifest themselves rapidly on matrix materials. In the CO chondrites, clear compositional trends are observed in the matrix as a function of petrologic type. For example, the bulk matrix and olivine compositions become increasingly Mg rich, consistent with equilibration between Mg-rich chondrules and Fe-rich matrix [14,16].

CV chondrites, such as Allende, have often been considered to record a relatively pristine record of nebular processes. However, recent observations suggest that a reappraisal of these meteorites is in order. It has been argued that the fayalitic olivines in CV chondrite matrixes are nebular condensates based on their distinct, tabular morphologies and high minor-element contents [17]. However, the presence of inclusions of pentlandite, chromite, and poorly graphitized C [18] in matrix olivines suggests that formation by dehydration of hydrous phases such as serpentine [19] is more likely.

Conclusions: Although the matrixes of chondrites are extremely sensitive to the effects of parent-body processes such as aqueous alteration and metamorphism, a very small group of the most highly unequilibrated chondrites do appear to have retained a relatively well-preserved record of nebular processes.

References: [1] Scott E. R. D. et al. (1988) in *Meteorites and the Early Solar System* (J. F. Kerridge and M. S. Matthews, eds.), pp. 718–745, Univ. of Arizona, Tucson. [2] Brearley A. J. (1996) in *Chondrules and the Protoplanetary Disk* (R. H. Hewins et al., eds.), p. 137, Cambridge Univ. [3] Ashworth J. R. (1977) *EPSL, 35,* 25. [4] Alexander C. M. O'D. et al. (1989) *EPSL, 95,* 187. [5] Brearley A. J. (1993) *GCA, 57,* 2291. [6] Greshake A. (1997) *GCA, 61,* 437. [7] Huss G. R. et al. (1981) *GCA, 45,* 33. [8] Matsunami S. (1984) *Proc. NIPR, 35,* 126. [9] Nagahara H. (1994) *GCA, 48,* 2581–2595. [10] McSween H. Y. Jr. and Richardson S. M. (1977) *GCA, 4,* 1145. [11] Klöck W. et al. (1989) *Nature, 339,* 126. [12] Brearley A. J. (1989) *GCA, 53,* 2395. [13] Zolensky M. E. and McSween H. Y. (1998) in *Meteorites and the Early Solar System* (J. F. Kerridge and M. S. Matthews, eds.), p. 114. [14] McSween H. Y. (1977) *GCA, 44,* 477. [15] Keller L. P. and Buseck P. R. (1991) *GCA, 65,* 1155. [16] Brearley A. J. (1994) *LPS XXV,* 165. [17] MacPherson G. et al. (1985) *GCA, 44,* 2267. [18] Brearley A. J. (1996) *Meteoritics & Planet. Sci., 31,* A21. [19] Kojima T. and Tomeoka K. (1993) *Meteoritics, 28,* 649.

CHLORINE-BEARING MELT INCLUSIONS IN OLIVINE FROM UNEQUILIBRATED ORDINARY CHONDRITES.

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Introduction: Melt inclusions are a common but little studied component of chondrules within UOCs. They are most visible within olivine phenocrysts. These inclusions are composed of silicate glasses with variable compositions. In thin section they characteristically have elliptical outlines and a mauve color. They formed as a result of melt being trapped during crystallization of the surrounding phase—olivine in the case of chondrites—and therefore can potentially provide information about chondrule melt compositions.

Preliminary results of analyzing the composition of melt inclusions and the effects of artificial heating and cooling are reported here. Some melt inclusions were found to contain Cl. The presence of halogen-bearing and alkali-rich phases in chondrites has often been attributed to alteration processes—nebular or planetary [1,2]. In contrast it has been suggested elsewhere [3,4] that some Cl-bearing phases within UOCs crystallized from chondrule melts and are not the result of alteration. The inclusions studied here provide further information about the distinction between primary Cl-bearing phases and those that formed through alteration.

Techniques: Thin sections of Bishunpur (LL3.1), Chainpur (LL3.4), Tieschitz (H3.6), and Parnallee (LL3.6) were searched for
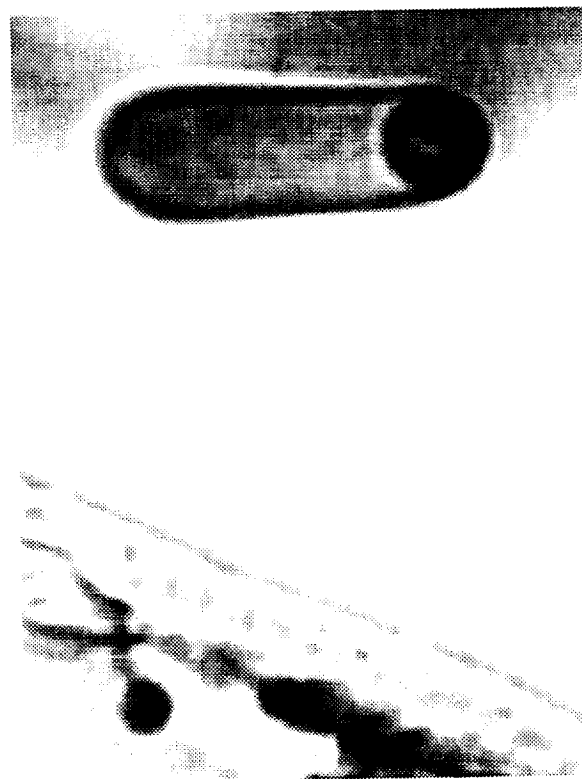
Fig. 1. Melt inclusion (25-μm diameter) enclosed within an olivine grain. The bubble at the right hand side is a void space formed during shrinkage of the glass. Sample is a porphyritic chondrule from Tieschitz.

TABLE 1.   Composition of melt inclusions within oliving (wt%).

	Parnallee	Parnallee	Chainpur	Range
SiO_2	62.2	60.7	66.8	45.3–76.0
Al_2O_3	12.5	10.3	13.1	6.9–12.5
TiO_2	0.5	0.3	—	<0.5
Cr_2O_3	0.4	7.5	—	<4.6
FeO	2.8	4.2	2.1	0.8–7.6
MgO	6.2	1.2	1.5	0.3–12.4
MnO	0.2	—	—	<0.2
CaO	7.9	0.3	—	0.2–11.0
Na_2O	3.6	2.1	4.2	2.4–4.8
K_2O	2.7	4.4	3.9	1.1–4.4
Cl	0.1	0.1	—	<0.1
Total	99.1	91.1	91.6	

Range of compositions calculated from 29 melt inclusions within sections of Bishunpur, Chainpur, Parnallee, and Tieschitz.

glassy melt inclusions within the olivine of chondrules. Chemical compositions were determined with a Hitachi 2500 SEM/EDS system at 15kV and 2nA. Long counting times were used (150 s) in order to achieve relatively low detection limits (~0.07 wt% for Cl). Only those melt inclusions that were not on cracks were used, in an effort to minimize the risk of contamination.

A demountable thin section of Tieschitz was prepared and, following optical identification of melt inclusions, was studied using a heating/cooling stage. The effects of heating and cooling the melt inclusions were monitored with an optical microscope.

Results: *Petrography.* Melt inclusions were found in all the sections studied. They were identified by their mauve color and elliptical outlines, and range in size up to 80 μm maximum diameter (Fig. 1). Most of the melt inclusions also contained "bubbles" at the margins. These occupy <30 vol% of the inclusions. Although the inclusions are predominately glass, some appeared to have undergone limited devitrification as they contained a few Ca-pyroxene dendrites and Cr spinels. No signs of corrosion or alteration were present.

The melt inclusions have a variable range of compositions. One common characteristic, however, is the relatively high K_2O contents for chondritic material (up to 4.4 wt%). This is, for instance, higher than the typical K_2O contents of chondrule mesostases. Chlorine was detected in some melt inclusions (0.1 wt%). The composition of 3 individual melt inclusions from Tieschitz and Parnallee are given in Table 1, together with a range of compositions from 29 melt inclusions located in Bishunpur, Chainpur, Tieschitz, and Parnallee.

Heating stage. Melt inclusions within olivine from Tieschitz were cooled to –196°C and heated to 600°C. Between these temperatures the "bubbles" at the margins of the inclusions did not undergo any changes in volume or leakage of fluids. This is consistent with their being void space, created during contraction of the melt pockets as they cooled during chondrule formation.

Discussion: The glassy, unaltered nature of the melt inclusions shows that remobilization of alkali elements seen in some components (e.g., matrix) of Tieschitz and other UOCs [5] has not affected them. Instead the K and Cl contents of the inclusions were determined when the chondrules were still molten. Therefore, the concentration and sometimes remobilization of labile elements within chondrules of UOCs took place in several stages. An early stage was

trapping during chondrule formation. This may be due to the presence of a relatively high pressure of volatile-rich gases at the same time as chondrules were forming. It has been suggested elsewhere that such a process may have operated because Cl-, alkali-rich phases within chondrules, and bulk enrichments of alkali elements in some chondrules, are not always easily explicable by alteration [3,6]. The hydrous alteration and associated corrosion sometimes seen in UOCs, which is responsible for some remobilization of alkali elements and halogens, occurred at a late parent-body stage [5]. Determining the setting for the initial, primary concentration of volatile phases within some chondrules will depend on which model concerning the site of chondrule formation—nebular or planetary—is favored. The latter setting is preferred here because localized compositional heterogeneities, as shown by the presence of some volatile-rich phases and other chemically differentiated components in UOCs [7], are more easy to explain through processes of planetary differentiation, rather than within the nebula.

Conclusions: Volatile elements, notably Cl, are present in small but significant amounts in melt inclusions trapped within olivine from UOC chondrules. These inclusions are unaffected by alteration and so suggest that some Cl-bearing, volatile-rich gases were trapped during chondrule formation. Melt inclusions provide evidence that not all halogen-bearing (and alkali-rich) phases within chondrules can be attributed to alteration. The initial trapping of volatile-rich gases is believed to have occurred in a planetary/parent-body setting as is therefore, by this model, all subsequent remobilization of these elements seen in some UOCs.

Some of the melt inclusions will be analyzed by an irradiation and laser fusion technique. This will provide further information about their halogen and volatile-element contents.

References: [1] Kimura M. and Ikeda Y. (1995) *Proc. NIPR Symp. Antarct. Meteorites, 8,* 123–138. [2] Krot A. N. et al. (1995) *Meteoritics, 30,* 748–775. [3] Bridges J. C. et al. (1997) *Meteoritics & Planet. Sci.,* submitted. [4] Bridges J. C. et al. (1995) *Proc. NIPR Symp. Antarct. Meteorites, 8,* 195–203. [5] Hutchison R. et al. (1994) *Meteoritics, 29,* 476–477. [6] Kurat G. et al. (1984) *EPSL, 68,* 43–56. [7] Bridges J. C. and Hutchison R. (1997) *Meteoritics & Planet. Sci., 32,* in press.

A SEARCH FOR ACCRETIONARY TEXTURES IN CM CHONDRITES. L. Browning, Hawai'i Institute of Geophysics and Planetology/School of Ocean and Earth Science and Technology, University of Hawai'i at Manoa, Honolulu HI 96822-2219, USA.

Introduction: It has been reported that examples of pristine asteroidal materials can be observed in most CM chondrites [1]. These "primary accretionary rocks," according to [1], experienced no aqueous alteration or brecciation on the CM asteroidal parent body and can be identified by their texture—a densely packed agglomeration of rim/core components with no interstitial matrix materials. These authors claim that the meteorite Y 791198 is made up exclusively of "primary accretionary rock" (or "primary rocks") while fragments of similarly pristine material are present as lithic clasts in most other CM samples.

Metzler et al. [1] propose the following multistage scenario to explain the origin of primary accretionary rocks: Both altered and unaltered CM phases were present in the solar nebula as isolated grains; coarse-grained CM components accreted a mantle (or "accretionary rim") of fine-grained alteration phases as they passed through one or more nebular dust clouds; and finally the CM asteroidal parent body accreted as an agglomeration of these rim/core components. Primary rocks are lithified samples of these accretionary agglomerates.

There are several interesting implications of this model. As one example, it requires that aqueous alteration generally preceded the formation of all CM rim textures, including chondrule rims, and the accretion of the CM asteroidal parent body. Because all CM rims contain abundant phyllosilicate minerals that dehydrate at temperatures on the order of a few hundred degrees Celsius [2], their model also implies that relatively cool rim materials accreted onto similarly cool core components. This contrasts sharply with the widely held hypothesis that rim materials in other types of chondrites were sintered onto hot chondrule cores immediately following the chondrule-forming event [3]. Although the location and relative timing of CM alteration has been discussed on several different grounds [1,4,5], the primary rock textures described by Metzler et al. [1] have not been reexamined by different researchers. This work represents an effort to identify, characterize, and reevaluate the origin of primary rock textures in Y 791198 and 10 CM falls.

Analytical Techniques: Two thin sections of the meteorite Y 791198, plus sections from 10 CM falls, were characterized by petrographic and scanning electron microscopy. Compositional data are currently being collected using an electron microprobe.

Results: Several observations argue that Y 791198 experienced *in situ* aqueous alteration. For example, multiple phyllosilicate veinlets (<2 μm thick) extend from the interior of one chondrule and then cut across a major fraction of the surrounding chondrule rim. These cross-cutting veinlets indicate that the rim was already emplaced around the chondrule when alteration occurred. Similar features are observed in the other CM chondrites examined in this study. Although no relationship has been detected between the chemistry or mineralogy of CM rims and various core types [1], these cross-cutting veinlets show that fluid-rock reactions caused the local redistribution of dissolved components between at least some CM core and rim materials. Similar occurrences of veinlets are also commonly observed around individual olivine fragments in Y 791198 and other CM chondrites. These phyllosilicate veinlets generally occur as fragile dendritic patterns that are interwoven with the surrounding fine-grained materials. The dendritic patterns of these veinlets probably reflect the fluid pathways that dissolved components took on the CM parent body, while their delicate nature argues against the plausibility of their having survived the type of multistage physical processing described by [1]. In a similar fashion, most calcite grains in Y 791198 are extensively embayed and possess very delicate spiderlike morphologies that are best reconciled with an origin by *in situ* precipitation/dissolution processes. Analogous calcite morphologies are present in most other CM chondrites, suggesting that these formational processes are typical of CM alteration.

This evidence for *in situ* aqueous alteration indicates that Y 791198 is not made up exclusively of primary accreted materials from the CM parent body, as suggested [1]. However, because the effects of aqueous processing are superimposed upon preexisting materials in complex ways, these results do not negate the possibility that CM materials were aqueously altered in some preaccretionary environment, as well as the CM parent body.

The current study indicates that agglomeritic textures are confined to discrete portions of Y 791198 and do not define the general fabric of this meteorite. Alternate textures include coarse-grained core components without rims and relatively broad regions of fine-grained materials (i.e., "matrix") that do not appear as rims. Observations indicate that some lithic fragments in other CM chondrites possess these textures while others don't. Moreover, regions containing densely packed agglomerates of rim/core components are not always contained within these clasts. The nature of the agglomerates themselves also varies widely. For example, some are made of discreet rim/core components, but the majority are smaller and appear to be lumps of rim or matrix materials with no obvious core component. Browning et al. [6] point out that different types of agglomerates may have formed by different processes and suggest that some of these smaller agglomerates may have formed when individual grains were imperfectly replaced during *in situ* serpentinization. In contrast, the densely packed agglomeritic texture of primary accretionary rocks is interpreted by [1] as evidence for a lack of *in situ* brecciation. Unraveling the origin of the various agglomerate types and the significance of densely packed agglomeritic textures requires more work.

To summarize, primary accretionary rock textures are present in Y 791198 and other CM chondrites, but probably do not represent pristine accretionary materials. Moreover, although the thin sections examined in this study contain many of the petrologic features described by [1], a comparison with other CM chondrites suggests that Y 791198 may not be as unusual as previously thought.

References: [1] Metzler et al. (1992) *GCA, 56,* 2873–2897. [2] Johannes (1968) *Contrib. Mineral. Petrol., 19,* 309–315. [3] Hewins R. et al., eds. (1996) *Chondrules and the Protoplanetary Disk,* Cambridge Univ. [4] Browning et al. (1996) *GCA, 60,* 2621–2633. [5] Brearley and Geiger (1991) *Meteoritics, 26,* 323. [6] Browning et al. (1997) *GCA,* submitted.

USE OF OXYGEN ISOTOPES TO CONSTRAIN THE NEBULAR AND ASTEROIDAL MODIFICATION OF CHONDRITIC MATERIALS.

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On the scale of individual chondrules and CAI, O isotopic variations appear to be dominated by exchange and mixing interactions between two principal reservoirs: a ^{16}O-rich dust reservoir and a ^{16}O-poor gas reservoir [1]. Each of these reservoirs may have had a somewhat variable isotopic composition as a consequence of their interaction with one another. At low temperatures in the nebular cloud, chemical interactions between these reservoirs were probably not significant. However, isotopic exchange of O between solid or molten silicates with nebular gases (CO and H_2O) must have occurred during transient heating events such as chondrule formation. Laboratory experiments show that this process occurs on a time-scale of minutes [2]. At some times or places in the solar nebula, conditions favored condensation of liquid or solid water to form wet planetesimals. This provided an environment for low-temperature chemical and isotopic interactions [3].

An important property of stable isotope exchange processes is the strong dependence of isotopic fractionation factors on temperature [4]. For O isotopes, equilibrium fractionations between the phases at the temperatures of molten silicates are generally less than 3‰, whereas fractionations between minerals and water are commonly greater than 20‰ at 0°C [5].

On the basis of measurements of constituents of the carbonaceous chondrites, it has been proposed that the initial dust component in the solar nebula was enriched in ^{16}O relative to the larger gaseous reservoir by about 70‰ [3]. Thus, high-temperature processes, in which mass-dependent fractionation effects are small compared to reservoir differences, lead to mixing lines in the O three-isotope diagram. These lines for chondrules and CAI typically have slopes close to 1, reflecting the compositions of the two primary reservoirs.

In the H, L, and LL ordinary chondrites, O isotopic compositions of chondrules follow a single, slope 1 mixing trend, independent of the Fe group of the host meteorite [6]. Thus, ordinary chondrite chondrules appear to be drawn from a single population with common chemistry. The distinction among Fe groups of the subsequently assembled parent bodies is probably the result of sorting processes [7]. The O isotope evidence implies that chondrules acquired their isotopic composition in high-temperature events in the nebula, before parent-body formation.

Chondrules in unequilibrated enstatite chondrites also form a linear array in the O isotope diagram, which does not overlap that of ordinary chondrite chondrules [8]. The range of variation is small, and thus the slope of the mixing line is not well constrained. The separation from the O chondrite and C chondrite compositions implies a dust component with a somewhat different isotopic composition.

Some chondritic materials have Δ^{17}O exceeding the highest values found in chondrules of the ordinary chondrites. These samples provide lower limits on Δ^{17}O of the gaseous nebular component. R chondrites have chondrules with Δ^{17}O = 3.0 [9]; silica xenoliths in some ordinary chondrites also have Δ^{17} = 3 [10], and magnetite with Δ^{17} = 5 has been found in unequilibrated ordinary chondrites [11].

The various carbonaceous chondrite groups exhibit the isotopic effects of both high- and low-temperature interactions between reservoirs. In CV and CM chondrites, both CAIs and chondrules follow a slope 1 mixing line, indicative of exchange between nebular gas and solids or liquids at high temperatures [1]. Chondrule rims in Allende also show this behavior, which implies acquisition of the rims in the nebular environment.

Low-temperature water-rock interaction (often leading to the production of hydrous minerals) is most evident in CI and CM chondrites, where it produces large heavy-isotope enrichment in O [3]. The same processes are operative (under similar conditions) in terrestrial sea-floor "weathering" in which basalts are altered to clay minerals [12]. The heavy-isotope enrichment is due to the mass-dependent isotopic fractionation between clay minerals and water. Small degrees of heavy-isotope enrichment due to incipient aqueous alteration are also evident in CO3 and some UOC [6].

It has been postulated that many occurrences of fayalitic olivine in chondrules, chondrule rims, dark inclusions, and chondrite matrix result from dehydration of phyllosilicate precursors [13]. If the proposed phyllosilicates had been formed in low-temperature parent-body processes such as those that produced CI and CM phyllosilicates, they should have acquired the heavy-isotope enrichment characteristic of these processes. Subsequent dehydration would

not obliterate this signature, since dehydration produces very small changes in O isotopic composition [14]. The observed isotopic compositions of these materials show no evidence for low-temperature hydration, but rather follow extrapolations of the variations in carbonaceous chondrite chondrules. Thus, the reservoir interactions that produced the observed compositions must have involved the nebular gas at temperatures high enough that the mass-dependent fractionation should be small. A rough estimate of the lower temperature limit is about 300°C. Most importantly, the gaseous reservoir must have been the same one with which chondrules and CAI interacted, i.e., the solar nebular gas, rather than an isolated parent-body fluid. Thus the O isotope data for dark inclusions and CV matrix do not themselves suggest a hydration-dehydration origin. If such a scenario is required by other evidence, the O data imply that the hydration step took place in the nebula at temperatures above 300°C.

References: [1] Clayton R. N. (1993) *Annu. Rev. Earth Planet. Sci., 21,* 115–149. [2] Yu Y. et al. (1995) *GCA, 59,* 2095–2104. [3] Clayton R. N. and Mayeda T. K. (1984) *EPSL, 67,* 151–161. [4] Urey H. C. (1947) *J. Chem. Soc. Lond.,* 562–581. [5] Onuma N. et al. (1972) *GCA, 36,* 169–188. [6] Clayton R. N. et al. (1991) *GCA, 55,* 2317–2337. [7] Dodd R. T. (1981) *Meteorites: A Petrologic-Chemical Synthesis,* Cambridge. [8] Clayton R. N. and Mayeda T. K. (1985) *LPS XVI,* 142–143. [9] Weisberg M. K. et al. (1995) *Proc. NIPR Symp., 8,* 11–32. [10] Bridges J. C. et al. (1994) *Meteoritics, 29,* 448–449. [11] Choi B.-G. et al. (1997) *LPS XXVIII,* 227–228. [12] Muehlenbachs K. and Clayton R. N. (1972) *Can. J. Earth Sci., 9,* 172–184. [13] Krot A. N. et al. (1995) *Meteoritics, 30,* 748–775. [14] Clayton R. N. et al. (1997) *Meteoritics & Planet. Sci., 32,* in press.

TURBULENT SIZE SELECTION AND CONCENTRATION OF CHONDRULE-SIZED OBJECTS: REYNOLDS NUMBER INVARIANCE AND IMPLICATIONS. J. N. Cuzzi[1], R. Hogan[2], A. Dobrovolskis[3], and J. Paque[4], [1]NASA Ames Research Center, Moffett Field CA 94035, USA (cuzzi@cosmic.arc.nasa.gov), [2]Symtech Inc., Mountain View CA 94035, USA, [3]Board of Studies in Astronomy, University of California, Santa Cruz CA, USA, [4]SETI Institute, Mountain View CA, USA.

It is generally agreed that individual chondrules formed as entities in a gaseous nebula prior to being accumulated into a meteorite parent body, where they incur various forms of modification. There are major unanswered questions about the properties of the nebula environment in which chondrules formed. This process, by which the most primitive meteorites are formed overwhelmingly from chondrules, must then be an aspect of "nebula processing." Textures in certain fragments of primitive meteorites might be summarized as being primarily chondrules and clastic, chondrule-sized fragments of other minerals. Each of these is covered with a rim of dust containing physical and chemical properties that are independent of the composition and mineralogy of the underlying chondrule. This (unfortunately rather rare) texture was called "primary accretionary texture" by [1] to reflect their belief that it precedes subsequent stages of fragmentation, comminution, mixing, heating, and other forms of alteration occurring on the parent body(ies). The size distribution of these chondrules and fragments, and the properties of their dusty rims, are key clues regarding the primary nebula accretion process. Key chondrule properties (e.g., mean size, density, and rims) remain

relatively well defined, even in the more abundant meteorites that have clearly suffered internal mixing, abrasion, grinding, and mineralogical alteration or replacement (due presumably to the collisional growth and heating process itself).

It has been our goal to infer the key nebula processes indirectly from the properties of the earliest primitive meteorites by using a theoretical framework in which the nebula possesses a plausible level of isotropic turbulence. We have shown that turbulence has the property of concentrating one particular particle size by orders of magnitude. The preferentially concentrated size depends primarily on the intensity of the turbulent kinetic energy (represented by the Reynolds number of the nebula). Specifically, the preferentially concentrated particle has a stopping time equal to the turnover time of the smallest eddy [2]. The intensity level of turbulence implied by chondrule sizes can be maintained by a small fraction of the energy released by the radially evolving disk. (It must be noted that the details of the transfer of energy actually occurring remain obscure.)

We have carried our studies of the turbulent concentration process to a deeper level and have obtained several new and interesting results. We have established that two critical aspects of the process can be described in a way that is Reynolds number independent [3]. In our previous results, we needed to rely on large extrapolations between computational turbulence regimes and nebula turbulence regimes (5 orders of magnitude in Reynolds number).

First, we ran numerical calculations of particle density fields in turbulence for a range of particle sizes with uniform initial spatial distribution. We then determined the distribution of particle sizes within the high-density regions. We have not only shown that the shape of the particle distribution resident in dense clumps is quite similar to that found in chondrites, but it is also Reynolds number independent (according to our mapping of factor 3–4 in Reynolds number). Chondrule size distributions provided by our numerical models might by expected to persist even at much higher nebula Reynolds numbers. Results will be shown and compared with size distributions from [8] and from our own experiments [5]. In the newer data, chondrules are disaggregated so their size and density can be measured separately. This is critical because in the aerodynamic sorting provided by turbulence, the defining parameter is the aerodynamic stopping time, which is proportional to the product of the particle radius and density.

Second, we have developed a new way of describing the particle density fields that is also invariant to Reynolds number. The mathematics of fractals has been shown to be particularly appropriate to describe the spatial distribution of certain properties of turbulence, specifically the dissipation rate of turbulent kinetic energy [6]. This means that the spatial distribution of the turbulent energy dissipation rate is scale-independent, and that higher intensities have a different spatial structure, or dimensionality, than lower intensities (i.e., are concentrated in smaller regions). We have shown that that same mathematics applies to the particle density field when the particle size is close to the preferentially concentrated size [3]. The density field (or concentration factor) for these particle sizes can then be described by a probability distribution that has only two elements: a Reynolds-number-independent scaling function (which we determine in our numerical calculations at three relatively low Reynolds numbers) and the Reynolds number itself. The entire particle density probability distribution can be predicted at any Reynolds number from this universal function. The particle concentrations predicted this way are in general accord with simple extrapolations published previously [2]. We discuss the implications for particle concentration in nebula turbulence and some remaining uncertainties.

References: [1] Metzler K. et al. (1992) *GCA, 56,* 2873–2897. [2] Cuzzi J. N. et al. (1996) in *Chondrules and the Protoplanetary Disk* (R. H. Hewins et al., eds.), Cambridge Univ. [3] Hogan et al. (1997) in preparation. [4] Hughes D. W. (1978) *EPSL, 38,* 391–400. [5] Paque J. and Cuzzi J. N. (1997) *LPS XXVIII.* [6] Meneveau C. and Sreenivasan K. R. (1991) *J. Fluid Mech., 224,* 429–484.

EFFECT OF REVISED NEBULAR WATER DISTRIBUTION ON ENSTATITE CHONDRITE FORMATION.

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The unique chemical and mineral composition of enstatite chondrites has been difficult to explain and accurately reproduce in chondrite formation models. Enstatite chondrites consist of highly reduced phase assemblages: the silicates contain almost no FeO while the Fe metal contains significant amounts of Si. Further, enstatite chondrites also contain a variety of unusual minerals, the majority of which are not found in ordinary or carbonaceous chondrites [1]. It is generally believed that the mineral assemblages seen in the enstatite chondrites could not have resulted from equilibrium condensation of a solar composition gas at the low pressures, 10^{-2}–10^{-6} atm, thought to have existed in the solar nebula [2].

In her Ph.D. dissertation [1], M. L. Hutson constructed a formation model for enstatite chondrites based on the assumption that condensation occurred in nebular regions of nonsolar composition. The modal mineralogy and bulk chemistry of the chondrites were best fit by a model requiring two chemical fractionations from gas of solar composition. The first was "refractory element" fractionation [3], which removed condensates at a temperature of around 1270 K. The second was the removal of water from 1–5 AU by diffusional transport. Loss of water vapor in gas increases the reducing nature and the C/O ratio of that gas. Hutson found that the depletion of 80–85% of the cosmic water abundance from 1–5 AU alone could explain many of the chemical and mineralogical signatures of enstatite chondrites; however, it was not sufficient, and thus the prior fractionation process was also posited.

Hutson based her water-depletion analysis on Stevenson and Lunine [4]. In their model water vapor is tranported across the condensation front by eddy diffusion and rapidly condenses out as ice. The ice is assumed to suffer little effect from gas drag or other transport processes and so remains in the condensation zone. The model predicts that the inner 5 AU of the nebula becomes severely depleted in water vapor in as little as 10^5 yr.

However, in recent work [5] we found that gas drag effects in [4] had been underestimated and that ice particles could drift back significant distances inward of 5 AU and sublimate, reinjecting the nebula with water vapor. Our expanded water transport model, which incorporated both diffusion and drift processes, still predicts an overall depletion in water vapor, but with a zone of local vapor enhancement on the order of 20–100% from 1–2 AU, which gradually drops off out to 5 AU. Thus, unlike [4], we find a radical dependence to the water vapor depletion pattern and thus to the reducing nature and C/O ratio in the inner nebula.

We will reinterpret Hutson's enstatite chondrite formation model and her conclusions in light of the revised nebula water depletion model, in particular considering the changes in condensation sequence of materials and the overall effect of the radial dependence of water depletion on nebular chemistry.

References: [1] Hutson M. L. (1996) Ph.D. thesis, Univ. of Arizona, Tucson. [2] Wood J. A. and Morfill G. E. (1988) in *Meteorites and the Early Solar System* (J. F. Kerridge and M. S. Matthews, eds.), p. 329, Univ. of Arizona, Tucson. [3] Larimer J. W. and Wasson J. T. (1988) in *Meteorites and the Early Solar System* (J. F. Kerridge and M. S. Matthews, eds.), p. 394, Univ. of Arizona, Tucson. [4] Stevenson D. J. and Lunine J. I. (1988) *Icarus, 75*, 146. [5] Cyr K. E. et al. (1997) *Icarus,* submitted.

INTERSTELLAR HYDROXYLS IN METEORITIC CHONDRULES: IMPLICATIONS FOR THE ORIGIN OF WATER IN THE INNER SOLAR SYSTEM.

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Introduction: Water-rich bodies in the solar system, including comets and chondritic meteorites, show a systematic D enrichment relative to the protosolar nebula (see Table 1). Deciphering the origin of H_2O in solar system objects hinges on a correct interpretation of this isotopic enrichment.

Mineralogical Identification of Water in Chondrules: Transmission electron microscopy diffraction patterns of excentroradial pyroxene chondrules (type I) from Bishunpur show that the zone-axis containing the [010]* reciprocal direction show an extreme disorder in the sequence of (010) planes. The corresponding high-resolution micrographs reveal a structure constituted by two types of narrow bands with approximately equal areas, both types being exactly parallel to the trace of the (010) pyroxene plane. One type of bands clearly shows lattice fringes typical of the clinoenstatite structure. The other type of bands is attributed to lamellae of amphiboles. This assumption is supported by the electron microprobe analyses: the rules for cation site occupancy in pyroxenes indicate that the ratio of the atomic concentration of octahedral to tetrahedral cations is <1, as expected in hydroxylated enstatite.

Parent-Body Alteration as Recorded by the D/H Ratio of the Mesostasis: In radial pyroxene type I chondrules, mesostasis exhibits D/H ratios much lower (D/H = 150×10^{-6}) than those found in the crystals (D/H up to 460×10^{-6}). Based on these observations, the following interpretation can be proposed. Type I chondrules were originally enriched in D. Their mesostasis was subjected to secondary alteration by an isotopically distinct source of H_2O (D/H = $89 \pm 9 \times 10^{-6}$), likely during the parent-body hydrothermal event. However, hydroxylated pyroxenes did not undergo isotopic reequilibration with this hydrothermal H_2O. Therefore the pyroxenes have

TABLE 1. The highest D/H ratios measured in LL3 matrix clays (interstellar water) are assumed to represent a minimum for the interstellar value; the lowest D/H value (protosolar water) in LL3 chondrules stands for water that underwent an isotopic exchange with the protosolar H and is calculated from the statistical mean of D/H ratios measured in the range $62-99 \times 10^{-6}$.

D/H ($\times 10^{-6}$)	Speciation	Location	References
Galactic			
40 ± 10	H	Big-Bang (primordial)	[1]
23 ± 5	H	Quasar 1937–1009	[2]
16 ± 1	H	Local interstellar medium	[3]
210 ± 120, 150	H_2O	Interstellar clouds	[4]
Protosolar Nebula			
36 ± 10, 31.5 ± 4.0	H_2	Presolar gas 4.5×10^9 ago	[5]
Planets and Comets			
20 ± 8	H_2	Jupiter	[6,7]
15 ± 11	H_2	Saturn	[8]
149 ± 3	H_2O	Bulk Earth	[9]
320 ± 30	H_2O	Comet P/Halley	[10]
280 ± 40	H_2O	Comet Hyakutake	[11]
LL3 Meteorites			
Interstellar Water			
730 ± 120	–OH	In clays	[12]
Protosolar Water			
88 ± 11	–OH	In chondrules	Present work
Carbonaceous Meteorites			
140 ± 10	–OH	Mean statistical value	
130 < D/H < 170 (66%)			

retained their preaccretional interstellar isotopic signature. These data demonstrate that at least two sources of H_2O were intimately mixed in the solar system. This is attested by the markedly different D/H ratios preserved in chondrule pyroxenes and in their associated mesostasis.

Interstellar Chondrule Precursors Recorded by Their High D/H Ratios Preserved in Pyroxene: As clearly demonstrated by their high D/H ratios, hydroxylation of pyroxenes took place before the incorporation of chondrules in the parent body. Two possible interpretations can be proposed to account for their high H_2O concentrations: (1) H_2O-rich solids were present among the chondrule precursors; (2) chondrules formed in a H_2O-rich environment and were subsequently altered after or during their cooling. In both cases, high D/H ratios suggest that this H_2O was of interstellar origin.

No geochemical test is known that would discriminate unequivocally between 1 and 2. We favor the interpretation according to which the chondrule melt was water supersaturated, amphibole crystallizing under disequilibrium conditions during the rapid cooling of the chondrule. Such a hypothesis has been tested experimentally by flash heating an enstatite-smectite mixture at 1900°C, followed by rapid cooling of this synthetic chondrule. If correct, this interpretation implies that H_2O was initially present among the chondrule precursors as phyllosilicates (or ice?) similar to those previously reported in the matrix of these meteorites.

Implications for the Solar System D/H Ratio: Interpretation of the D/H ratio in bulk meteorite samples over the last 40 years was confronted by the problem of possible terrestrial contamination of anhydrous minerals. Our results solve this problem and show that the majority of H in the anhydrous meteoritic minerals is indigenous to the minerals. This conclusion is based on a central observation: The distribution of isotopic ratios in chondrules exhibits minimum (D/H = $88 \pm 11 \times 10^{-6}$) and maximum values (D/H = $479 \pm 8 \times 10^{-6}$ in pyroxenes), which cannot conceivably be attributed to terrestrial contamination. Two mechanisms are proposed for these two end members: (1) The low D/H ratio ($88 \pm 11 \times 10^{-6}$) probably results from an isotopic exchange between protosolar H_2O and HD. For heuristic purposes this H_2O is designated as "protosolar water." (2) D/H ratios $> 200 \times 10^{-6}$ can be reached only via interstellar chemistry. Crude calculations show that f reaches a value of 15 (i.e., $479 \times 10^{-6}/31 \times 10^{-6}$) at T = 130 ± 10 K in less than a million years, via ion-molecule reactions. This type of interstellar chemistry likely took place in the molecular cloud that predates the formation of the protosolar nebula. Such an isotopic distribution provides a tool to distinguish between *in situ* and preaccretional alteration processes.

Interstellar and Cometary Water Budgets on Earth: Based on these isotopic estimates and assuming that the mixing process between the different H_2O carriers identified in LL3 chondrites is a general rule for solar system objects, the cometary (D/H = $300 \pm 50 \times 10^{-6}$) and interstellar contributions (D/H = $730 \pm 120 \times 10^{-6}$) to the Earth (D/H = $149 \pm 3 \times 10^{-6}$) can be calculated: Less than 10% of H_2O on the present-day Earth was inherited from the early cometary bombardment, and thus >90% was outgassed from the primitive mantle. Of the resulting 100%, $14 \pm 3\%$ is of interstellar origin and thus $86 \pm 3\%$ resulted from the oxidation of the protosolar gas.

References: [1] Gloeckler G. and Geiss J. (1996) *Nature, 381,* 210–212. [2] Tytler D. et al. (1996) *Nature, 381,* 207–209. [3] Linsky J. L. (1993) *Astrophys. J., 402,* 694–709. [4] Gensheimer P. D. et al. (1996) *Astron. Astrophys., 314,* 281–294. [5] Gautier D. and Morel P. (1997) *Astron. Astrophys.,* in press. [6] Lécluse C. et al. (1996) *Planet. Space. Sci., 44,* 1579–1592. [7] Niemann H. B. et al. (1996) *Science, 272,* 846–849. [8] Noll K. S. and Larson P. L. (1990) *Icarus, 89,* 168–189. [9] Cordier et al. (1988). [10] Eberhardt P. et al. (1995) *Astron. Astrophys., 302,* 301–318. [11] Gautier D. et al. (1996) in *ACM 96,* p. 46, Versailles, France, July 8–12, 1996. [12] Deloule E. and Robert F. (1995) *GCA, 59,* 4695–4706.

THEORETICAL MODELS AND EXPERIMENTAL STUDIES OF GAS-GRAIN CHEMISTRY IN THE SOLAR NEBULA.   B. Fegley Jr., Planetary and Chemistry Laboratory, Department of Earth and Planetary Sciences, Washington University, One Brookings Drive, St. Louis MO 63130-4899, USA (bfegley@levee.wustl.edu).

Introduction: "Here today, gone tomorrow" describes the ephemeral existence of the solar nebula. The question of how long the gaseous nebula existed is fundamental for models of nebular chemistry because the underlying assumption of all condensation calculations [1–3] is that enough time was available for equilibrium to be reached between gases, gas and grains, and between different grains. However, different chemical reactions proceed at different rates, which generally vary exponentially with temperature. Hence, it is unclear that all reactions, especially low-temperature reactions between gas and grains and between different solid grains could reach equilibrium before the nebular gas dissipated and chemistry ceased. Here I revisit this question and discuss reactions forming Fe sulfides, magnetite (Fe_3O_4), and hydrated silicates.

Nebular Lifetime: Astronomical observations of young stars, isotopic studies of meteorites, and theoretical models of accretion disks suggest a nebular lifetime of 0.1–10 m.y. [4,5]. A widely used earlier estimate was 10^{13} s (~300,000 yr) [6].

Gas-Grain Reactions: Condensation calculations [1–3] predict that troilite, Fe_3O_4, and hydrated silicates form by reaction of nebular gas with solid grains at low temperatures. The gas molecules must collide with solid grains to react with them. Initially, reaction rates depend on the temperature, gas partial pressure, and grain size (surface-to-volume ratio). Higher temperatures, higher pressures, and smaller grains increase the reaction rate. "Fluffy" and porous grains react faster because the surface-to-volume ratio is increased. Conversely, lower temperatures, lower pressures, and larger grains decrease reaction rates. Reaction rates shift from linear kinetics (chemical control) to parabolic kinetics (diffusion control) and slow down once a sufficiently thick nonporous product layer coats the unreacted solid. The critical thickness varies for each reaction and depends on the temperature.

SCT Models: I used simple collision theory (SCT) to quantify these ideas and to model gas-grain kinetics for troilite, magnetite, and hydrated silicate formation in the solar nebula and in the subnebulae believed to exist around Jupiter and Saturn during their formation [7–9]. The models assume fully dense, monodispersed spheres (0.1 μm radius) comparable in size to interstellar dust and fine-grained meteorite matrix. The kinetic theory of gases and kinetic data from the literature were used to calculate gas collision rates with grains and the fraction of collisions that led to chemical reaction. The chemical lifetime (t_{chem}) for a reaction must be less than or equal to the nebular lifetime (t_{neb}) for the reaction to proceed during the nebular lifetime.

Iron Sulfides: Simple collision theory modeling predicts that FeS formation is rapid (~320 yr in the nebula) [7], so we studied FeS formation first [10–14]. Our experimental data show that corrosion

of Fe metal and Fe-Ni alloy (Fe meteorite metal) in H_2/H_2S mixtures is rapid, even at H_2S concentrations of 23, 50, and 100 parts per million by volume (ppmv), which span the expected value of 33 ppmv H_2S in the solar nebula. We observe the transition from linear to parabolic kinetics and find characteristic chemical signatures in sulfides formed from Fe-Ni alloys: (1) bulk Fe/Ni in sulfide and metal are similar, if not identical, (2) increasing Ni concentration from the metal-sulfide to the sulfide-gas interface, (3) pentlandite inclusions in the monosulfide solid solution. These features can be destroyed during thermal metamorphism, and hold the potential for distinguishing nebular from parent-body sulfides [11,14]. Detailed microprobe studies of Ni-bearing sulfides in chondrites are needed to see which (if any) Ni-bearing sulfides are nebular remnants and which are parent-body products.

Magnetite: The SCT models predict that Fe_3O_4 formation takes ~320,000 yr in the nebula, but is more rapid in the higher-pressure subnebulae. However, the activation energy (E_{act}) for wüstite formation had to be used to calculate the t_{chem} for Fe_3O_4 because the E_{act} for Fe_3O_4 formation kinetics in H_2/H_2O mixtures is not known. Intuitively, we would think that "rusting" is rapid, but reaction of ~1 μbar H_2O vapor with Fe at 130°C and below is probably slow. Our initial experiments [15] show that Fe_3O_4 forms by reaction of Fe with H_2O, but also suggest that the linear rate is slower than that for FeS formation. Also, the transition from linear to parabolic kinetics and the effect of Ni plausibly decrease the Fe oxidation rate even more. I consider bulk Fe_3O_4 formation in the solar nebula unlikely, although Fe_3O_4 rims may form on metal. Magnetite formation is kinetically and thermodynamically favorable in the jovian subnebulae.

Hydrated Silicates: The SCT models predict that hydrated silicate formation (serpentine, talc) takes ~4.5 b.y. in the solar nebula. Hydrating rock in a near-vacuum at or close to room temperature is a slow process. The SCT models predict that hydrated silicates can form in the subnebulae around Jupiter and Saturn [8,9]. The higher pressures in the subnebulae lead to faster reaction rates. Also, hydrated silicates become stable at higher temperatures, since condensation temperatures generally increase with increasing pressure. Mica dehydration experiments in my laboratory [16] show that H_2O loss is more rapid than breakdown to the thermodynamically stable reaction products. Cation diffusion is the slow step for forming the predicted anhydrous assemblage. This implies that cation diffusion is also the rate-limiting step for hydration of anyhydrous minerals. Formation of hydrated silicates in jovian protoplanetary subnebulae, inside parent bodies, or in temporary atmospheres (of large planetesimals) that could form by adiabatic gas capture from the solar nebula seems more plausible than nebular gas-grain reactions.

References: [1] Larimer J. (1967) *GCA, 31*, 1215. [2] Grossman L. (1972) *GCA, 36*, 597. [3] Lewis J. S. (1972) *EPSL, 15*, 186. [4] Podosek F. A. and Cassen P. (1994) *Meteoritics, 29*, 6. [5] Cameron A. G. W. (1995) *Meteoritics, 30*, 133. [6] Cameron A. G. W. (1978) *Moon and Planets, 18*, 5. [7] Fegley B. Jr. (1988) in *LPI Tech. Rpt. 88-04*, 51. [8] Fegley B. Jr. and Prinn R. G. (1989) in *The Formation and Evolution of Planetary Systems*, p. 171, Cambridge Univ. [9] Fegley B. Jr. (1993) in *The Chemistry of Life's Origins*, p. 75, Kluwer, Dordrecht. [10] Lauretta D. et al. (1996)

Icarus, 122, 288. [11] Lauretta D. et al. (1996) *Proc. NIPR Symp. Antarct. Meteorites, 9*, 97 and 111. [12] Lauretta D. et al. (1996) *Meteoritics & Planet. Sci., 31*, A78. [13] Lauretta D. et al. (1997) *LPS XXVIII*. [14] Lauretta D. et al., this volume. [15] Hong Y. and Fegley B. Jr., this volume. [16] Zolotov M. Yu. and Fegley B. Jr. (1997) unpublished results.

THE CHONDRITE-ACHONDRITE TRANSITION: DE-COUPLING OF OXYGEN ISOTOPE AND GEOCHEMICAL CHANGES.

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Chondrites and Achondrites: Chondrites represent primitive, undifferentiated solar system material. In terms of nonvolatile element composition, they closely match the solar photosphere [1]. Their textures (chondrules) result from nebular processes [2]. And although they have been metamorphosed they have not been melted on their parent bodies [1]. In contrast, the bona fide achondrites (HEDs, SNCs, and lunar meteorites) resemble terrestrial igneous rocks in texture, mineralogy, and bulk composition, allowing us to understand them as products of igneous differentiation on their parent bodies (4 Vesta, Mars, Moon). They have ages that are younger than those of chondrites [3,4], consistent with this understanding.

On a $\delta^{17}O$-$\delta^{18}O$ plot, chondritic materials plot along lines of slope ~1 and differentiated materials plot along lines of slope ~1/2 (0.52). The slope ~1 lines are believed to be mixing lines, reflecting an inhomogeneous distribution of ^{16}O-rich material in the solar nebula [5]. Slope ~1/2 O isotope lines result from mass fractionation, which occurs during chemical processes such as igneous differentiation. The SNC and HED groups each plot along their own slope ~1/2 mass-fractionation lines, distinct from the Earth-Moon line, indicating that their parent bodies formed from distinct O reservoirs.

There is evidence that (with the exception of volatile elements) achondrite parent bodies were similar to chondrites in bulk chemical composition [6–8]. In particular, Ca/Al (wt) ratios inferred for the EPB and Mars (1.09) are identical to those of chondrites [9]. Thus, there has emerged a general view that the terrestrial planets and asteroids accreted from more or less chondritic material [10] with heterogeneous O isotopes [11], and that they evolved (in proportion to their size) toward isotopic homogenization and progressively more fractionated rock types as heating occurred. The primitive achondrites and ureilites, which appear to be transitional between chondrites and bona fide achondrites, provide an opportunity to test this view.

Primitive Achondrites and Ureilites: Primitive achondrites (winonaites-IAB inclusions, brachinites, acapulcoites, lodranites) have been defined as meteorites that are close to chondritic in bulk composition but have igneous textures and appear to have lost an (Fe,Ni)S melt and in some cases a low-melting-T silicate melt [12]. Thus, they are either tacitly [12] or explicitly [10,13] considered to be residues of very low degrees of partial melting. Recently [14] have informally redefined primitive achondrites as meteorites "derived from parent bodies that avoided isotopic homogenization and thus retained some of their primary chemical and isotopic characteristics," and have included ureilites in this class. Depletion in lithophile incompatible and plagiophile elements can be used as a measure of degree of "primitiveness" (Fig. 1). Depletion increases in the
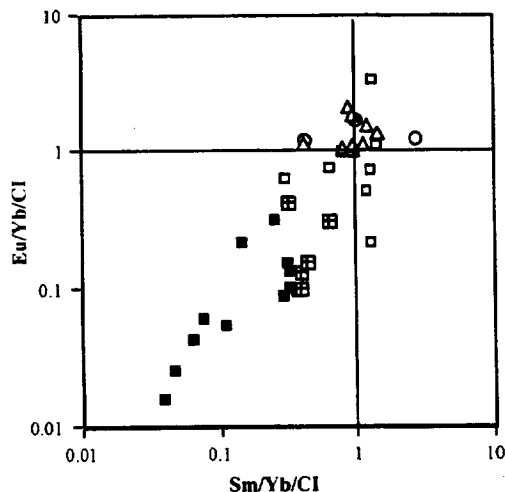
Fig. 1.   Ureilites (black boxes), Iodranites (boxes with crosses), winona-ites-IAB (open boxes), acapulcoites (open triangles), brachinites (open circles), Allende chondrules (black triangles), and chondrule rims (crosses).

Fig. 3.   See Fig. 1 for description of symbols.

Fig. 2.   See Fig. 1 for description of symbols.
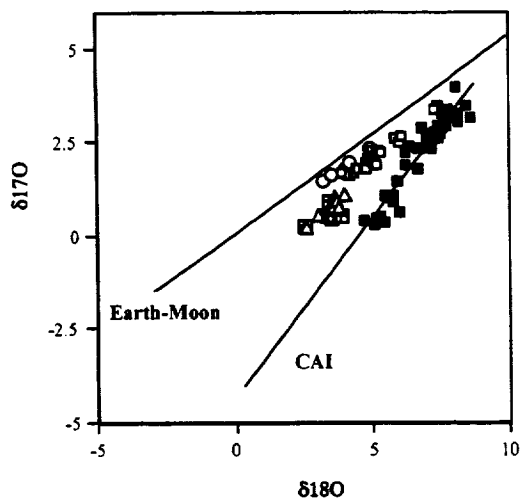
Fig. 4.   See Fig. 1 for description of symbols.

order (brachinites, acapulcoites) → winonaites and IAB inclusions → Iodranites → ureilites.

If the view that primitive achondrites and ureilites have been depleted to various (small) degrees with corresponding degrees of (incomplete) O isotopic homogenization makes sense, then there should be a simple relation between degree of depletion of a group and the degree to which its O isotopic compositions deviate from a slope ~1 line and tend toward a slope ~1/2 line on a $\delta^{17}O$-$\delta^{18}O$ diagram. The least-depleted groups should plot on slope~1 lines and the most-depleted groups should tend toward slope ~1/2 lines. This is not the case (Fig. 2). Ureilites, which are the most depleted, plot along the slope ~1 CAI line. Winonaites, brachinites, and acapulcoites, which are the least depleted, plot on nearly slope ~1/2 lines

(winonaites: slope -0.55 $r^2 = 0.92$; brachinites: slope -0.49 $r^2 = 0.94$). Of acapulcoites and Iodranites, which plot on a single slope ~1/2 (0.47) line and so may be from the same parent body, it is Iodranites that are more depleted and so should show the least scatter, and yet they show more scatter than acapulcoites (acapulcoites form a line with slope -0.57 and $r^2 = 0.83$, while Iodranites scatter about a poor line of slope -0.27 and $r^2 = 0.24$). These observations are precisely the opposite of what would be expected.

In addition, if mg-$\Delta^{17}O$ correlations are of nebular origin, the quality of the correlation should decrease with increasing degree of depletion of a meteorite group. Chondritic materials should show the best correlation and ureilites should show the worst. Again, this is not the case (Figs. 3,4). The ureilite correlation is of the same quality

as that of Allende chondrule rims ($r^2 = 0.76$ for ureilites and 0.71 for Allende rims), and much better than that of Allende chondrules ($r^2 = 0.29$) (Fig. 3). Of acapulcoites and lodranites (Fig. 4), acapulcoites should show a better correlation, but they show no significant correlation ($r^2 = 0.14$) compared to lodranites ($r^2 = 0.38$). And the lodranite correlation should be better than that of ureilites (Fig. 4), but it is not (but see [15]). Again, the observations are the opposite of what would be expected.

There is not a simple transitional sequence of coupled O isotopic and geochemical changes among the primitive achondrites and ureilites. This raises some questions about our understanding of the chondrite-achondrite transition: (1) Are the incipient melting conditions that explain the textures and compositions of winonaites and acapulcoites sufficient to equilibrate O isotopes? If not, (2) Is it possible that winonaites and acapulcoites accreted from material that was already O isotopically equilibrated but not chemically fractionated? If so, (3) Why did ureilites not equilibrate O isotopes? (4) Is it possible that ureilites accreted from material that was not chondritic in bulk composition, in particular with superchondritic Ca/Al? (5) Are mg-Δ^{17}O correlations really nebular?

Acknowledgments: This work was supported by my mother.

References: [1] McSween H. Y. (1987) *Meteorites and Their Parent Planets*, Cambridge Univ. [2] Grossman J. N. (1988) in *Meteorites and the Early Solar System* (J. F. Kerridge and M. S. Matthews, eds.), p. 680, Univ. of Arizona, Tucson. [3] Jacobsen S. B. and Wasserburg G. J. (1980) *EPSL, 50*, 139. [4] McSween H. Y. (1994) *Meteoritics, 29*, 757. [5] Clayton R. N. et al. (1973) *Science, 181*, 485. [6] Jones J. H. (1984) *GCA, 48*, 641. [7] Dreibus G. and Wänke H. (1985) *Meteoritics, 20*, 367. [8] Treiman A. H. et al. (1986) *GCA, 50*, 1071. [9] Ahrens L. H. (1970) *EPSL, 10*, 1. [10] Taylor G. J. et al. (1993) *Meteoritics, 28*, 34. [11] Clayton R. N. et al. (1991) *GCA, 55*, 2317. [12] Prinz M. et al. (1980) *LPS XI*, 902; (1983) *LPS XIV*, 616. [13] Benedix G. K. et al. (1995) *LPS XXVI*, 99. [14] Clayton R. N. and Mayeda T. K. (1996) *GCA, 60*, 1999. [15] McCoy T. J. (1997) *GCA*, in press.

PROGRESSIVE ALTERATION OF CM2 CHONDRITE MATRIXES: DETERMINING RELATIVE PHYLLOSILICATE CONTENTS BY X-RAY DIFFRACTION.

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Introduction: Fine-grained matrix is the most volumetrically abundant component in CM2 chondrites [1,2]. It is a complex mixture of phyllosilicate minerals, sulfides (including tochilinite), carbonate, and high-temperature mineral fragments [3]. CM2 carbonaceous chondrites have suffered hydrothermal alteration to various levels, a process that might have occurred either on the parent body [1,4] or in a nebular setting [5], but the conditions (P, T, eH, pH) under which the alteration took place are still subject to debate [2]. The extent to which matrix alteration has occurred is an important parameter that must be determined before secondary alteration effects can be distinguished from primary parent-body variations. Unfortunately, however, the extremely fine-grained and highly intergrown nature of carbonaceous chondrite matrix has made constructing a reliable index of alteration a difficult task. The most recent and comprehensive index relies on calculation of an average matrix

phyllosilicate composition [6], a parameter that can only be obtained after painstaking electron microprobe analysis of many sections.

Recent advances in the application of X-ray diffraction techniques to the characterization of mixtures of minerals have resulted in the development of a rapid, whole-pattern profile-stripping method for the quantification of multiphase samples [7]. This method has been further developed to deconvolute mixtures of clay minerals in environmentally important deposits [8]. Analyses can be carried out on either powdered samples or thin sections, with a data acquisition time of only 5–10 min (although a useable pattern for identification purposes can be obtained in seconds). Given that the main matrix component in CM2 chondrites might well be described as a mixture of clay minerals, it was thought that application of the XRD technique might be appropriate as a rapid and simple method for tracing the mineralogical variations in carbonaceous chondrite matrixes brought about by aqueous alteration. To this end, a suite of CM2 chondrites will be examined; initial results for Cold Bokkeveld and Murray are reported here. Cold Bokkeveld is the most altered CM2 chondrite in the alteration sequence proposed by Browning et al., while Murray occurs midway through the sequence [6].

Method: A preliminary optical examination of thin sections of Cold Bokkeveld and Murray identified areas approximately 5 × 5 mm² relatively free from large olivine grains, clasts, etc. X-ray diffraction data were acquired with an Enraf-Nonius diffractometer system utilizing a curved position-sensitive detector (PSD) with simultaneous detection of diffracted X-rays over 120° of arc; tube operating conditions were 45 kV and 45 mA. The monochromated X-ray beam (Cu-Kα_1 radiation) was delimited by a combination of horizontal and vertical slits, resulting in beam dimensions ~5 mm × 0.25 mm; a stationary beam-sample-detector geometry was employed. Each section was aligned using a collimated laser to position the selected area under the glancing-angle incident X-ray beam.

Two analyses were made of a polished thin section surface of Cold Bokkeveld, firstly for an acquisition time of 10 min with the section stationary, the second with the section rotating in its own plane for an acquisition period of 1 hr. Although a clearer pattern, with less noise and better count statistics resulted from the experiment of longer duration and larger area irradiated, no advantage was gained, thus subsequent analysis of the section of Murray was carried out for an acquisition time of 10 min with a stationary sample. Fluorescence from Fe is induced by the Cu-Kα_1 radiation; correction for this effect gives a total Fe content for the specimen. Sequential pattern matching between sample and patterns from single phases, followed by profile stripping allows identification of each phase present, and their relative abundances [7,8].

Results: Preliminary results from Cold Bokkeveld and Murray indicate that in both meteorites the two major phyllosilicates present were, as anticipated, a serpentine-group mineral (2θ ~ 12°) and smectite (2θ ~ 6°). Comparison between the two chondrites showed that although both meteorites contained similar quantities of smectite, Cold Bokkeveld has approximately twice as much serpentine as Murray, as befits its more altered nature [6]. A complete sequence of CM2 chondrites will be measured. Matching the meteorite profiles with patterns from single mineral standards covering the spectrum of serpentine-group compositions from cronstedtite (Fe-rich) to serpentine (Mg-rich) phyllosilicates should allow determination of the cronstedtite-to-serpentine ratio of each meteorite, reflecting the extent to which Fe-bearing phyllosilicates have been converted to Mg-rich end members during alteration.

References: [1] McSween H. Y. (1979) *GCA, 43,* 1761–1770.
[2] Zolensky M. E. et al. (1993) *GCA, 57,* 3123–3148. [3] Zolensky
M. E. and McSween H. Y. (1988) in *Meteorites and the Early Solar
System* (J. F. Kerridge and M. S. Matthews, eds.), pp. 114–143,
Univ. of Arizona, Tucson. [4] Tomeoka K. and Buseck P. R.
(1985) *GCA, 49,* 2149–2163. [5] Metzler K. et al. (1992) *GCA,
56,* 2873–2898. [6] Browning L. B. et al. (1996) *GCA, 60,* 2621–
2633. [7] Cressey G. and Schofield P. F. (1996) *Powder Diffr., 11,*
35–39. [8] Batchelder M. and Cressey G. (1997) *Clays & Clay
Minerals,* submitted.

PRIMITIVE MATRIX COMPONENTS OF THE UNIQUE CARBONACEOUS CHONDRITE ACFER 094: CLUES TO THEIR ORIGIN.

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The vast majority of meteorites found meet, more or less per-
fectly, the mineralogical and geochemical criteria to be assigned to
one of the known meteorite classes. However, since the intensive
search for new extraterrestrial material in cold and hot deserts, a few
meteorites were found appearing to be unique [e.g., 1,2]. Such
samples naturally attract the interest of research because they may
contain information about unknown parent bodies as well as about
processes occurring in the solar nebula.

The Saharan meteorite Acfer 094 is such a promising meteorite.
Found on the Tademait Plateau of the Algerian Sahara in 1990, this
82-g stone could not be unambiguously classified applying the usual
criteria [3–5]. Chemical, mineralogical, and isotopic characteristics
were unable to distinguish between a CO3 vs. CM2 classification.
Additionally, general surveys of presolar phases in Acfer 094 have
shown that it contains the highest SiC concentration of any meteor-
ites measured to date [6]. This and studies on stable isotopes charac-
terize Acfer 094 as extremely primitive, which classifies it as a good
candidate to contain unprocessed material, e.g., pristine matrix com-
ponents.

Acfer 094 consists of abundant chondrules, chondrule fragments,
CAIs, and mineral fragments embedded in a fine-grained ground-
mass. The abundance of grains <50 µm is 62.5 vol% and approxi-
mately 30–40 vol% of the meteorite consist of grains <10 µm [3–5].

Fig. 1.   TEM image of the fine-grained matrix. Olivines (Ol), pyroxenes
(Px), and pyrrhotites (Pyr) are embedded within an amorphous (am)
groundmass.

In order to study the fine-grained matrix material (<3 µm), four
matrix-rich areas of the meteorite were investigated by TEM. The
matrix is dominated by an amorphous material that is also present in
a sample produced by crushing, excluding an origin as a result of ion-
beam irradiation (Fig. 1). The most abundant phases enclosed in the
amorphous material are tiny rounded olivines (200–300 nm), rounded
pyroxenes (300–400 nm), and Fe,Ni-sulfides (100–300 nm). Some
15–80-nm-sized olivines (Fa <1) are rimmed by material of un-
known composition. Larger olivines and pyroxene grains up to 2 µm
in size are rare. A few angular pyroxene and olivine fragments have
been detected. Serpentine and chlorite are present in small portions
in the amorphous material. Serpentine occurring in cracks and
ferrihydrite are the most common secondary minerals. The character-
istics and possible formation of these components will be discussed
below.

Amorphous Material: The amorphous material acts as an in-
tergranular groundmass to all crystalline components. Analyses in-
dicate a chemical inhomogeneity of the glass on a nanometer scale.
The material is rich in SiO_2 (42.6–54.1 wt%), FeO (22.8–31.6 wt%),
and MgO (7.8–16.3 wt%). All analyses contain considerable amounts
of NiO (2.0–8.5 wt%), Al_2O_3 (2.8–5.2 wt%), and S (0.4–2.6 wt%).
High-resolution TEM shows that in some regions local ordering
occurs. Microcrystallites of serpentine and chlorite have been ob-
served. Four different mechanisms have to be considered for the
formation of the amorphous material:

Fragmentation of chondrules. Feldspathic mesostasis produced
by fragmentation of chondrules is present in the matrix of ordinary
chondrites [7]. However, in the case of Acfer 094 this origin can be
ruled out due to the low Ca/Al ratios (0.2–0.7) of the amorphous
material.

Shock-induced melting. Mainly because of the total lack of any
shock effects in the constituent minerals such an origin can also be
excluded. In addition, the amorphous material in Acfer 094 is rich in
Ni and S whereas in shock-produced melts Ni and S form separated
globules of sulfides and metals.

Weathering of FeO-rich olivines. The total absence of FeO-rich
olivines is one of the surprising characteristics of the Acfer 094
matrix. It might, therefore, be suggested that these olivines have been
altered to an amorphous gel-like phase. However, studies on terres-
trial olivines have shown that during weathering, mainly phyllosili-
cates and magnetite and not amorphous material were formed [8].
Also, from the thermodynamic point of view, such glass would be
metastable and recrystallize immediately.

Disequilibrium condensation. Silicon-rich amorphous materi-
als have been the products of several disequilibrium condensation
experiments [e.g., 9] and at least two astrophysical environments
are possible for such a scenario: the early solar nebula and certain
circumstellar regions. Excluding formation by 1–3, it seems most
likely that the amorphous material condensed in either of these
locations.

Matrix Olivines: Most olivines are 200–300 nm in size,
anhedral to subhedral, and show rounded morphologies. They are
Fe-poor ($Fa_{<2}$) and typically occur isolated within the amorphous
matrix. Some of them are surrounded by a 5–15-nm thin rim of
unknown composition. Three different mechanisms have to be con-
sidered for the formation of the olivines:

Fragmentation of chondrules. Because no matrix olivine con-
tained more than 1.9 wt% FeO and because nearly all grains exhibited
rounded morphologies a formation by fragmentation of chondrules
seems unlikely. Chondrule olivines in Acfer 094 generally have $Fa_{>3}$.

Annealing of the amorphous material. In order to recrystallize Mg-rich olivines from a Fe-rich groundmass, highly reducing conditions are required, which would simultaneously result in the formation of Fe-metals. Such are absent in the fine-grained matrix of Acfer 094. However, considering the matrix ferrihydrite as an alteration product of former Fe-metals, recrystallization of the amorphous material cannot be completely ruled out.

Condensation in the solar nebula. The condensation of olivines containing more than 10^{-2} Fa mol% requires strongly oxidizing conditions. Such conditions may have been present locally in the solar nebula, possibly due to vaporization of volatile components [10]. On balance, the fact that mixing of a disequilibrium condensation product (amorphous material) and an equilibrium condensate (olivines) so intimately would be quite difficult, a formation by partial annealing is favored.

Matrix Pyroxenes: Two different pyroxenes are present: enstatites (Fs_{0-3}) and Ca-rich pyroxenes (Wo_{20-45}). The few Ca-rich pyroxenes are fragmental grains of probably clastic origin. Enstatitic pyroxenes are mostly abundant and typically occur as 300–400-nm rounded individual grains. Nearly all pyroxenes studied are intergrowths of orthoenstatite and clinoenstatite. The odd and even number of clinoenstatite (100) repeats and the presence of different orientated twins proves that they formed by rapid cooling (1000°–5000°C/hr) from high temperatures [11]. Excluding fragmentation and recrystallization, the small Mg-rich pyroxenes (Fs_{0-3}) with rounded morphologies are thought to have condensed in the solar nebula at highly oxidizing conditions. However, high cooling rates are contrary to an assumed slowly cooling nebula. Therefore, the formation of the rounded pyroxenes remains uncertain.

Ferrihydrite and Phyllosilicates: Ferrihydrite, chlorite, and serpentine were identified as the only hydrous phases in Acfer 094. Whereas the formation of chlorite and serpentine found in the amorphous material is attributed to a first recrystallization, ferrihydrite and serpentine occurring in cracks and pore spaces have formed by hydrous alteration. Based on mineralogical criteria it is impossible to distinguish between parent-body and terrestrial alteration.

Although some similarities exist, comparing the fine-grained matrix of Acfer 094 with the matrixes of the unequilibrated CO3 chondrite ALHA 77307, and the unusual type 3 chondrite Kakangari, Acfer 094 remains unique. The presence of an amorphous phase, most probably representing an unprocessed pristine condensate, supports the idea that such material of variable chemical composition could be the precursor of other matrix components [12].

References: [1] Brearley A. (1989) *GCA, 53,* 2395–2411. [2] Brearley A. (1993) *GCA, 57,* 1521–1550. [3] Bischoff A. and Geiger T. (1994) *LPS XXV,* 115–116. [4] Newton J. et al. (1995) *Meteoritics, 30,* 47–56. [5] Greshake A. (1997) *GCA, 61,* 437–452. [6] Gao X. et al. (1996) *Meteoritics & Planet. Sci., 31,* A48. [7] Alexander C. et al. (1989) *EPSL, 95,* 187–207. [8] Banfield J. et al. (1991) *GCA, 55,* 2781–2793. [9] Rietmeijer F. (1996) *LPS XXVII,* 1069–1070. [10] Palme H. and Fegley B. (1990) *EPSL, 101,* 180–195. [11] Brearley A. and Jones R. (1988) *Eos Trans. AGU, 69,* 1506. [12] Scott E. et al. (1996) *LPS XXVII,* 1161–1162.

CHEMICAL ALTERATION OF CHONDRULES ON PARENT BODIES.
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Introduction: How well do chondrites preserve primitive chondrule compositions? Chondrules in most meteorites have been chemically altered by secondary processes after they solidified. Thermal metamorphism on parent bodies affected most chondrites, causing elements to migrate across chondrule borders, e.g., olivine and pyroxene equilibrate as Mg and Fe diffuse across grain and chondrule boundaries at metamorphic temperatures. Secondary minerals such as plagioclase and phosphates form metamorphically, accompanied by a similar migration of alkalis, Ca, and rare earth elements. Shock metamorphism on the parent body also may cause elements to move into or out of chondrules as phases such as metal and sulfide become mobilized. A third parent-body process, aqueous alteration, severely affected chondrules in CM and CR chondrites, again almost certainly resulting in the transport of elements between chondrules and matrix. Depending on the extent of thermal and shock metamorphism and aqueous alteration, the compositions that chondrules had just after accretion may be partially or completely erased, and will certainly be obscured.

Thus, researchers use the unmetamorphosed, unshocked, least-altered, petrographic type 3 meteorites such as the unequilibrated ordinary chondrites (UOCs) and CV3, CO3, EH3, and EL3 chondrites to measure the compositions that chondrules had at the time of accretion, and thereby to learn about their formation and nebular history. But, do even these chondrites preserve chondrule compositions?

Metamorphism: The UOCs themselves encompass a wide range of metamorphic grades. Petrologic subtypes 3.3 to 3.9 have a narrower range of Fe/Mg ratios in their olivine than do lower subtypes, and experienced mild thermal metamorphism on the parent body resulting in movement of cations across chondrule borders [1]. A similar range of metamorphic effects is present in the type 3 carbonaceous and enstatite chondrites [2,3], leaving only a few good candidates for preserving primitive chondrule compositions.

Metasomatism: *Bleaching.* Among the most primitive UOCs (including Semarkona, Bishunpur, Krymka, Sharps, and Tieschitz), the effects of light aqueous alteration have been known for a number of years, but most of the affected phases are in the extremely fine-grained matrix or as rare, altered patches in chondrules [4–6]. However, we recently rediscovered and documented [7] the observation that the finest-grained chondrules, either cryptocrystalline (C) or radial pyroxene (RP) in texture, in most UOCs and type 4 chondrites have thick "bleached" zones at their surfaces and along cracks [8–9]. The unaffected areas of these chondrules commonly have normative compositions consisting of ~90% low-Ca pyroxene plus ~10% highly albitic plagioclase (glass). The bleached zones have much less normative feldspar and are porous. The ion probe shows that in Semarkona these zones are also rich in H_2O and halogens. The albitic glass has most likely been dissolved and transported out of the chondrules by circulating aqueous fluids, leaving holes and small amounts of alteration products behind. Thus, the bulk compositions of such chondrules are not primary, and have been lowered in alkalis, Al, and Si; only analyses of the cores of these chondrules give data relevant to chondrule formational conditions. We note that if this type of process affected coarser-grained chondrules, etching away just the outer few micrometers of large areas of glass, it might be extremely difficult to identify.

Where did this aqueous alteration occur? In Semarkona, there is convincing evidence that this process happened on the parent body after compaction: Some chondrules have only partially bleached surfaces, and are altered where matrix contacts the chondrule, but not

where one chondrule touches another; the porous matrix acted as a conduit for fluid flow. In Bishunpur, which is more crushed and brecciated than Semarkona, there exist chondrule fragments that are bleached along the original surface, but not along the broken surface, indicating impact processing after alteration. In the higher-petrologic-type ordinary chondrites, bleached chondrules are found in the absence of hydrated minerals, implying that metamorphism (and dehydration) postdated an episode of aqueous alteration, so it is possible that virtually all ordinary chondrites experienced some aqueous alteration during their history.

Metasomatism: *Alteration of glass.* Another effect of secondary processes acting on chondrules in primitive UOCs (thus far studied in Semarkona and Bishunpur) is the compositional zoning of mesostases in low-FeO chondrules [10,11]. Glass near the outer surfaces of these chondrules is commonly much richer in volatile lithophile elements than glass deep inside the chondrules: alkalis (Na, K, Rb, and Cs), H (probably as H_2O), halogens (Cl and F), and Mn all show this effect, with enrichment factors of 10 or more observed in some cases. The D/H ratio is also much higher in volatile-rich glass zones. The glass of the same chondrules shows weaker zoning of major elements, apparently caused by the fractional crystallization of clinopyroxene near the chondrule surface during solidification; cooling was too rapid for melt near the surface to equilibrate with melt within the chondrule. This primary igneous process gave rise to bright yellow cathodoluminescence in the outer zones of these chondrules and also must have resulted in a slight enrichment of the mostly incompatible volatiles (assuming that they were not all lost at this stage; see below). In any case, the observed magnitude of volatile-element zoning is far too great to be caused by this primary igneous effect (and for elements like Na, diffusion in silicate melts is probably too fast to preserve such effects); the D/H fractionation also could not be igneous in origin. We must appeal to secondary processes to explain these.

Volatiles must have entered the chondrules in a subsolidus alteration process. Simple diffusional migration of the elements into the chondrules, such as might happen during nebular condensation or recondensation, or during thermal processing on the parent body, is unlikely because zoning profiles are similar for elements with very different diffusion coefficients and condensation temperatures. The presence of up to 1% H_2O in the volatile-enriched zones is evidence that the alteration process occurred in the presence of an aqueous fluid phase that reacted with the glass and transported the volatile elements. Clearly, the glass has not completely reacted away, as it is still isotropic (albeit browner in color) and cathodoluminescent.

We conclude that the parent body is the most likely setting for this alteration process as well. The matrix material surrounding chondrules would be an excellent source of volatile elements that could be transported into chondrules by the fluid. Indeed, complementary fractionations are observed between chondrules and matrix for a number of volatile element ratios in Semarkona. The matrix also has a high D/H ratio [11,12], and would be a good source of D for the metasomatic fluid. It seems likely that this fluid is the same one that altered the C and RP chondrules: the anorthitic glass in low-FeO chondrules probably responded quite differently to the fluid than the albitic glass in most C and RP chondrules.

Glass in the cores of many low-FeO chondrules appears to be unaffected by aqueous alteration: zoning profiles are commonly U-shaped across the chondrules, with flat, unzoned central regions (which we note are not completely volatile free). But the most-

altered glass is found in the pyroxene-rich outer zones of these (commonly) igneously zoned chondrules, making it tricky to reconstruct, and impossible to measure directly the preaccretionary bulk compositions of the whole chondrules.

The glass in a few low-FeO chondrules appears to be completely altered. These chondrules do not show zoning of volatiles in their glass, but are instead uniformly high in volatiles throughout. In the one example we studied, the glass composition lies along the volatile-rich ends of the alteration trends shown by zoned chondrules. In Semarkona, the group A5 chondrules, characterized by highly albitic mesostasis [13], may also be thoroughly metasomatized objects. In one large example, glass inclusions trapped in the olivine have very low Na/Al ratios compared to the mesostasis surrounding the olivine. The mesostasis is also high in H_2O and other volatiles in ratios similar to that found in the altered parts of low-FeO chondrules. Some other high-FeO chondrules (type II or group B) contain similar glass inclusions in their olivine, hinting at metasomatic effects in these as well.

We believe that the presence of volatile-rich, hydrated glass in chondrules is generally diagnostic of parent-body aqueous alteration. It is important to note that this does not rule out the possibility that nebular alteration also affected these or other chondrules.

Conclusions: There are abundant effects of aqueous alteration on the parent body in chondrules from UOCs, making it more difficult than previously thought to read the compositional record left from the time of chondrule formation. Much of the data in the literature may need to be reinterpreted in light of these results. Indeed, there may not be any ordinary chondrites with chondrules completely free from secondary parent-body processing.

References: [1] McCoy et al. (1991) *GCA, 55,* 601–619. [2] Scott and Jones (1990) *GCA, 54,* 2485–2505. [3] Zhang et al. (1995) *JGR, 100,* 9417–9438. [4] Hutchison et al. (1987) *GCA, 51,* 1875–1882. [5] Alexander et al. (1989) *GCA, 53,* 3045–3057. [6] Alexander et al. (1986) *Meteoritics, 21,* 328. [7] Grossman (1996) *LPS XXVII,* 467–468. [8] Kurat (1969) in *Meteorite Research,* pp. 185–190. [9] Christophe Michel-Levy (1976)*EPSL, 30,* 143–150. [10] Grossman (1996) *Meteoritics & Planet. Sci., 31,* A55–A56. [11] Grossman et al. (1997) *LPS XXVIII,* 481–482. [12] Deloule and Robert (1995) *GCA, 59,* 4695–4706. [13] DeHart et al. (1992) *GCA, 56,* 3791–3807.

THERMAL QUENCHING OF SILICATE GRAINS IN PROTOSTELLAR SOURCES.

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Turbulent convection of hot vapor and dust into cooler regions of protostellar disks can result in abrupt thermal quenching of freshly condensed grains. Laboratory experiments on initially amorphous dust analogs provide a unique opportunity to study the thermal processing of silicate grains in protostellar sources. Infrared spectroscopy and analytical electron microscopy of these laboratory samples will aid in the identification of primitive materials preserved in chondritic meteorites and comets, and may be a useful way of relating infrared observations of cometary dust to the chemical composition and mineralogical content of such grains.
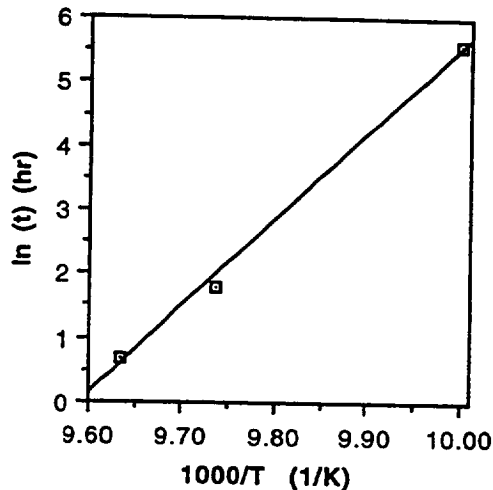
Fig. 1. Arrhenius plot of the annealing time required for the 10-μm IR feature of the amorphous silicate to shift from 9.3 to 9.7 μm over the temperature range 1000–1038 K.

Magnesium silicate smoke was prepared in a condensation flow apparatus [1] from Mg metal and a mixture of SiH_4 diluted in He and O_2 at ~770 K at a total pressure of 80 torr. The freshly condensed smoke was deposited on a collection sheet at ~300 K and removed from the vacuum chamber after the furnace had cooled. The IR spectrum of the initial Mg silicate condensate, a chaotic mixture of Mg metal and silicon oxides with a Mg:Si atomic ratio of 1:3, displayed two broad bands of 9.3 and 21.3 μm, attributed to Si-O stretching and O-Si-O bending vibrations respectively.

Samples of the Mg silicate were annealed in vacuum and monitored by IR spectroscopy as a function of annealing time, focusing on the evolution of the 10-μm feature. As annealing proceeded, the maximum shifted to longer wavelengths and was eventually observed at 9.7 μm, the value typically reported for silicates in the interstellar medium and in circumstellar outflows of O-rich stars. The rate of spectral evolution was measured as a function of temperature from 1000 to 1038 K. At 1000 K, 11 days of annealing were required for the maximum to shift from 9.3 to 9.7 μm. At 1027 K, the maximum was observed at 9.7 μm after 6 hr, while only 2 hr of annealing was needed at 1038 K in order to produce the same spectral changes. An Arrhenius plot of the annealing time required before the maximum in the IR spectra of the amorphous silicate had reached 9.7 μm over the temperature range 1000–1038 K is presented in Fig. 1. Given the very rapid rate at which the 9.3-μm maximum shifts to 9.7 μm, observations of dust with maxima in the range between 9.3 and 9.7 μm in either optically thin protostellar sources or in cometary dust would imply the existence of very high thermal gradients combined with rapid mass transport necessary to quench the annealing of this early state.

Transmission electron microscope analysis of the Mg silicate samples revealed zoned entities 2–3 μm in diameter that contained cores of pure silica that were either polycrystalline tridymite or dense, fine-grained amorphous silica smoke. These silica cores may be experimental artifacts of the vapor condensation process. The cores were mantled with mixed Mg silicates with a bulk composition of dehyroxylated serpentine ($Mg_3Si_2O_7$) or smectite ($Mg_6Si_8O_{22}$).

No olivine (Mg_2SiO_4) or pyroxene ($MgSiO_3$) compounds were present at this stage in the annealing process.

In the primitive solar nebula the conditions necessary to produce quenched silicates may only have existed in relatively low-density environments such as in bipolar outflows above the interface between the accreting Sun and the nebular accretion disk. In denser regions one would expect that the cooling rate would be too low to preserve such highly amorphous materials due to the high nebular opacity. However, in late stages of planetary accretion, following the loss of much of the insulating gas and dust of the nebular accretion phase one might find conditions suitable for the preservation of such signatures. In particular, immediately following the impact of two planetary-scale bodies, such as has been hypothesized to have formed the Earth-Moon system, one expects the formation of a massive, silica-rich atmosphere, the outermost portions of which should be rapidly quenched by radiative cooling to space. Dust lost from such an environment could be accreted by cometessimals prior to their ejection into the Oort Cloud or Kuiper Belt. Such grains could also be accreted as asteroidal regolith on growing planetissimals and could be preserved as meteorite matrix. Finally, it may be possible to indirectly gather evidence for planetary accretion by observing the infrared spectra of optically thin dust in T Tauri stars and searching for the signature of quenched dust produced by planetary-scale impacts.

References: [1] Nelson R. J. et al. (1989) *Proc. LPSC 19th*, pp. 559–563.

IRON-RICH AUREOLES AS RECORDERS OF *IN SITU* AQUEOUS ALTERATION IN THE CM CARBONACEOUS CHONDRITES MURRAY, MURCHISON, AND ALLAN HILLS 81002. N. P. Hanowski and A. J. Brearley, Institute of Meteoritics, Department of Earth and Planetary Sciences, University of New Mexico, Albuquerque NM 87131, USA.

Introduction: Iron-rich aureoles in aqueously altered CM carbonaceous chondrites represent compositionally distinct areas of fine-grained secondary material (e.g., matrix) surrounding altered metal inclusions. These inclusions have diameters up to >100 μm and occur in matrix, chondrules, and chondrule fragments. The aureoles show characteristic elemental enrichments and depletions due to element mobilization into and out of altered metal inclusions. Several Fe-rich aureoles (>500 μm in diameter) have been identified previously as the result of *in situ* aqueous alteration of metal inclusions in the CM chondrite [1]. Here we present additional occurrences of such aureoles in the CM chondrite Murchison (with a low alteration degree similar to Murray) and the highly altered CM chondrite, ALH 81002. An understanding of the mechanisms involved in the formation of Fe-rich aureoles has considerable potential for further elucidating the conditions and duration of the alteration process.

Observations: Backscattered electron (BSE) images from three thin sections of Murchison show between two and six well-developed, Fe-rich aureoles several hundred micrometers in diameter in each section. Some of these aureoles can be directly related to altering metal inclusions in the matrix or chondrules. The majority, however, is apparently imaged in a plane that does not include the altered metal inclusion (Fig. 1a). Quantitative X-ray maps usually show that the fine-grained material inside the aureoles has an Fe
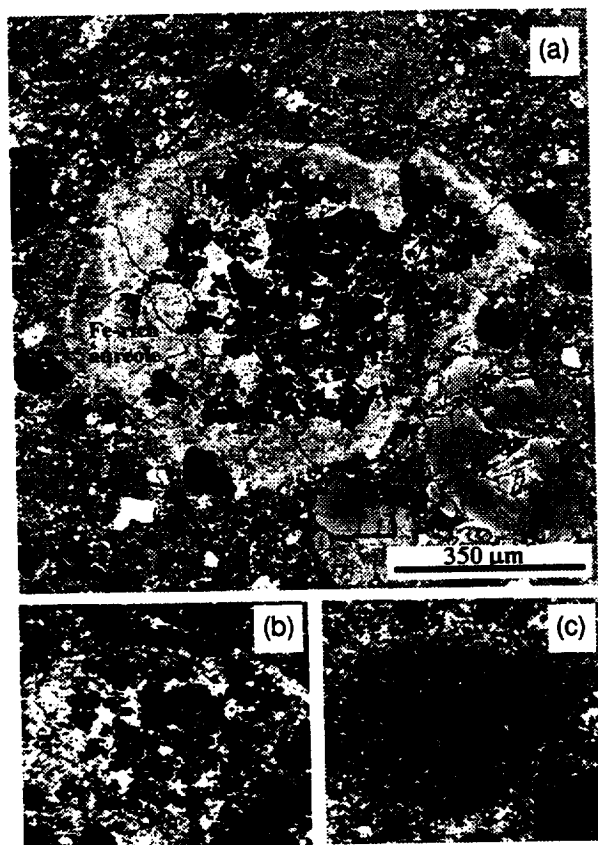
Fig. 1. (a) Backscattered electron image of an Fe-rich aureole in the CM carbonaceous chondrite Murchison. (b) Quantitative X-ray map of the Fe concentrations in the aureole shown in (a) (maximum intensity corresponds to ~35 wt% Fe). (c) Quantitative X-ray map of the S concentrations in the same aureole (maximum intensity corresponds to ~3 wt% S).

content 2–10 wt% higher than equivalent material outside the aureoles. The Fe enrichment is often highest in the outer margins of the aureoles. Areas of Fe enrichment (Fig. 1b) also show a depletion in S from ~3 wt% (a typical S content of matrix and rim material in CM chondrites [2,3]) to <1 wt% (Fig. 1c). Magnesium and Si are also slightly depleted (by <~2 wt%) in the aureoles, whereas other elements, such as Ni and Al, are apparently not enriched or depleted relative to surrounding material. The metal inclusions are entirely replaced by a phase rich in Fe (~40 wt%), S (~13 wt%), Ni (~3–4 wt%), and Cr (~1–2 wt%) with minor amounts of Si and Mg (both <2 wt%). The composition, size, and morphologies of Fe-rich aureoles and altered metal inclusions in Murchison are similar to equivalent features in the CM chondrite Murray.

Both Fe-rich aureoles found in two sections of ALH 81002 are distinctly larger (>1500 μm) than any aureole present in Murray or Murchison. The aureoles in ALH 81002, as well as those in Murchison and Murray, enclose adjacent fragments, fine-grained material, and often other chondrules. The Fe enrichment in aureoles in ALH 81002 is usually <5 wt% and the S depletion <2 wt%. They show, however, a distinct Fe enrichment (often >15 wt%) along the outer edges of the aureoles, forming a reaction front. These reaction fronts

are the most characteristic feature of Fe-rich aureoles in ALH 81002 and the detection of aureoles in BSE images of this meteorite would be extremely difficult without them. The altered metal inclusion associated with one aureole in ALH 81002 is compositionally similar to inclusions in Murchison and Murray (but with a higher S content of ~20 wt%) and affects the altered mesostasis of the chondrule in which the inclusion is located. Altered mesostasis in proximity to this in-clusion (<150 μm from the inclusion) is slightly enriched in Fe (~5 wt%) and S (~2 wt%) compared to more distant altered mesostasis.

Discussion: The presence of Fe-rich aureoles in Murchison and ALH 81002 is consistent with evidence from Murray [1] that their aqueous alteration occurred (probably exclusively) in a parent-body environment. The undisturbed appearance of the aureoles and the fact that they enclose chondrules and chondrule fragments indicate early *in situ* alteration of the metal inclusions after brecciation ceased to play a significant role. The compositional behavior of the altered metal inclusions in Murchison and ALH 81002 (depletion in Fe and enrichment in S, Mg, and Si) appears to complement the behavior of their surrounding aureoles (enrichment in Fe and depletion in S, Mg, and Si). This is consistent with earlier mass balance calculations on inclusions and aureoles in Murray [1] indicating a coupled exchange between them. Although some aureoles, especially in Murchison, bear a strong resemblance to Fe-rich chondrule rims, they are clearly the result of a chemical exchange process. Chondrule rims in CM chondrites generally have a slightly higher S content than surrounding matrix [3], which is the reverse of what is observed in Fe-rich aureoles.

With analogy to terrestrial alteration processes, the radial morphologies and limited (submillimeter) range of elemental exchange indicated by most Fe-rich aureoles suggest a diffusion process in which elements are probably exchanged in solution in an H_2O-rich fluid without advective transport [4]. The relatively large aureoles in ALH 81002 indicate that their spatial extent may be related to the higher degree of alteration in this meteorite, resulting from more extensive interaction with aqueous fluid

The Fe enrichment is clearly coupled with S depletion (and minor Mg and Si depletion) in all the aureoles found in Murray, Murchison, and ALH 81002. This process must involve the preferential breakdown of S-bearing phases in the fine-grained matrix. One possible candidate for the source of the S is tochilinite, which is believed to be an important matrix phase in CM chondrites [5]. However, the observation that at least some tochilinite is stabilized in the altering metal inclusion seems to be more compatible with the breakdown of sulfides as the main carriers of S in the matrix.

References: [1] Hanowski N. P. and Brearley A. J. (1997) *LPS XXVIII*, 503. [2] Metzler K. et al. (1992) *GCA, 56*, 2873. [3] Zolensky M. et al. (1993) *GCA, 57*, 3123. [4] Rose A. W. and Burt D. M. (1979) in *Geochemistry of Hydrothermal Ore Deposits*, p. 173. [5] McSween H. Y. (1987) *GCA, 51*, 2469.

TRANSPORTATION OF GASEOUS ELEMENTS AND THEIR ISOTOPES IN A THERMALLY EVOLVING CHONDRITIC PLANETESIMAL. K. Hashizume[1] and N. Sugiura[2], [1]Department of Earth and Space Science, Osaka University, Toyonaka, Osaka 560, Japan (kohash@ess.sci.osaka-u.ac.jp), [2]Department of

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Ordinary chondrites are considered to have experienced thermal metamorphism in small bodies. We are interested in the behavior of volatile elements in such a thermally evolving planetesimal. Volatile elements generally have high vapor pressures at high temperature. In porous bodies, with a high gas permeability, volatile elements are transported efficiently over a long range. The behavior of volatile elements transported by permeable gas flow can be handled by an equation whose form is similar to that of the equation of thermal diffusion. We can follow the transportation of heat and volatile elements in planetesimals, when the parameters in these equations, initial conditions, and the chemical behavior of volatile elements are given. Numeric simulations for C transportation in a thermally evolving chondritic planetesimal have been previously studied, concluding that the efficiency of C transportation from the interior of the planetesimal to its surface largely depends on the gas permeability near the surface [1]. In this study, we carried out numeric simulations for transportation of C, N, and H in a planetesimal using a similar scheme. Using the simulation, we intend to explain several new constraints recently observed among equilibrated ordinary chondrites [2].

We discovered that N in equilibrated H chondrites is mainly trapped in taenite (f.c.c. γ-Fe,Ni), probably dissolved in the interstitial sites of the metals. The N concentrations in taenite were around 10 ppm, and the isotopic compositions ranged $-40 < \delta^{15}N < +120\%_o$ among the chondrites [2]. From the diffusion coefficient of N in γ-Fe,Ni, we estimated the closure temperature of N in taenite to be approximately 500°C. We concluded that N presently trapped in taenite was in equilibrium with the N components surrounding the metal grains, possibly the gas phase (N_2) existing among pores during the thermal metamorphic event, and were trapped in there when the parent body cooled down to 500°C. We noted several unresolved problems in [2], which we focus on in this study. The problems are as follows: (1) Can we explain the N concentrations in taenite by dissolution equilibrium between the N_2 gas and the metal phase? At 500°C, the N gas pressure is required to be around 1 bar to be equilibrated with 10 ppm of N dissolved in taenite, if the dominant N gas species were N_2. If the gas transportation in the H chondrite parent body occurred very efficiently, the gaseous elements may be totally lost from the interior of the parent body. (2) Can we maintain N isotopic heterogeneity within a single thermally evolving parent body? If the gas transportation (isotope homogenization) occurred very effectively at the interior, we may not expect any isotopic heterogeneity remaining among the equilibrated ordinary chondrites, even if there existed a large spatial-scale isotopic heterogeneity among the accreted materials [2,3].

We carried out numeric simulations solving the transportation equations described in the next paragraph, combined with calculations for heat transportation and chemical reactions. Many of the basic parameters are the same as in [1], and the thermal model is entirely the same as in [1]. We assumed an isochemical starting material, containing volatiles (H, C, N, and O) homogeneously. We also assumed a homogenous heat source in the parent body, in this case ^{26}Al, whose amount is enough to make the maximum temperature at the center of the parent body 850°C. In addition, we added slightly different amounts of ^{15}N so that the N isotopic composition in the starting material differs from the planetesimal. Starting from

these initial conditions, we simulated two-dimensional gas flows in radial (r) and longitudinal (θ) directions. During the thermal metamorphic event, we calculated chemical reactions between gas species and their dissolution into metal phases. We assumed that the O pressure is buffered by redox reaction between fayalite and metallic Fe.

In order to simulate the gas transportation, we formulated the transportation equations, modifying the equations described in [2,4] to better simulate the gas transportation of minor species and isotopes. Two equations are formulated depending on the two flow modes, viscous flow (1 « L) and molecular flow (1 » L), where L is the effective diameter of the flow path, which is comparable to the pore size or the crack opening size, and 1 is the mean free path of the gas molecules. The flow equation in the viscous case is described as

$$v_{i(vis)} = -[k_0/u_0 \times dP_0/dy + D \times d(\ln X_i)/dy]$$

where v is gas flow velocity, P is gas pressure, X is gas fraction ($= P_i/P_0$), k is gas permeability, u is viscosity, and D is the gas diffusion coefficient. The suffixes 0 and i are the total fraction and respective gas species (therefore $P_0 = \Sigma P_i$, for example). The first term in the equation is called Darcy's law. The gas permeability k of ordinary chondrites is estimated by [5]. In the viscous case, the flow speed determined by Darcy's law is proportional to the total pressure gradient. Since we assume isochemical starting materials, there is no total pressure gradient in the θ direction. Therefore, the homogenization of N isotopes within the θ direction can be driven only by gas diffusion, the second term of the equation. Comparing $k_0/u_0 \times P_0$ and D, both parameters with a dimension of m^2/s, D is smaller than the first parameter at a high-pressure region such as $P_0 \approx 10^7$ (Pa). Therefore, we expect inefficient isotopic homogenization effects during the viscous flow mode. The isotope homogenization occurs much more efficiently in the molecular flow mode, whose flow equation is described as

$$v_{i(mol)} = -[(1 - L/l) k_i/u_i \times dP_i/dy + L/l \times v_{i(vis)}]$$

However, the total mass transported during the molecular mode is less than the amounts transported during the viscous mode because the molecular mode is applied only when the total pressure is low, for example, below 10^5 (Pa).

References: [1] Sugiura N. et al. (1986) *EPSL, 78,* 148–156. [2] Hashizume K. and Sugiura N. (1997) *GCA, 61,* 859–872. [3] Sugiura N. and Hashizume K. (1992) *EPSL, 111,* 441–454. [4] Sugiura N. et al. (1987) *Mem. NIPR Spec. Issue, 46,* 216–225. [5] Matsui T. et al. (1986) *Meteoritics, 21,* 109–116.

AN EXPERIMENTAL STUDY OF MAGNETITE FORMATION IN THE SOLAR NEBULA.

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Introduction: Chemical equilibrium calculations predict magnetite formation at low temperatures [1,2] in the solar nebula via the net thermochemical reaction: 3Fe (alloy) + $4H_2O$ (gas) = Fe_3O_4 (magnetite + $4H_2$ (gas). Using a simple collision theory (SCT), Fegley concluded that Fe_3O_4 formation under nebular conditions
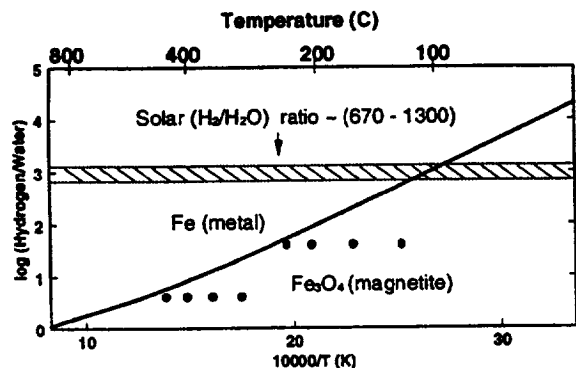
Fig. 1. Equilibrium between Fe (metal) and Fe_3O_4 (magnetite). The shaded area is the solar H_2/H_2O ratio range. Magnetite is stable at ≤100°C under nebular conditions. The experimental points are shown by dots.

from 0.1-μm-radius Fe grains required ~10^{13} s and thus may or may not be kinetically inhibited over the solar nebular lifetime of ~10^{13} s [3,4]. However, no work on Fe_3O_4 formation kinetics at low temperatures in H_2/H_2O gases is available to test the SCT model predictions. Our goal is to study the kinetics and mechanism of Fe oxidation at low temperatures in gas compositions relevant to the solar nebula to evaluate the possibility of magnetite formation in the solar nebula.

Experimental Methods: Magnetite formation was studied by heating high-purity Fe foil (99.998%) in H_2/H_2O gas mixtures at different temperatures for known periods of time. This approach is analogous to that in our experimental studies of Fe-sulfide formation [5]. Thin Fe foil (~0.5 cm × 0.5 cm × 0.025 cm) was placed next to a Pt-Pt Rh thermocouple in the isothermal zone of the furnace, with 40 cm³ min⁻¹ (STP) H_2/H_2O flow passing by the Fe foil. The H_2O vapor content was controlled by the temperature of an H_2O saturator and the flow rate was regulated by electronic mass flow controllers. Gas chromatography and water uptake by $Mg(ClO_4)_2$ both gave H_2O concentrations in agreement with the expected value at the saturator temperatures. The reaction products were analyzed by X-ray diffraction (XRD) and the reaction extent was monitored by the weight gain of the reacted sample.

Thermodynamic Calculations: The equilibrium between Fe metal and magnetite was calculated using updated thermodynamic data and elemental abundances [6,7]. The results are shown in Fig. 1. Iron is stable above the equilibrium line, while magnetite is stable below the equilibrium line, and both phases coexist on the line. Within the solar H_2/H_2O ratio range, magnetite is stable at ≤100°C. (The distribution of C between CO and CH_4 affects the solar H_2/H_2O ratio.)

Results: The black dots in Fig. 1 show our experimental conditions. X-ray diffraction shows that Fe_3O_4 is formed on our samples. No wüstite or hematite were detected in these runs. Magnetite formation is reversible and depends on the H_2/H_2O ratio. Pure Fe foil heated at 205°C for 7 days in a gas mixture with an H_2/H_2O ratio ~41 gained 60 μg cm⁻² and was partially converted to Fe_3O_4. X-ray diffraction showed only Fe and Fe_3O_4 lines. The color change on the surface of the reacted sample indicates the thickness of the Fe_3O_4 layer [8]. The reacted sample returned to its original weight after heating at 205°C for 4 days in purified H_2. The oxide color disap-

peared, the sample returned to its original appearance, and XRD showed only Fe lines. These observations show that magnetite formed by the oxidation of Fe by H_2O, and that magnetite can be reduced back to Fe when H_2O is not present. Further kinetic experiments are under way.

Summary: Thermodynamic calculations show a magnetite stability field at ≤100°C for the solar H_2/H_2O ratio range. Our experimental data show magnetite formation from Fe oxidized in H_2/H_2O mixtures. The reaction 3Fe (alloy) + $4H_2O$ (gas) = Fe_3O_4 (magnetite) + $4H_2$ (gas) can be reversed when the H_2/H_2O ratio is reduced, proving Fe oxidation by water vapor.

References: [1] Larimer (1967) *GCA, 31,* 1215–1238. [2] Grossman (1972) *GCA, 36,* 597–619. [3] Fegley (1988) in *LPI Tech. Rpt. 88-04,* 51–60. [4] Fegley and Prinn (1989) in *The Formation and Evolution of Planetary Systems,* pp. 171–211, Cambridge Univ. [5] Lauretta et al. (1996) *Icarus, 122,* 288–305. [6] Robie and Hemingway (1995) *USGS Bull. 2131.* [7] Grevesse and Noels (1993) in *Origins and Evolution of the Elements,* pp. 14–25, Cambridge Univ. [8] Kubaschewski and Hopkins (1953) *Oxidation of Metals and Alloys,* Butterworth, London.

LIGHTNING AND SHOCK HEATING AS CANDIDATE PROCESSES FOR CHONDRULE FORMATION.   M. Horányi, Laboratory for Atmospheric and Space Physics, University of Colorado, Boulder CO 80309-0392, USA.

We report on our continued theoretical and experimental investigations on dusty gas and plasma dynamics that lead to short-duration momentum and energy exchange heating events. We have extended our previous test particle simulations to describe aerodynamic shocks and lightning discharges. We are now considering the self-consistent coupling (mass, momentum, energy, and electrostatic charge) between the gas/plasma and the evaporating/condensing chondrule precursor grains. We estimate heating/cooling rates, size distributions, and the depth of the molten-solid interface for the surviving grains as a function of the initial parameters and grain size distributions.

In collaboration with S. Robertson (University of Colorado) and B. Walch (University of Northern Colorado) we have modified an existing experimental plasma physics facility to produce conditions that imitate lightning discharges in the early solar system. We have developed an experimental setup where small precursor grains can be exposed to electrostatic discharges. The first two sets of experiments (~10 samples) showed little or no heating. We are now working on several improvements: (1) fabricating smaller precursors, (2) better electrostatic isolation, and (3) better placement of the samples. We rely on our collaborators to analyze the produced artificial chondrules. R. Hewins (Rutgers University) provided precursor grain material and examined the returned samples.

Independently of the details of their generation, lightning discharges produce an ionized plasma column. The initial plasma parameters (density, electron and ion temperature, and the size of the discharge channel) fully determine the subsequent evolution. In our model calculations we quantitatively describe the history of the discharge channel simultaneously with the thermodynamics of the

embedded dust grains. The expected plasma conditions of a discharge in the early solar system cannot be reproduced in our laboratory experiments. We adapt the theoretical models to the laboratory plasma conditions to verify the calculations. Using the measured history of the plasma parameters of our experimental device as model inputs we calculate energy deposition rates and predict critical grain sizes that could produce fully or partially melted samples.

Lightning discharges are likely to occur in high-dust-density regions of the solar nebula where dust grains have a wide particle size distribution. One expects that a larger population of particles, smaller than the characteristic chondrule size, fully vaporize and produce plasma and neutral gas, mass loading the original plasma. Also, the bigger particles can get entrained and drain the momentum of the expansion. In collaboration with A. Körösmezey (KFKI, Budapest, Hungary) we now self-consistently model the expansion of a dusty plasma discharge. The energy deposition, heating, and mass loss from the grains is coupled with continuity equations for the mass, momentum, and energy of the expanding plasma.

The requirement of low electrical conductivity points toward regions in the disk with high dust densities where the grains become the major charge carriers. In these regions, consecutive shocks or density waves could cumulatively build up large electrostatic fields. In a shocked high-gas-temperature region the ionization fraction increases significantly and dust particles can swiftly collect the free electrons and ions via collisions except for the charges residing on the dust grains, since grain-grain collisions are likely to be rare. As the shock passes or dissipates, the gas cools and recombines. Different sizes and/or compositions of the grains can result in different charging histories. For example, due to the higher secondary or photoelectron production, small particles (micrometer-sized) are more likely to collect positive charges and bigger grains (millimeter-sized) are more likely to end up negatively charged. Naturally, at any point charge neutrality is maintained

$$e(n_e - n_i) + \int_{a_{min}}^{a_{max}} Q(a)n(a)da = 0$$

where e is the charge of an electron, n_e and n_i are the electron and ion densities respectively, Q(a) is the average charge (positive or negative) of the particles with radius a, and n(a) is the grain size distribution with the a_{min} the smallest and a_{max} the largest grain considered. Drag sorting separates the oppositely charged small and large particles, perhaps leading to the buildup of large-scale electric fields.

FAYALITIC HALOS WITHIN FORSTERITES FROM CARBONACEOUS CHONDRITES. X. Hua[1] and P. R. Buseck[2], [1]Department of Geology and Chemistry, Arizona State University, Tempe AZ 85287-1404, USA, [2]Department of Biochemistry, Arizona State University, Tempe AZ 85287-1404, USA.

Introduction: Spindle-shaped fayalitic halos occur in forsterites of the Allende, Kaba, Mokoia, Vigarano, and Ningqiang carbonaceous chondrites. The halos (1) are ellipsoidal or round in shape, (2) have round, bleblike inclusions of Ni-rich metal and sulfide in their centers, and (3) have their long axes parallel to each other within given host crystals. The Fe and Mg compositional profiles are well approximated by the error function, which is consistent with a diffusional origin. The relatively high Ni contents of the metal inclusions

relative to kamacite indicates Fe depletion. We propose that the halos formed by the oxidation of the Fe-Ni metal in the inclusions and subsequent Fe^{2+} diffusion into adjoining forsterite.

Petrography and Mineral Chemistry: The fayalitic halos occur either near the surfaces of chondrules or along fractures. All halos within a given host grain have the same shapes in polished surfaces, but they can differ from one grain to another. Some halos appear round, while others are elliptical. By observation of halos in many olivine grains, we conclude that their three-dimensional shapes are ellipsoidal. Using optical microscopy, we determined that the long axes of the elliptical halos are roughly parallel to the c axis of the host olivine. The largest halos are 20 μm long and 6 μm wide. Round inclusions of metal and sulfide occur in the centers of most halos. Some inclusions are elongated; multiple adjacent halos look like several ellipsoids superimposed on one another.

The Fe contents are highest next to the metal and sulfide inclusions and decrease gradually with distance from the inclusions. The most Fe-rich parts of the halos have compositions of ~Fa$_{80}$, and those of the host forsterite are ~Fa$_{1.0}$. The rate of compositional change along specific directions within a given halo depends on their crystallographic orientations; the gradients are flatter parallel to crystallographic c than parallel to other directions. The plots of compositional profiles can be well approximated by the error function. In the case of the multiple fayalitic halos around the elongate inclusions, the Fa contents differ from one analyzed spot to another, even though all the spots are at roughly similar distances from the inclusions.

Inclusions in the centers of the fayalitic halos are polymineralic, probably mixture of Ni-rich metal, Ni-rich sulfides, and minor apatite (whitlockite or other meteoritic phosphates), and silicates.

Discussion: We propose that oxidation and diffusion were important factors in halo formation. The standard Gibbs energies (in joules per mole) were calculated for the formation of FeO and NiO as a function of temperature between 300 and 2000 K. The results show that Fe is more readily oxidized than Ni over this entire temperature range. The residual metal after the oxidation will be Ni rich, which is consistent with the composition of the metal (Ni up to ~50 wt%) in the inclusions. Oxidation of the metal inclusions was accompanied by the production of Ni-rich sulfides.

Both the relative dimensions and the shapes of the compositional profiles indicate that the fayalitic halos formed via diffusion. We assume that the forsterite initially contained small metal inclusions. An increase in f_{O_2} resulted in the development of some Fe^{2+}. Based on experiments [1] and calculations [2], the diffusion of divalent cations in olivine is highly anisotropic and is fastest parallel to the c crystallographic direction. For Fe^{2+}, diffusion parallel to c is 4× faster than along a and 5× faster than along b [1]. Using the relationship, $x^2 = Dt$, we calculated that $x_c:x_b:x_a = 20:9:10$. The most elongated halos have dimensions roughly proportional to the calculated ratios, although some halos have larger ratios.

We generated time-temperature curves by assuming that the maximum diffusion distances are 5, 10, 15, and 20 μm respectively. The plot shows that (1) it would take >10^{10} yr to form even the shortest halo (5 μm) by diffusion at ~560 K; this lifetime is longer than the age of the solar system (4.6 × 10^9 yr); (2) if we take the nebula lifetime as the upper limit for the diffusion, the lowest temperature required to form a 5-μm halo is ~650 K, and ~700 K is needed for a 20-μm halo; and (3) the halos could have formed within a matter of a few years or tens of years at temperatures above 1000 K.

The meteorites that contain the fayalitic halos are all CCs and contain low-temperature minerals such as layer silicates and organic species. The upper temperature limit for such materials depends on the specific species, but it seems highly unlikely that the host meteorites could have been heated sufficiently to permit the halos to have formed *in situ*. The temperatures inferred as feasible from the above alternatives suggest a parent-body origin is unlikely because all organic components would have been destroyed and phyllosilicates would have been dehydrated at the temperatures required to produce the halos.

We are thus left with the possibilities that the halos formed in the nebula prior to incorporation on their respective parent body(ies), or the forsterites have been recycled from an earlier parent body that was heated sufficiently to allow the halos to form. Such a recycled origin would help explain the observed nonequilibrium coexistence of forsterite and fayalite [3], but it makes it difficult to understand the primitive bulk compositions of these meteorites.

Another unresolved problem is what happened to the Mg that was presumably replaced by the Fe in the halos? It is possible that SiO_2 was introduced [4] or that Mg left via a gas phase through minor fractures. This hypothesis is in agreement with the unpublished experimental results of Palme et al. (personal communication). It is clear that important questions remain regarding these intriguing features.

References: [1] Buening D. K. and Buseck P. R. (1973) *JGR*, *78*, 6852. [2] Lasaga A. C. (1980) *Am. Mineral.*, *65*, 1237. [3] Hua X. and Buseck P. R. (1995) *GCA*, *59*, 563. [4] Palme H. and Fegley B. Jr. (1990) *EPSL*, *101*, 180.

PRESOLAR GRAINS AS TRACERS OF NEBULAR AND PARENT-BODY PROCESSING OF CHONDRITIC MATERIAL.

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Presolar grains such as diamond, SiC, graphite, and Al_2O_3 are present in the least-altered members of all chondrite classes [1,2]. These grains reside in the fine-grained "matrix" and did not experience the chondrule-forming process. Because most types of presolar grains are chemically unstable in putative nebular conditions and in chondritic meteorites, they serve as sensitive monitors of nebular and parent-body conditions.

Tracers of Metamorphism: Isotopic and trace-element characteristics of some presolar material and the abundances of presolar grains in "matrix" are functions of the metamorphic history of the host meteorite [1–4]. Currently recognized presolar grains show a range of resistance to metamorphism. If all meteorite classes acquired similar initial mixtures of presolar grains, then the relative abundances of the different types of presolar grains can be used as probes of metamorphism in the host meteorite. In most meteorite classes, graphite and the diamond fraction that carries P3 noble gases are least resistant; SiC is moderately resistant; and diamond and Al_2O_3 are most resistant to parent-body metamorphism. However, in the highly reduced EH chondrites, SiC and diamond are both more stable, and SiC becomes more resistant to metamorphism than diamond [1,2]. These relationships provide a relative scale of metamorphic intensity. An absolute temperature scale for low-grade meta-

morphism may be provided by the P3 noble-gas carrier in presolar diamonds, which appears to release its gases over a limited temperature range, independent of the nature of the surroundings [3].

Tracers of Nebular Processing: In the least metamorphosed meteorites of each class, matrix-normalized abundances of presolar diamonds vary by only a factor of ~2.2 [1,2]. There is also increasingly compelling evidence that each chondrite class acquired the same mixtures of diamonds [3–5] and SiC [6–8]. These observations show that a single widespread reservoir of presolar grains was sampled by all chondrite classes. This reservoir is most plausibly the dust from the solar system's parent molecular cloud.

The CI chondrite, Orgueil, and the matrixes of CM2 chondrites have the highest matrix-normalized abundances of silicon carbide, and graphite, have among the highest diamond abundances, and have diamonds with high N contents and the highest contents of P3 noble gases [1–4]. These characteristics indicate that CI chondrites and the matrixes of CM2 chondrites contain the least-processed sample of the presolar grains' reservoir from the Sun's parent molecular cloud. The CI chondrites and the CM2 matrixes also have the bulk chemical compositions that are most like the composition of the Sun [e.g., 9,10]. As the bulk compositions of the meteorite classes become more fractionated relative to the CI composition, the abundances and characteristics of presolar grains also become increasingly different from those in CI chondrites. For example, EH chondrites are much enriched in total Fe and are much more reduced than CI chondrites. The EH chondrites also acquired higher matrix-normalized abundances of diamond and SiC than CI chondrites and no detectable graphite [1,2]. The CV3 chondrites are enriched in refractory elements such as Ca and Al and in ^{16}O relative to CI chondrites. They also have higher diamond abundances and much lower SiC and graphite abundances than CI chondrites. In both of these classes, the most resistant presolar grains (diamonds and, under reducing conditions, SiC) have higher abundances in the more chemically fractionated material, while the more reactive graphite and the carrier of P3 noble gases are strongly depleted. These correlations suggest that the same processes were responsible for both the abundance differences and the differences in bulk composition and provide insight into those processes.

A nebular model in which the bulk compositions of chondrite classes reflect different degrees of nebular condensation [e.g., 9,11] is inconsistent with presolar-grain abundance data. Presolar grains cannot survive in a solar-composition gas hot enough to evaporate most nebular dust [e.g., 12]. If presolar grains represent a minor component added to the nebula after condensation, then very efficient mixing in the meteorite-formation region would have been required to produce the near-constant diamond abundances in meteorite matrixes. This mixing would have to have taken place without destroying the chemical fractionations produced by condensation. Not only is such a mixing scenario unlikely, this model does not predict or explain the observed correlations between bulk compositions of chondrites and abundances and characteristics of presolar grains. Efficient mixing apparently occurred prior to nebular chemical fractionations and processing of the presolar-grains complex. If so, then chondrite groups could not have resulted from partial condensation of hot nebular gas followed by isolation of the condensates from the nebula [e.g., 9,11].

The currently known presolar grains are only the most recognizable part of a much larger complex of presolar material. This presolar dust, processed in various ways in the solar system, but not evapo-

rated and recondensed, may have been the principal raw material for meteorites and planets. Bulk presolar matter would have had CI (= solar) bulk composition, with the elements partitioned between different kinds of solids ranging from stellar condensates like SiC and graphite to interstellar amorphous material and dirty ices. Similar abundances of refractory presolar grains would be expected in all classes because chondrites would be modified samples of a single initial mixture. Nebular evaporative processing acting on the initial presolar mixture could have produced the chemical fractionations that define the meteorite classes while at the same time producing the variations in abundances and properties of presolar grains [1,2]. If so, then the characteristics and relative abundances of different kinds of presolar materials in unmetamorphosed chondrites are potential probes of nebular processing.

References: [1] Huss G. R. and Lewis R. S. (1995) *GCA, 59,* 115–160. [2] Huss G. R. (1997) in *Astrophysical Implications of the Laboratory Study of Presolar Grains* (T. Bernatowicz, ed.), AIP. [3] Huss G. R. and Lewis R. S. (1994) *Meteoritics, 28,* 811–829. [4] Russell S. S. et al. (1996) *Meteoritics & Planet. Sci., 31,* 343–355. [5] Huss G. R. and Lewis R. S. (1994) *Meteoritics, 28,* 791–810. [6] Huss G. R. et al. (1997) *GCA, 61,* submitted. [7] Huss G. R. et al. (1994) *LPS XXV,* 585–586. [8] Huss G. R. et al. (1995) *LPS XXVI,* 645–646. [9] Larimer J. W. and Anders E. (1967) *GCA, 31,* 1239–1270. [10] Anders E. and Grevesse N. (1989) *GCA, 53,* 197–214. [11] Grossman L. and Larimer J. W. (1974) *Rev. Geophys. Space Phys., 12,* 71–101. [12] Mendybaev R. A. et al. (1997) *LPS XXVII,* 937–938.

CHRONOLOGIC CONSTRAINTS ON SECONDARY ALTERATION PROCESSES.

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A central goal of meteoritics is understanding the chronology of events leading to the transformation (a.k.a. modification) of interstellar precursor material inherited by the nascent solar nebula to form first meteorites and then small planetary bodies by processes of evaporation and condensation, melting and recrystallization, accretion, brecciation, and metamorphism. There is a particular need to distinguish, to the extent possible, chronological differences between nebular and parent-body processes related to specific features in chondritic meteorites. The most direct and readily interpreted information on the timescale of chondrite metamorphism comes from radiometric age dating of "secondary" minerals, i.e., phases produced as a result of metasomatic events in the solar nebula or on parent bodies. Carbonates in CI and CM chondrites and most Ca-phosphates and many feldspars in equilibrated ordinary chondrites are secondary minerals that have been used for this application [1–3]. Two short-lived radionuclide systems have provided strong evidence that metamorphic processes began less than 10 m.y. after formation of the first solar system solids. Excesses of ^{53}Cr, from the decay of ^{53}Mn ($\tau_{1/2} = 3.7$ Ma) in carbonates from Orgueil, indicate an early onset of aqueous activity on the CI planetesimal, only ~15 m.y. after the formation of CAIs [4,5]. This timescale is also commensurate with that inferred for the formation of Fe-Mn-phos-

phates in the IIIAB irons, presumably by (secondary) oxidation of P originally contained in metal [6]. Evidence of radiogenic ^{26}Mg in plagioclase from Ste. Marguerite [7] provides additional evidence for the rapid growth of chondrite parent bodies with cooling below the Al-Mg closure temperature within ~6 m.y. of CAI formation. Data from the ^{129}I-^{129}Xe and U-Pb systems are complementary, supporting the early onset scenario while also indicating that metamorphic activity on some chondrite parent bodies continued over a protracted interval of up to ~60 m.y. [8,9]. Unfortunately, while the range of metamorphic ages from both the I-Xe and U-Pb systems is very similar, most attempts to correlate I-Xe and Pb-Pb ages of individual meteorites have proved unsuccessful. An important exception is recent work demonstrating good agreement for phosphate mineral separates [10]. Most of the chronological data relating to the times of formation of secondary minerals in chondrites, excluding CAIs, indicate relatively long times and appear to "date" parent-body processes, since timescales appear incommensurate with anticipated nebular lifetimes.

References: [1] Richardson S. M. (1978) *Meteoritics, 13,* 141–159. [2] Van Schmus W. R. and Wood J. A. (1967) *GCA, 31,* 747–765. [3] Perron C. et al. (1988) *Meteoritics, 27, 275.* [4] Endress M. et al. (1996) *Nature, 379,* 701–703. [5] Hutcheon I. D. and Phinney D. L. (1996) *LPS XXVII,* 577–578. [6] Hutcheon I. D. et al. (1992) *LPS XXIII,* 565–566. [7] Zinner E. K. and Göpel C. (1992) *Meteoritics, 27,* 311–312. [8] Swindle T. D. and Podosek F. A. (1988) in *Meteorites and the Early Solar System* (J. F. Kerridge and M. S. Matthews, eds.), pp. 1127–1145, Univ. of Arizona, Tucson. [9] Göpel C. et al. (1994) *EPSL, 121,* 153–171. [10] Brazzle P. R. and Hohenburg C. M. (1996) *Meteoritics & Planet. Sci., 31,* A20–A21.

ELEMENTAL REDISTRIBUTION BY AQUEOUS FLUIDS IN UNEQUILIBRATED ORDINARY CHONDRITES: TIESCHITZ AND SEMARKONA COMPARED.

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Introduction: A number of UOCs show signs of hydrous alteration [1,2]. Kurat [1] suggested that in Tieschitz, feldspathic or nepheline-rich mesostases of some pyroxene-rich chondrules had been selectively removed by leaching to produce voids. He found no evidence for redeposition of the leached material elsewhere, but this was disputed [3]. The products of aqueous alteration were discovered in Semarkona (and Bishunpur) by Hutchison et al. [2]. Chondrule mesostases, anhydrous silicates, and sulfide have been partially altered to smectite [4] with little production of voids. Tieschitz matrix contains a second generation of Fe-rich olivine, whereas in the matrix of Semarkona Fe-rich olivine is absent [4,5]. We compare the mineralogical and chemical characteristics of the matrixes of the two meteorites to try to identify the processes that acted on the respective parent bodies.

Tieschitz: Tieschitz has a chemical composition between H and L groups, is petrographic subtype 3.6 [6], and is texturally

unique. The presence of fine-grained opaque rims—dark matrix [3]—around chondrules and other objects is not uncommon in UOCs, but additionally, in Tieschitz, white matrix fills channels between the chondrules. These channels are a few tens of micrometers wide and their filling generally abuts the dark rims of the bounding chondrules. In polished thin section, white matrix is transparent (white), with low birefringence and low reflectivity. In the SEM it appears dark and blocky on a 5–20-mm scale [3]. Grains of albite and nepheline may be present [7] and the norm has 50% albite and 25% nepheline [8]. Rare ferromagnesian mineral fragments occur and unidentified, Na-, Al-rich phases may be abundant [5]. Christophe Michel-Levy [3] agreed with [1] that some chondrule mesostases had been removed, but argued that the material had been redeposited to form white matrix. Hutchison et al. [7] disagreed and suggested that white matrix formed by the crystallization of mesostases expelled from hot, deforming chondrules. New observations, however, led Hutchison et al. [9,10] to accept that leaching and elemental redeposition had also occurred.

Reinvestigation of Tieschitz [9,10] was prompted by the accidental discovery of two types of mesostasis coexisting within five porphyritic olivine (PO) chondrules. The proportion of chondrules with voids was determined from a photomosaic of backscattered electron images representing a 35-mm² area: 30 of 101 chondrules contain discernible voids. As observed by [3], some voids have acicular crystals—parts of augite dendrites—extending inward from their walls, so the voids are natural. Thus, primary voids or voids due to leaching are an important feature of the meteorite. In the SEM, some mesostasis appears to be dark and blocky, like white matrix, whereas most is bright and smooth. Augite dendrites are present throughout both types of mesostasis but are absent in white matrix. In a porphyritic olivine-pyroxene (POP) chondrule the two types are present without augite dendrites. Dark, blocky mesostasis proved to be chemically similar to white matrix, being rich in Al_2O_3, Na_2O, K_2O, Ba, Cl, and F and poor in Ca [10] relative to bright, smooth mesostasis.

The five PO chondrules are typical of Tieschitz. Their longest dimensions range from 0.6 to 1.0 mm, they are largely surrounded by opaque, fine-grained rims and they are somewhat misshapen. Departure from a circular outline is the result of abrasion or of mutual indentation by neighboring objects. Chondrule outlines are flattened and the dark rims attenuated or absent at their contacts. In all five PO chondrules the phenocrysts are zoned, Ca-poor pyroxene is absent, and, as in most Tieschitz chondrules [3], augite dendrites are present throughout the mesostases. In one chondrule the olivines have cores of Fo_{90} with Fo_{75} rims, zoned to Fo_{57} at the chondrule margin. In this chondrule the augite dendrites have a uniform composition close to $Wo_{38}En_{43}Fs_{19}$, with 1–2 wt% Cr_2O_3, whether set in bright and smooth or dark and blocky mesostasis.

As already noted, except for the presence of augite dendrites, blocky mesostasis in the five PO chondrules resembles white matrix. Kurat [1] and Christophe Michel-Levy [3] observed that the mesostases of pyroxene-rich chondrules are most suceptible to leaching; such chondrules are more likely to contain voids, especially near their margins. One porphyritic olivine-pyroxene (POP) chondrule was found with its mesostasis largely intact. This chondrule has no augite dendrites but has both types of mesostasis. Olivine phenocrysts (Fo_{69-52}) are overgrown by platy, Ca-poor pyroxenes (Wo_3 En_{67}) with thin, irregular overgrowths of Ca-rich pyroxene ($Wo_{<17}$ $En_{53}Fs_{>30}$). The pyroxene phenocrysts extend across the contact

between the two types of mesostasis without compositional change, which indicates that a single chondrule liquid was involved. They make straight, sharp contacts with bright, smooth mesostasis, but their contacts against dark mesostasis are irregular and marked by voids.

Dark, blocky mesostasis probably formed *in situ* by the aqueous alteration of primary bright mesostasis. White matrix may have formed by the alteration of mesostases expelled from deforming chondrules [see 3, Fig. 2] with no dendritic augite. Dendrites would have inhibited the expulsion of mesostasis from chondrules.

Semarkona: Semarkona belongs to petrographic subtype 3.0 [6]. As in Tieschitz, aqueous alteration affected chondrules and matrix together. Semarkona, however, contains few optically observable voids, but porosity is revealed in the TEM (Fig. 3 in [4]). Textural relationships indicate that smectite and other products directly replaced mesostasis, olivine, pyroxene, and sulfide, without large-scale elemental redistribution. Because of the volume increase entailed in converting anhydrous precursors to smectite, some elemental loss or redistribution is required. For example, during hydrous alteration, Ca was not taken up by smectite but was fixed in calcite [4].

Discussion: The question arises, could Tieschitz have undergone aqueous alteration to a similar degree to that experienced by Semarkona, followed by dehydration and mild thermal metamorphism? Alexander et al. [5] noted that Semarkona matrix is significantly enriched in Al ($\times 1.6$–2.0), Na ($\times 2.4$–2.9), and K ($\times 6.8$–7.0), and depleted in Ca ($\times 0.4$–0.5) relative to the bulk meteorite. In contrast, Tieschitz dark matrix is only slightly enriched in Al ($\times 1.3$) and Na ($\times 1.4$–1.8), highly enriched in K ($\times 6.3$–6.5), and undepleted in Ca relative to the bulk meteorite. Is it possible, then, that Semarkona matrix could have been chemically fractionated by dehydration and recrystallization to yield the mineral assemblages found in Tieschitz white and dark matrix?

Simple chemical calculations argue against this. The silicate component of Semarkona matrix (Table 1, no. 1) could yield 66 wt% olivine, Fo_{47}, within the range of Tieschitz matrix olivines [5], plus 34 wt% of a felsic component. The felsic component is then recalculated to 100 wt% for comparison with white matrix (Table 1, nos. 4 and 5). White matrix is significantly poorer in SiO_2 and K_2O than the felsic component of Semarkona matrix. Loss of these oxides from the felsic component could indeed produce a composition similar to white matrix. Tieschitz may therefore have suffered a net loss, albeit

TABLE 1.

	1*	2*	3*	4*	5*
SiO_2	46.7	22.8	23.9	70.5	58.7
Al_2O_3	5.2	—	5.2	15.3	19.1
FeO	28.9	28.9	—	—	5.0
MgO	14.4	14.4	—	—	3.5
CaO	1.26	—	1.26	3.7	4.0
Na_2O	2.77	—	2.77	8.2	9.3
K_2O	0.76	—	0.76	2.2	0.4
Sum	99.9	66.1	33.9	99.9	100.0

*1 = Semarkona matrix silicate (Table 2, no. 8, in [2]) recalculated to 100 wt%; 2,3 = analysis 1 apportioned into olivine, Fo_{47}, and felsic components; 4 = the felsic component, 3, recalculated to 100 wt%; 5 = white matrix [5, Table 3, no. 1].

small, of SiO_2 and K_2O. The question is, when? If matrix is largely the product of comminution of chondrules [5], Tieschitz chondrules, on average, may have been less siliceous and less potassic than those in Semarkona. Certainly, many Tieschitz chondrules have nepheline-normative mesostases [7] whereas many Semarkona chondrules have quartz-normative mesostases [5]. Alternatively, leaching by aqueous fluid may have removed some SiO_2 from Tieschitz. In any case we are left with the conclusion that the two chondrites differ in primary silicate chemistry or in postaccretional history.

References: [1] Kurat G. (1969) in *Meteorite Research* (P. M. Millman, ed.), pp. 185–190, Reidel, Dordrecht. [2] Hutchison R. et al. (1987) *GCA, 51*, 1875. [3] Christophe Michel-Levy M. (1976) *EPSL, 30*, 143. [4] Alexander C. M. O'D. et al. (1989) *GCA, 53*, 3045. [5] Alexander C. M. O'D. et al. (1989) *EPSL, 95*, 187. [6] Sears D. W. G. et al. (1980) *Nature, 287*, 791. [7] Hutchison R. et al. (1979) *Nature, 280*, 116. [8] Wlotzka F. (1983) in *Chondrules and their Origin* (E. A. King, ed.), pp. 296–318, LPI, Houston. [9] Hutchison R. (1992) *Meteoritics, 27*, 236. [10] Hutchison R. et al. (1994) *Meteoritics, 29*, 476.

ANHYDROUS ALTERATION OF ALLENDE CHONDRULES IN THE SOLAR NEBULA.

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All the Allende chondrules experienced more or less secondary anhydrous alteration after their consolidation. The anhydrous alteration includes three different processes: (1) formation of secondary olivine zonation, (2) replacement of phenocrystic enstatite by ferroan olivine, and (3) replacement of groundmassic plagioclase and feldspathic glass by nepheline and sodalite. The degree of each process varies among Allende chondrules.

Formation of Secondary Olivine Zonation: Olivine in most Allende chondrules shows normal Mg-Fe zoning from magnesian cores to ferroan rims; the olivine cores range mainly from Fo_{90-100}, and the rims are mostly Fo_{70-95} [1]. The normal zoning of chondrule olivine was not due to igneous processes in the chondrule liquid droplets, because the coexisting pyroxenes that crystallized after olivine in chondrules have much larger Mg/(Mg + Fe) ratios than the ferroan olivine rims. The normal zoning of chondrule olivine may have been produced by Mg-Fe exchange with an ambient oxidized gas through body diffusion in olivine. The Mg-Fe diffusion coefficients of olivine suggest that the normal zoning formed at temperatures higher than 600°C [1]. As the coexisting pyroxenes never show Mg-Fe zoning, the Mg-Fe diffuison in olivine must have taken place under conditions where Mg-Fe diffusion was blocked for pyroxenes.

Replacement of Phenocrystic Enstatite by Ferroan Olivine: Phenocrystic enstatite in Allende chondrules is often replaced by ferroan olivine especially in the peripheral portions of chondrules. The replacing olivine has a compositional range of Fo_{50-70}, and is more ferroan than the rims of the normally zoned olivine, suggesting that the replacement took place after the formation of the secondary olivine zonation.

Replacement of Groundmass Plagioclase and Feldspathic Glass by Nepheline and Sodalite: Cryptocrystalline groundmasses in Allende chondrules are often devitrified and opaque under a microscope especially in the peripheral portions of chondrules. This devitrification was caused by secondary anhydrous alteration mainly

due to replacement of the plagioclase component of cryptocrystalline groundmasses by nepheline and sodalite. In addition, groundmass plagioclase in Allende chondrules sometimes suffers replacement by nepheline or sodalite. This replacement was caused by substitution of Ca of plagioclase component by 2Na that were introduced from outside chondrules:

$$CaSi_2Al_2O_8 + 2Na \rightarrow Na_2Si_2Al_2O_8 + Ca$$
An component   Gas   Nepheline   Ca phases
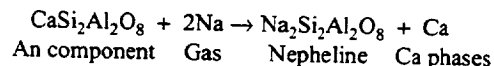
where the Ca atoms in the right hand of the reaction equation were partly expelled outside the chondrules and partly used to produce Ca-rich phases in the same chondrules. The Ca-rich phases are hedenbergite, andradite, grossular, kirschsteinite, and wollastonite, and commonly occur in close association with nepheline and sodalite [2]. The secondary altered groundmasses including nepheline and sodalite often contain fine-grained ferroan olivine grains with Fo_{50-70}, suggesting that the replacement took place at the same time as the replacement of phenocrystic enstatite by ferroan olivine. Heating experiments to produce nepheline from plagioclase crystals and feldspathic glass beads were performed to estimate the formation conditions, and the results suggest that the formation of nepheline in Allende chondrules took place at temperatures of 400°–600°C [3].

Nebular Process for the Secondary Anhydrous Alteration: According to O three-isotope plot [4], Allende chondrules form "a chondrule mixing line," which differs from "an inclusion mixing line." The highly altered chondrules studied are plotted on the chondrule mixing line and never deviate toward the inclusion mixing line, indicating that the secondary anhydrous alteration took place in an oxidized gas that is different in O isotopic composition from those for Allende inclusions, matrix, and dark inclusions. This difference in O isotopic composition, as well as the features of the anhydrous alteration of Allende chondrules stated above, suggests that nebular process is preferable to parent-body processes for the secondary anhydrous alteration of Allende chondrules.

References: [1] Ikeda and Kimura (1995) *Proc. NIPR Symp. Antarct. Meteorites, 8*, 97–122. [2] Kimura and Ikeda (1995) *Proc. NIPR Symp. Antarct. Meteorites, 8*, 123–138. [3] Ikeda and Kimura (1996) *Proc. NIPR Symp. Antarct. Meteorites, 9*, 51–68. [4] Clayton et al. (1983) in *Chondrules and Their Origins* (E. A. King, ed.), pp. 37–43, LPI, Houston.

THE KAIDUN METEORITE: EVIDENCE FOR PRE- AND POSTACCRETIONARY AQUEOUS ALTERATION.

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The processes of aqueous alteration of carbonaceous chondrite constituents are still the subject of fiery debates. Some evidence exists supporting that such processes took place on or in meteorite parent bodies, but evidence for preaccretionary aqueous alteration of chondritic constituents, possibly in the solar nebula, also exists. Evidence for some hydrous chondritic constituents being precipitated directly from the gas phase, presumably in a locally fractionated solar nebula, is also apparent.

We found abundant evidence of aqueous alteration in an EH chondrite fragment #02.04 from the Kaidun heterogeneous breccia [1]. The fragment consists of enstatite, albite, silica, graphite, kamacite, perryite, schreibersite, troilite, niningerite, and "hydrodaubreelite," and contains three types of Fe-rich oxide phases, which apparently formed from preexisting metal and schreibersite. Analyses obtained by EMP are all characterized by low totals, which indicates the presence of a light element, very likely H. The phases are distinguished by both their chemical composition and their location within the fragment. Phases I and II are characterized by a large variation of both major (SiO_2 2.6–41.6 wt% and Fe 23.1–69.5 wt% respectively) and all minor element contents and usually have a high content of Cl (<2.4 wt%) and a Na_2O/K_2O ratio >1. Phase I has high Ni (<24.6 wt%) and S (<16.5 wt%) contents and low Al_2O_3 (<1.5 wt%) and MgO (<1.4 wt%) contents. In contrast, phase II has low Ni (<1 wt%) and S contents (<1.7 wt%) and high Al_2O_3 (<21 wt%) and MgO contents (<16.5 wt%).

Phase III is characterized by a rather homogeneous chemical composition and low contents of minor elements. It is rich in SiO_2 (41.3 wt%) and FeO (43.3 wt%), poor in all other elements, has a Na_2O/K_2O ratio near 1, and is free is of Cl.

Phases I and II occur in the peripheral zones of Ni,Fe-metal grains located near the surface of the fragment. Sometimes a complete replacement of the metal grain is observed, but the primary "metallic" morphology of the grain is preserved. No regularity in a real distribution of phase III was found. It is present mainly as irregular grains, in which small enstatite grains are occasionally included. This situation is rather typical for Ni,Fe-metal grains of the unaltered sample.

The chemical composition, morphology, and location of phases I and II permit us to identify them as the product of aqueous alteration of Ni,Fe metal and schreibersite, which very likely took place late and at low temperatures. This low-temperature alteration could have taken place in the Kaidun parent body [2]. Another possible place could have been some porous zones within the rock that permitted fluids to percolate.

The chemical homogeneity of phase III appears to indicate that formation took place under equilibrium conditions, a situation that is different from phases I and II. The difference in the formation conditions is reflected in a different chemical composition. This equilibrium alteration must be due to higher temperatures and/or longer duration as compared to those that formed in phases I and II.

Considering the widespread survival of highly reactive and reduced phases in the Kaidun breccia [1,3], it is hard to conceive that the alterations described here all took place in the Kaidun rock. At least, the high-temperature alteration must be of pre-Kaidun age, whatever the origin of that complex chondritic breccia might be. The type of alteration found in this fragment is typical of aqueous alterations in many other meteorites: (1) Alteration did not uniformly affect the meteorite, or even the fragment in question. It therefore must have occurred before the final assemblage. (2) Alteration did not convert metal completely into oxides, reflecting the very limited extent of this aqueous alteration in meteorites. No evidence for large amounts of water penetrating the meteorite exists, in spite of the fact that it contains abundant CI/CM-type chondrite fragments. The kind of alteration seen here and in other meteorites is, therefore, much more easily rationalized in terms of reaction of solids with vapor before accretion of the meteorite.

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References: [1] Ivanov A. V. et al. (1989) *Geochem. Intl., 26,* 84–91. [2] Ivanov A. V. et al. (1993) *Geochem. Intl., 30,* 11–19. [3] Kurat G. et al. (1997) *Meteoritics & Planet. Sci.,* submitted.

ALTERATION OF PLAGIOCLASE-RICH CHONDRULES IN CO3 CHONDRITES: EVIDENCE FOR LATE-STAGE SODIUM AND IRON METASOMATISM IN A NEBULAR ENVIRONMENT.

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Introduction: A suite of plagioclase-bearing chondrules in CO3 chondrites shows evidence for extensive Na and Fe metasomatism. An important question to address is whether this metasomatism took place in the nebula, as a result of interactions with a low-temperature gas, or whether it took place on the CO parent body after accretion. The CO parent body is known to have undergone an episode of thermal metamorphism, so it is possible that some or all of the observed alteration was associated with this episode. However, this style of metasomatism is also commonly associated with CAIs, in which it is understood to have happened in the nebula. Petrographic observations suggest that the metasomatism did indeed occur in the nebula, and that parent-body metamorphism left a secondary overprint on the metasomatized chondrules after accretion.

Observations: We have studied nine chondrules from CO3 chondrites that have a "basaltic" texture, with primary pyroxene and plagioclase phenocrysts. These chondrules were first described by [1] in Lancé. A similar object from Ornans was described by [2]. We have searched 19 thin sections of a total of 13 different CO chondrites, and the nine chondrules we found are in four different chondrites: Kainsaz, subtype 3.1 [3,4], Lancé, subtype 3.4 [3], and ALHA 77003, and its paired chondrite, ALH 83108, subtype 3.5.

These chondrules have complex primary mineralogies and crystallization histories. They are reduced and contain Fe,Ni metal and FeS, and their silicate mineralogy consists of plagioclase (An_{80-90}) and pyroxene phenocrysts that usually consist of orthopyroxene cores with augite overgrowths. Many of the chondrules also contain discrete units of clinoenstatite with olivine enclosed in a poikilitic texture. Primary compositions of olivine and pyroxene are inferred to have high Mg/(Mg+Fe) ratios (Fa and Fs <2), consistent with the presence of metal. The primary groundmass contains silica and glass. One chondrule contains an inclusion of plagioclase and nepheline with numerous spinel inclusions. A similar inclusion was observed in one of the chondrules described by [1]. Russell et al. [5] describe a CAI in Isna with a similar texture, which is a potential precursor for the spinel-rich inclusions in the plagioclase-bearing chondrules.

The chondrules appear to have undergone extensive secondary Na and Fe metasomatism. Introduction of Na into the chondrules resulted in partial nephelinitization of plagioclase. Nepheline occurs as an intergrowth texture within the plagioclase crystals (Fig. 1). Introduction of Fe resulted in Fe-Mg exchange in olivine and spinel to form zoned grains, and reactions with silica in the groundmass to form ferrosalite (Fe and Ca-rich pyroxene).

Location of Metasomatism: It is important to understand whether Fe and Na were introduced contemporaneously. Iron-magnesium exchange in olivine and spinel also occurs during parent-body metamorphism, as a result of equilibration of FeO-poor minerals in chondrules and FeO-rich matrix. It is necessary to disentangle

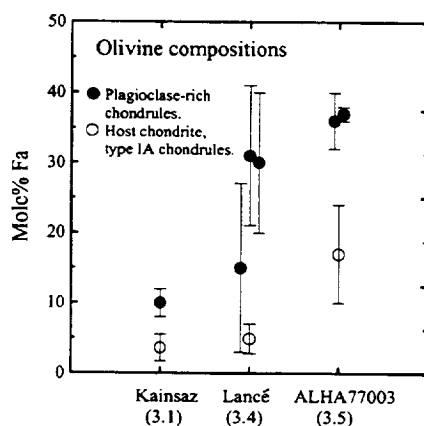Fig. 1. Metasomatic textures in a Kainsaz chondrule.

Fig. 2. Olivine compositions compared with olivine in type IA chondrules in the host chondrites.

the effects of metamorphism in order to understand the metasomatic process clearly. One way to evaluate this question is to compare the composition of olivine in the plagioclase-bearing chondrules with olivine of similar primary composition from ferromagnesian chondrules in the same chondrites. In all cases, Fa contents of olivines in the plagioclase-bearing chondrules are considerably higher than values expected from metamorphism *in situ* (Fig. 2). For Kainsaz, Lancé, and ALHA 77003/ALH 83108 mean Fa contents are 10, 15–30, and 37, compared with Fa contents of 4, 5, and 17 respectively for type IA chondrules from the host meteorites [6]. This suggests that at least some Fe was introduced prior to incorporation of the chondrules into the parent body. The Fa contents of olivines in the plagioclase-bearing chondrules correlate with petrologic subtype. This is probably the result of a secondary metamorphic overprint on the metasomatized compositions.

The question of where metasomatism occurred can also be addressed by examining the degree of alteration of similar objects in the

same chondrite. For the two chondrules in Kainsaz, low degrees of nephelinitization and preservation of significant amounts of silica in the mesostasis indicate a similar, low degree of metasomatism. Qualitatively, the chondrules in Lancé show similar degrees of alteration to each other, including almost complete replacement of silica and intermediate degrees of nephelinitization. However, one chondrule has significantly lower Fa in olivine than the others (Fig. 2). In ALHA 77003 and ALH 83108, three chondrules show distinctly different degrees of alteration, from almost no nepheline in one chondrule to very high proportions of nepheline in the other two. For the chondrule with the low proportion of nepheline, olivine compositions (Fa_{37}) are similar to compositions in a heavily metasomatized chondrule a few millimeters away in the same thin section (Fa_{36}). This implies that the degree of Fe metasomatism is considerably higher than the degree of Na metasomatism, and that the two processes are decoupled. The degree of alteration of silica in the groundmass of such a chondrule would help to clarify if this were the case, but unfortunately no silica or its reaction product has been observed in this chondrule. In all the other chondrules studied, the degrees of Fe and Na metasomatism appear to be quite well correlated.

These observations suggest that the metasomatism did not take place on the parent body of the CO chondrites. It appears to have taken place in the nebula, before accretion. This is consistent with the style of alteration observed in CAIs in the CO chondrites [5].

Timing of Metasomatism: If metasomatism took place in the nebula this has further implications for the nebular environment. Obviously, metasomatism must have occurred after formation of the plagioclase-bearing chondrules. A study of Mg isotopes in the two Kainsaz chondrules [7] shows no evidence for the presence of excess ^{26}Al, indicating that they formed ~3 Ma after most CAIs. Either metasomatism occurred over an extended period of time, or it took place very late in solar nebula evolution, affecting both chondrules and CAIs at the same time. The latter scenario is more consistent with a period in which volatile elements were condensing at a late stage. Formation of the plagioclase-bearing chondrules apparently preceded formation of ferromagnesian chondrules in which no effects of metasomatism are observed.

References: [1] Kurat G. and Kracher A. (1980) *Z. Naturforsch., 35a,* 180–190. [2] Palme H. and Wlotzka F. (1981) *Meteoritics, 16,* 373–374. [3] Jones R. H. and Brearley A. J. (1994) *LPS XXV,* 641–642. [4] Jones R. H. and Hutcheon I. D. (1996) *Meteoritics & Planet. Sci., 31,* A67–A68. [5] Russell S. S. et al. (1997) *GCA,* submitted. [6] Scott E. R. D. and Jones R. H. (1990) *GCA, 54,* 2485–2502. [7] Hutcheon I. D. and Jones R. H. (1995) *LPS XXVI,* 647–648.

A TRANSMISSION ELECTRON MICROSCOPE STUDY OF THE MATRIX MINERALOGY OF THE LEOVILLE CV3 (REDUCED-GROUP) CARBONACEOUS CHONDRITE: NEBULAR AND PARENT-BODY FEATURES. L. P. Keller, MVA, Inc., 5500 Oakbrook Parkway, Suite 200, Norcross GA 30093, USA (lkeller@mvainc.com).

Introduction: McSween [1] divided the CV chondrites into oxidized and reduced subgroups based on the chemistry and mineralogy of the opaque phases. The reduced members have been mini-

mally affected by thermal metamorphism and aqueous alteration and so appear to be mineralogically more primitive than the more altered oxidized subgroup, and their mineralogy and petrography may provide key data on nebular and parent-body processes that were operating in the early solar system. While a number of detailed studies on an oxidized subgroup of CV3 chondrites have been reported, little is known about the reduced members of the CV group. In this report, the results of a transmission electron microscope (TEM) study of the matrix mineralogy of the Leoville CV3 (reduced-group) carbonaceous chondrite are described.

Methods: Regions of interest were extracted from petrographic thin sections and prepared for TEM analysis by ion milling. The ion-milled specimens were analyzed using a JEOL 2010 TEM equipped with a NORAN thin-window energy-dispersive X-ray (EDX) spectrometer. Fourier transform infrared (FTIR) transmission spectra were collected using a Perkin-Elmer infrared microscope equipped with a thermal emission source. Spectra were obtained from 30-μm^2 regions of matrix in the ion-milled sections over the wavelength range 2.5–15 μm.

Results: Leoville matrix is dominated by fine-grained (typically <1 μm) olivine with a restricted compositional range between Fo_{40} and Fo_{50}. Coarser-grained olivine shows a broader range of compositions from Fo_{40} to Fo_{90}. The majority of olivines are highly strained, and are generally equant grains. The lath-shaped and tabular olivines common to oxidized CVs (e.g., Allende) are not observed in Leoville matrix. Only rarely are olivines with (100) stacking faults observed, whereas these defects are common in matrix olivines from the oxidized group (Bali, Kaba, Mokoia, and Grosnaja).

Low-Ca pyroxene is more abundant and coarser grained than high-Ca pyroxene in Leoville matrix. Low-Ca pyroxene is also more abundant in Leoville than in the oxidized CVs (based on TEM and FTIR results). The low-Ca pyx occurs as rounded grains and plates that are typically 0.5–1 μm in size; electron diffraction and HRTEM data indicate a mixture of ortho- and clinopyroxene intergrown on a fine scale. Rare twinned pyroxene grains showing only a 0.9-nm repeat (e.g., clinoenstatite) are also observed. No trace-element enrichments were noted by EDX (e.g., no pyx compositions with Mn/ Fe > 1 were observed). Low-Ca pyx is very Mg rich (>En_{96}) and contains trace Cr and Al in addition to the minor Ca and Fe. The low-Ca pyroxene occurs as isolated single crystals and in clusters of crystals. In both occurrences, the pyx is intimately associated with fine-grained metal and fayalitic olivine. Sparse grains of high-Ca pyx (augites) are intergrown with the fine-grained olivine in matrix and range in composition from $Di_{40}Hd_{60}$ to $Di_{80}Hd_{20}$.

Matrix is essentially devoid of feldspar/feldspathoids, and no phyllosilicates have been observed to date, although minor rust staining occurs throughout the section and is dominated by a poorly crystalline ferrihydrite-like phase. The only commonly encountered Al-rich phase in Leoville matrix is hercynitic spinel. The hercynites tend to be small, anhedral, and Cr-bearing. The hercynites are Fe rich with Mg/Mg + Fe (at.) clustering about 0.32.

Metal is the dominant opaque phase in Leoville matrix and appears to be uniformly distributed in matrix. Grain sizes are variable, but most of the metal is submicrometer in size and consists of kamacite (~5 atom% Ni) and taenite (with 40–55 atom% Ni). Electron diffraction confirms the presence of bcc and fcc metal and the lack of ordered variants (e.g., tetrataenite) and FeNi carbides. Poorly graphitized carbon (PGC) occurs as discontinuous rims up to 20 nm thick surrounding many of the submicrometer taenite grains in ma-

trix. Much of the metal in Leoville matrix shows an unusual morphology, occurring as highly anhedral grains (nearly skeletal) with numerous embayments and reentrant features. Most are single crystals, although some of the larger metal grains are polycrystalline.

Sulfides (mostly troilite along with minor low-Ni pyrrhotite) are uncommon in Leoville matrix, and tend to be coarse-grained relative to the other matrix phases.

Leoville matrix lacks the Fe-rich and Ni-rich phases such as hedenbergite, fayalitic olivine (Fa > 60), magnetite, pentlandite, and high-Ni taenite (awaruite) that are common in the oxidized CV chondrites. In addition, Leoville has been strongly deformed, resulting in chondrule flattening, compaction of matrix, and the deformation of individual mineral grains [e.g., 2].

Discussion: The TEM results on Leoville matrix show that it is mineralogically very primitive, consistent with thermoluminescence data, which indicate a petrologic type 3.0 [3]. Although Leoville displays a shock overprint, the deformation was not accompanied by significant thermal metamorphism. The lack of thermal effects combined with the absence of aqueous alteration products suggests that many of the phases in Leoville matrix should retain chemical and mineralogical features that were acquired prior to accretion. For example, a common assemblage in Leoville matrix is the coexistence of enstatite, kamacite, and fayalitic olivine that are in contact at the micrometer scale, yet show no evidence for equilibration or reaction. This result suggests that much of Leoville matrix is a mechanical mixture of minerals that formed prior to accretion. It is not clear whether the enstatite microstructures in Leoville matrix result from shock effects as suggested by [2], or whether they simply represent the inversion of protoenstatite to mixtures of clino- and orthoenstatite on cooling from high temperatures.

The metal grains rimmed by poorly graphitized carbon (PGC) in Leoville matrix are mineralogically and texturally similar to the metal-C assemblages in some IDPs [4] and ordinary chondrites [5]. In these occurrences, the PGC is believed to form by catalytic disproportionation of CO by fine-grained FeNi metal in a nebular setting. A similar origin is proposed here for the metal-PGC assemblages in Leoville. A nebular origin of the submicrometer metal in matrix is also suggested by its etched appearance. Chemical etching on the parent body is unlikely because of the paucity of aqueous alteration products in matrix. Futhermore, the PGC follows the irregular outline of the metal grains, which indicates that the metal had the morphology prior to being rimmed by PGC. The metal morphologies show some similarities to grains in IDPs that are believed to have been physically etched by ionizing radiation in a nebular or presolar environment [6].

Previous work has shown that Leoville is more strongly shocked than other CV chondrites [2], and while matrix olivines have been highly strained due to the deformation, there is no extensive formation of the characteristic (100) defects that are common in olivine from the matrixes of oxidized CVs. Because lattice offsets are associated with the olivine (100) defects (e.g., in Bali and Grosnaja), it was proposed that the defects resulted from deformation on the CV parent body [e.g., 7]. However, these defects are uncommon in the highly deformed olivines in Leoville matrix, suggesting that these defects in the oxidized CVs are somehow related to the aqueous alteration processes that have affected these meteorites or were exposed to a different strain rate environment.

Conclusions: TEM studies of the Leoville CV3 chondrite show that matrix contains a number of likely nebular products that

were accreted on the Leoville parent body, including enstatite-metal aggregates and metal-PGC grains. A parent-body shock event is superimposed on the matrix minerals and has resulted in considerable strain. There are several differences in the matrix mineralogy of Leoville (reduced group) relative to the oxidized members of the CV chondrites.

References: [1] McSween H. Y. (1977). [2] Nakamura T. et al. (1992) *EPSL, 114,* 159. [3] Guimon R. K. et al. (1995) *Meteoritics, 30,* 704. [4] Bradley J. P. et al. (1984). [5] Brearley A. J. (1990) *GCA, 54,* 831. [6] Bradley J. P. et al. (1996) *LPS XXVII,* 149. [7] Keller L. P. et al. (1994) *GCA, 58,* 5589.

RELATIONSHIP BETWEEN ANHYDROUS AND AQUEOUS ALTERATIONS IN CV3 CHONDRITES.

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Introduction: Almost all chondrules in Allende CV3 chondrite were secondarily subjected to anhydrous alteration: (1) alkali-Ca exchange reaction to form nepheline, sodalite, and Ca silicates such as hedenbergite and wollastonite, (2) secondary zonation of olivine, and (3) replacement of enstatite by ferroan olivine [1,2]. The other oxidized CV3 chondrites, such as Axtell, Y 86751, Ningqiang, and ALH 81258, also experienced such reactions ([3,4] and unpublished data). The anhydrous alteration weakly took place in Efremovka, Leoville, and Vigarano of the reduced subgroup [5].

On the other hand, aqueous alteration to produce phyllosilicate took place in some oxidized CV3 chondrites such as Kaba and Mokoia [6,7]. Thus, various alteration reactions have been noticed for CV chondrites. In order to explore the relationships between the anhydrous and aqueous alterations of chondrules, we carried out mineralogical and petrological study of chondrules in Kaba and Mokoia, in comparison with those in the other CV chondrites.

Aqueous Alteration in Kaba and Mokoia: Our observations also show that chondrules in Kaba and Mokoia were extensively subjected to aqueous alteration. Phyllosilicates occur commonly in the peripheral parts of chondrules. Saponite is identified in Kaba chondrules, consistent with previous works [e.g., 6]. On the other hand, Na phlogopite as well as saponite commonly occur in chondrules, as already noted [7]. Margarite rarely occurs in chondrules in Mokoia.

Phyllosilicates typically replaced glass and plagioclase in groundmass. Phyllosilicates often replaced pyroxenes in both CVs. However, low-Ca pyroxenes distinctly show replacement texture in comparison with high-Ca pyroxenes. In all chondrules of Kaba and Mokoia, olivines do not show any replacement texture by phyllosilicates. Resistance to the alteration increases in the order glass and plagioclase < low-Ca pyroxene < high-Ca pyroxene < olivine.

Anhydrous Alteration in Mokoia: Although both Kaba and Mokoia experienced aqueous alteration, their mineralogy of anhydrous phases is different. Phenocrystic olivines in Kaba chondrules are Fo_{95-100} without chemical zoning toward groundmasses. On the other hand, olivine phenocrysts in Mokoia chondrules are Fo_{81-99} in the cores, but Fo_{62-98} in the rims. They usually show normal zoning

toward groundmasses, despite the fact that phyllosilicate or plagioclase occur in the groundmasses. The ferroan rims are usually 10–20 μm wide, consistent with those in Allende olivines. Some olivines (Fo_{99-96}) in fragmental chondrules and isolated minerals in both CVs directly contact ferroan matrixes without zonation.

The atomic Mg/Mg + Fe ratios of pyroxenes are 0.97–1.00 in Kaba and Mokoia chondrules. Thus, the ferroan olivine rims were not equilibrated with coexisting pyroxenes in Mokoia. The olivine zonation was secondarily formed under subsolidus conditions like that in Allende chondrules [1]. Low-Ca pyroxenes in Mokoia are abundantly replaced by olivines (Fo_{53-77}), similar to those in Allende [1], whereas pyroxenes in Kaba do not show such texture.

Primary groundmass phases are devitrified glass and plagioclase (An_{80-98}) in Kaba and Mokoia. They typically occur in the central parts of chondrules. All chondrules in Kaba do not contain feldspathoid. On the other hand, nepheline and sodalite are encountered in some Mokoia chondrules. They replaced primary groundmass phases, like those in Allende. Two Mokoia chondrules contain hedenbergite ($En_{0-2}Fs_{49-50}Wo_{49-50}$) and wollastonite among phenocrysts. Such Ca-rich phases are byproducts of the alkali-Ca exchange reaction [2].

Therefore, chondrules in Mokoia show typical features of anhydrous alteration such as secondary olivine zonation, replacement of enstatite by ferroan olivine, alkali-Ca exchange reaction to form feldspathoids and Ca silicates. The former two reactions are noticed in all chondrules, and the alkali-Ca reaction features are noticed in more than 30% of chondrules.

Stage of Alteration Reactions: In Mokoia chondrules, phyllosilicates formed around zoned olivine, low-Ca pyroxene replaced by ferroan olivine and feldspathoids. Mokoia chondrules experienced both anhydrous and aqueous alterations. On the other hand, chondrules in Kaba do not show any features of anhydrous alteration. Phyllosilicate directly replaced primary low-Ca pyroxene and groundmass.

Aqueous alteration has been considered to take place in CV chondrite parent body at low temperatures, below 100°C [6]. Such low temperatures are consistent with no zoning of olivine in Kaba, because diffusion of Fe and Mg hardly occurs below about 600°C in the nebular lifetime [1]. On the other hand, olivines in Mokoia chondrules show distinct zonation. We suggest that the aqueous alteration, possibly in the parent body, may have followed anhydrous alteration at about 600°–800°C [2], possibly in the nebula [8].

Now we distinguish several kinds of alteration reactions for CV chondrites: anhydrous alteration, aqueous alteration, and dehydration for some dark inclusions [9]. CV chondrites of the reduced subgroup were hardly to weakly subjected to these reactions [5]. Chondrites of the oxidized subgroup show these alterations in various degrees. The anhydrous alteration took place extensively in some CVs such as Allende and others. Kaba was only subjected to the aqueous alteration, whereas Mokoia experienced the anhydrous reactions followed by the aqueous alterations.

References: [1] Ikeda and Kimura (1995) *Proc. NIPR Symp. Antarct. Meteorites, 8,* 97–122. [2] Kimura and Ikeda (1995) *Proc. NIPR Symp. Antarct. Meteorites, 8,* 123–138. [3] Murakami and Ikeda (1994) *Meteoritics, 29,* 397–409. [4] Krot et al. (1995) *Meteoritics, 30,* 748–775. [5] Kimura and Ikeda (1996) *Proc. NIPR Symp. Antarct. Meteorites, 10,* in press. [6] Keller and Buseck (1990) *GCA,*

54, 2113–2120. [7] Tomeoka and Buseck (1990) *GCA, 54*, 1745–1754. [8] Ikeda and Kimura, this volume. [9] Kojima and Tomeoka (1996) *GCA, 60*, 2651–2666.

MINERALOGICAL AND CHEMICAL MODIFICATION OF CV3 CHONDRITES DURING FLUID-ASSISTED METAMORPHISM IN THE CV3 ASTEROID.

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Calcium-aluminum-rich inclusions (CAIs), chondrules, matrixes, and dark inclusions (DIs) in CV3 chondrites experienced late-stage alteration processes resulting in many alteration features previously ascribed to the nebula [1,2]. These features include (1) oxidation and sulfidation of Ni- and Co-poor metal and troilite to magnetite, awaruite, Ni-rich taenite, Co-rich kamacite, wairauite, pyrrhotite, and pentlandite; (2) replacement of magnetite by fayalite, salite-hedenbergite$_{ss}$, pyroxenes, and andradite; (3) fayalitic olivine (Fa$_{30–60}$) rims around forsterite grains; (4) fayalitic olivine (Fa$_{30–60}$) veins in forsterite and low-Ca pyroxene; (5) tabular fayalitic olivine (Fa$_{30–60}$) in matrix; (6) salite-hedenbergite$_{ss}$-andradite inclusions in matrix; (7) Fe-alkali-halogen metasomatic alteration of chondrules and CAIs resulting in formation of grossular, anorthite, nepheline, sodalite, wollastonite, salite-hedenbergite$_{ss}$, andradite and kirsch-steinite; and (8) various phyllosilicates (margarite, clintonite, Na-phlogopite, saponite, chlorite, serpentine, montmorillonite, talc, bio-pyriboles). Inspired by the aqueous alteration-dehydration model suggested by Kojima and Tomeoka [3] for the Allende DI All-AF, we suggested that all oxidized CV3s [4] experienced variable degrees of fluid-assisted metamorphism resulting in the alteration features listed above [1]. Although the following mineralogical, petrographic, and chemical studies of CV3s and their DIs strongly support this suggestion [5–14], the time, duration and physical-chemical conditions of alteration, including p, T, and fluid composition (pH, f$_{O_2}$, concentrations of dissolved species), are still poorly constrained.

Formation of Magnetite, Nickel- and Cobalt-rich Metal, and Nickel-rich Sulfides: There are two major textural types of magnetite in CV3s: (1) magnetite nodules associating with Ni- and Co-rich metal and Ni-rich sulfides in chondrules and matrix, and (2) framboidal magnetite grains in matrixes in Mokoia and Bali [15,16]. The framboidal magnetite associates with phyllosilicates and is commonly attributed to aqueous alteration [15]; the origin of magnetite-metal-sulfide nodules remains controversial [1]. The observed differences in O isotopic compositions of the magnetite nodules and olivine phenocrysts in Allende chondrules [13] exclude the formation of the magnetite nodules by crystallization from metal-sulfide-oxide droplets [17] and support their origin by oxidation of metal after chondrule formation [18]. Although late-stage oxidation of metal in the solar nebula cannot be excluded (experiments on kinetics of magnetite formation by oxidation of Fe-Ni alloys may help to resolve this issue), the presence of oxidized and reduced opaque assemblages mixed in several brecciated CV3s [1,19] favors heterogeneous oxidation in an asteroid. The observed correlation of the degree of aqueous alteration of the Efremovka DIs [14] and composition of metal grains, which are similar to those in the oxi-

dized CV3s, support the origin of Ni- and Co-rich metal by preferential oxidation of Fe in asteroidal environment.

Formation of Pure Fayalite: Hua and Buseck [19] described pure fayalite in chondrules, CAIs, and matrixes in Kaba and Mokoia and suggested a multistage nebular process for its origin; it includes oxidation of metal to magnetite at low temperature (<400 K) by the reaction

$$3Fe(s) + 4H_2O(aq) = Fe_3O_4(s) + 4H_2(g) \qquad (1)$$
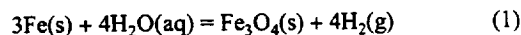
decomposition of enstatite during a high-temperature reheating event under reducing conditions to form SiO gas

$$2MgSiO_3(s) + H_2(g) = Mg_2SiO_4(s) + SiO(g) + H_2O(g) \qquad (2)$$

and formation of fayalite under oxidizing conditions

$$2Fe_3O_4(s) + 3SiO(g) + H_2O(g) = 3Fe_2SiO_4(s) + H_2(g) \qquad (3)$$
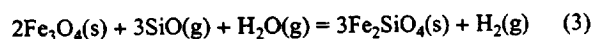
No physical model explaining these highly variable redox conditions in the late-stage solar nebula was proposed.

Our mineralogical study shows that fayalite replaces magnetite-sulfide nodules in chondrules, fine-grained rims, and matrixes in Kaba and Mokoia. The fine-grained rims are commonly crosscut by fayalite-magnetite-sulfide veins that may extend into the matrix where they connect with fayalite-sulfide-magnetite inclusions. Based on these observations, we conclude that fayalite-bearing assemblages postdate chondrule formation, accretion of fine-grained rims and matrixes in Kaba and Mokoia, and hence, formed in an asteroid. Salite-hedenbergite$_{ss}$ and andradite replace magnetite nodules and fayalite in chondrules, CAIs, and matrixes in Kaba and Mokoia. We infer that formation of the magnetite, fayalite, salite-hedenbergite$_{ss}$, and andradite resulted from a fluid-rock interaction by reactions

$$2Fe_3O_4(s) + 3SiO_2(aq) + 2H_2(g) = \\ 3Fe_2SiO_4(s) + 2H_2O(g) \qquad (4)$$

$$Fe_2SiO_4(s) + 3SiO_2(aq) + 2Ca^{2+}(aq) + 2H_2O(aq) = \\ 2CaFeSi_2O_6(s) + 2H_2(g) \qquad (5)$$

and

$$2Fe_3O_4(s) + 9SiO_2(aq) + 9Ca^{2+}(aq) + 10H_2O(aq) = \\ 3Ca_3Fe_2(SiO_4)_3(s) + 10H_2(g) \qquad (6)$$
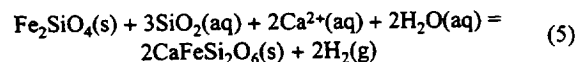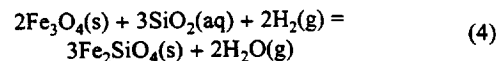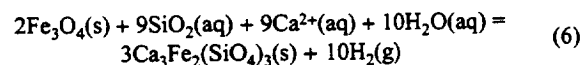
Silicon, Ca, Mg, and some Fe may have been released from primary minerals in matrix, chondrules, and CAIs replaced by phyllosilicates [15,20] and transported in the fluid, not in the nebular gas.

Formation of Fayalitic Olivine (Fa$_{30–60}$): There are several textural types of fayalitic olivine in CV3s: (1) tabular-to-equant grains in matrix [21–23], (2) rims around forsterite grains [21–23], (3) veins in forsterite [21–23], (4) olivine replacing low-Ca pyroxene [24], (5) rims around metal nodules in forsterite [22], and (6) veins crosscutting chondrules and fine-grained rims [6]. It seems likely that all these textural types are genetically related [6]. The most widely favored nebular scenario for the origin of fayalitic olivine involves high-temperature formation during condensation and/or reaction with an oxidizing nebular gas; the latter was suggested to be produced by evaporation of dusty nebular regions [2,21–23,25]. The

asteroidal models invoke various mechanisms: (1) solid-state oxidation [24] by the reaction

$$Fe(s) + MgSiO_3(s) + H_2O(aq) = FeMgSiO_4(s) + H_2(g) \quad (7)$$
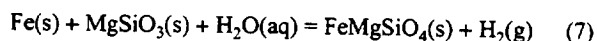
(2) progressive aqueous alteration of matrix and chondrule silicates, followed by metamorphic dehydration of the product phyllosilicates [6], and (3) metasomatic Fe-Mg exchange reactions, coupled with vapor growth, in the poorly consolidated portion of an early accreted parent body [26]. The mineralogical observations strongly supporting an asteroidal setting for the origin of fayalitic olivine include (1) microstructures of matrix olivine similar to those observed in dehydrated phyllosilicates in CM chondrites [6,8,9,11,27], including voids, inclusions of pentlandite, and poorly graphitized C (PGC) (pentlandite is not stable above 610°C and PGC formation is a thermodynamically irreversible process that is only known to occur by the thermal annealing of complex hydrocarbon precursors, which only form as a result of low-temperature processes [11]); (2) replacement textures, including pseudomorphs after chondrules and mineral grains [6,14]; (3) relict phyllosilicates left after dehydration [14]; (4) veins crosscutting fine-grained rims and extending into matrix [6,28]; and (5) talc and biopyriboles replacing low-Ca pyroxene in Allende chondrules and predating formation of fayalitic olivine replacing the low-Ca pyroxene [12]. Although these observations exclude high-temperature nebular models for the origin of fayalitic olivine, the exact mechanisms of its asteroidal growth are still poorly known. The observed significant variations in grain sizes of tabular fayalitic olivine in matrixes of CV3s [1] may indicate coarsening during thermal metamorphism.

Formation of Calcium-Iron-rich Silicates, Nepheline, and Sodalite: Salite-hedenbergite$_{ss}$ ± andradite ± wollastonite ± kirschsteinite assemblages are observed (1) in Kaba and Mokoia chondrules replacing magnetite nodules and pure fayalite, (2) as concentrically zoned inclusions in matrixes of all oxidized CV3s and Allende DIs [7], (3) as rims around heavily altered Allende CAIs and DIs in Allende and Efremovka [7,14,29], (4) in Allende chondrules replacing mesostasis [7,30–32], and (5) as veins in Allende and its DIs [7]. Although these minerals have been interpreted as direct condensates from an oxidized nebular gas or as products of nebular metasomatic alteration reactions [29–32], the evidence of *in situ* growth of salite-hedenbergite$_{ss}$ ± andradite ± wollastonite ± kirschsteinite rims around Allende and Efremovka DIs and the presence of salite-hedenbergite$_{ss}$ veins crosscutting Allende DIs and replacing fayalitic olivine rims strongly support their asteroidal formation [7,14]. We suggest that salite-hedenbergite$_{ss}$ ± andradite ± wollastonite ± kirschsteinite formed during fluid-rock interaction and subsequent thermal metamorphism, possibly by various mechanisms: (1) Replacement of fayalite and magnetite in Kaba and Mokoia chondrules and matrixes of the oxidized CV3s. Some of the salite-hedenbergite$_{ss}$ and andradite in the CV3 matrixes might have precipitated directly from a fluid by the reactions

$$Fe^{2+}(aq) + Ca^{2+}(aq) + 2SiO_2(aq) + 2H_2O(aq) = \\ 2H_2(g) + CaFeSi_2O_6(s) \quad (8)$$

and

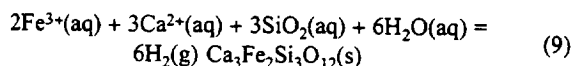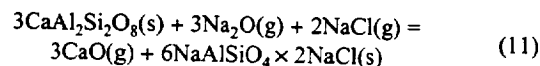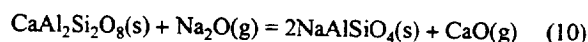$$2Fe^{3+}(aq) + 3Ca^{2+}(aq) + 3SiO_2(aq) + 6H_2O(aq) = \\ 6H_2(g) \, Ca_3Fe_2Si_3O_{12}(s) \quad (9)$$
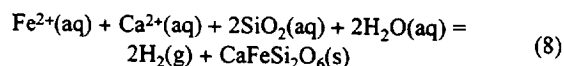
(2) The salite-hedenbergite$_{ss}$ ± andradite ± wollastonite ± kirschsteinite assemblages in Allende chondrules and CAIs formed during Fe-alkali-halogen metasomatism possibly by fluids released during dehydration of phyllosilicates by the reactions

$$CaAl_2Si_2O_8(s) + Na_2O(g) = 2NaAlSiO_4(s) + CaO(g) \quad (10)$$

$$3CaAl_2Si_2O_8(s) + 3Na_2O(g) + 2NaCl(g) = \\ 3CaO(g) + 6NaAlSiO_4 \times 2NaCl(s) \quad (11)$$

and

$$3NaAlSi_3O_8(s) + NaCl(g) = \\ 3NaAlSiO_4 \times NaCl(s) + 6SiO_2(g) \quad (12)$$
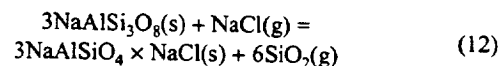
Although Ikeda and Kimura [30,31] suggested that nepheline and sodalite in Allende chondrules formed by anhydrous reactions [10–12] in the solar nebula, the presence of nepheline and sodalite enclosing tabular fayalitic olivine in Allende matrix and intergrowths of nepheline and fayalitic olivine replacing forsterite phenocrysts in Allende DIs support their asteroidal origin [6]. (3) The salite-hedenbergite$_{ss}$ ± andradite ± wollastonite ± kirschsteinite veins in Allende DIs and rims around Allende and Efremovka DIs may have resulted from redistribution of Ca, Fe, Si, and Mg by fluids released during dehydration.

Formation of Phyllosilicates: Although it is widely recognized that several oxidized CV3s (Kaba, Mokoia, and Bali) experienced aqueous alteration to various degrees probably in an asteroid [15,16,20], it was found only recently that phyllosilicates in Allende are not restricted only to CAIs [33–35], but also widespread in pyroxene-bearing chondrules [12,32]. These observations indicate that aqueous alteration may have affected all the components in Allende and hence are more likely to have occurred after accretion within an asteroid.

References: [1] Krot A. N. et al. (1995) *Meteoritics, 30,* 748. [2] Palme H. and Wark D. A. (1988) *LPS XIX,* 897. [3] Kojima T. and Tomeoka K. (1994) *Meteoritics, 29,* 484. [4] McSween H. Y. Jr. (1977) *GCA, 41,* 1777. [5] Kojima T. and Tomeoka K. (1996) *GCA, 60,* 2651. [6] Krot A. N. et al. (1997) *Meteoritics & Planet. Sci., 32,* 31. [7] Krot A. N. et al. (1996) *Meteoritics & Planet. Sci., 31,* A74. [8] Brearley A. and Prinz M. (1996) *LPS XXVII,* 161. [9] Brearley A. J. (1996) *Meteoritics & Planet. Sci., 31,* A21. [10] Clayton R. N. and Mayeda T. K. (1996) *Meteoritics & Planet. Sci., 31,* A30. [11] Brearley A. J. (1997) *LPS XXVIII,* 151. [12] Brearley A. J. (1997) *LPS XXVIII,* 153. [13] Choi B.-G. (1997) *EPSL, 146,* 337. [14] Krot A. N. et al. (1997) *LPS XXVIII,* 769. [15] Tomeoka K. and Buseck P. R. (1990) *GCA, 54,* 1745. [16] Keller L. P. et al. (1994) *GCA, 58,* 5589. [17] Rubin A. E. (1991) *Am. Mineral., 76,* 1356. [18] Blum J. D. et al. (1989) *GCA, 53,* 543. [19] Hua X. and Buseck P. R. (1995) *GCA, 59,* 563. [20] Keller L. P. and Buseck P. R. (1990) *GCA, 54,* 2113. [21] Peck J. A. and Wood J. A. (1987) *GCA, 51,* 1503. [22] Hua X. et al. (1988) *GCA, 52,* 1389. [23] Weinbruch S. et al. (1990) *Meteoritics, 25,* 115. [24] Housley R. M. and Cirlin E. H. (1983) in *Chondrules and Their Origins* (E. A. King, ed.), p. 141, LPI, Houston. [25] Palme H. and Fegley B. (1990) *EPSL, 101,* 180. [26] Weisberg M. K. et al. (1996) *Meteoritics & Planet. Sci., 31,* A150. [27] Akai J. (1988) *GCA, 48,* 1593. [28] Kojima T. et al. (1993) *Meteoritics, 28,* 649. [29] MacPherson G. J. et al. (1988) in *Meteorites and the Early Solar System* (J. F. Kerridge

and M. S. Matthews, eds.), p. 746, Univ. of Arizona, Tucson. [30] Ikeda Y. and Kimura M. (1995) *Proc. NIPR Symp. Antarct. Meteorites, 8,* 97. [31] Ikeda Y. and Kimura M. (1996) *Proc. NIPR Symp. Antarct. Meteorites, 9,* 51. [32] Kimura M. and Ikeda Y. (1996) *Meteoritics & Planet. Sci., 31,* A70. [33] Tomeoka K. and Buseck P. R. (1982) *Nature, 299,* 326. [34] Tomeoka K. and Buseck P. R. (1982) *Nature, 299,* 327. [35] Tomeoka K. and Buseck P. R. (1982) *GCA, 54,* 1745. [36] Hashimoto A. and Grossman L. (1987) *GCA, 51,* 1685.

THE METEORITE PARENT-BODY ALTERATION MODEL AND THE INCOMPATIBLE REALITY.

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Meteorites and, in particular, chondrites frequently contain objects that have signs of beginning, advanced, or almost complete changes in their mineralogy or mineral chemistry, a metamorphosis that is commonly referred to as "alteration." Such changes are to be expected to be omnipresent in meteorites because these rocks are the products of a large variety of processes that were operating in the solar nebula. Adaption of mineral assemblages and mineral chemistries to changing physicochemical conditions is a natural process that, of course, must have been working also in the solar nebula with its widely varying temperature and pressure regimes. Until the final product was formed, the constituting matter had to evolve from temperatures above the boiling point of most phases or compounds to temperatures below the freezing point of volatile constituents, such as H_2O, CO, CH_4, CO_2, etc. Equilibration of solid phases with a gaseous environment depend on the grain size of the solids, diffusivities of the species considered, and the changes in temperature. Thus, equilibrium is rarely achieved in meteorites, as amply shown by the nature of unequilibrated chondritic meteorites. Incomplete response to varying environmental conditions is often interpreted as low-temperature alteration within the parent body.

The attempts to stay in equilibrium with the environment cannot be successful for all phases under all circumstances. More likely, we can expect unsuccessful attempts and, actually, we can observe many such examples in almost all meteorites. This normal sequence of events, as documented by unsuccessful equilibration, has, however, commonly been interpreted as unlucky "secondary alteration." The place where such bad things can happen best is widely believed to be the meteorite's parent body, where it was exposed to conditions it was not designed for.

All meteorites show signs of unsuccessful attempts to reach equilibrium either with their peers, or with the environment, or both. Even the best "equilibrated" OCs, for example, have a number of phases that are out of equilibrium with their colleagues. This fact is usually repressed by meteoriticists, perhaps because it simply doesn't fit the model. Carbonaceous chondrites had less luck and that's why they are rich in examples of unsuccessful attempts of constituents to reach equilibrium with each other and a progressing, changing world. That world is commonly believed to be a planetary or planetesimal world for reasons that remain in the dark. This way we arrived at a pretty curious situation: the solar nebula, the parent of all meteorites, which had to change its conditions drastically during its evolution, is not eligible as the culprit in ruining our meteoritic constituents. According to widespread belief, they rather must emerge from the nebula in an immaculate state and subsequently become exposed to the bad and destructive world of parent bodies.

Naturally, observations can be interpreted in an alternative way and, actually, we are forced to interpret most of them in a different way when we consider all observations. For example, most CCs consist of constituents (chondrules, aggregates, etc.) set into a fine-grained carbonaceous matrix. These constituents usually bear the scars of incomplete equilibrium with some environment that, apparently, was quite different from that in which they originally formed. If this new environment was the one that was created locally in the parent body then one can expect that constituents of similar mineralogical and textural type should react in the new environment in a similar way, with the result that they become "altered" to similar degrees. In nature this is clearly not the case. The rule is rather that constituents of a given CC show all sorts of different "alterations" and rarely the same intensity. Almost totally hydrated objects are located right next to almost unchanged ones, highly sulfidized ones are next to unchanged, metal-rich ones, highly oxidized objects bearing magnetite are approaching or even touching nonoxidized ones, etc. What is even more impressive is the widespread survival of highly reactive phases, which were formed in strongly reducing environments, in the highly oxidizing environment of CCs (low-Ni metal, phosphides, sulfides of lithophile elements, etc.). Furthermore, hydrous objects (like anhydrous ones) commonly display delicate growth and aggregation features and a very large compositional variety on a micrometer scale. Moreover, because, e.g., serpentinization of olivine or pyroxene should produce at least two products, the serpentine and either a Mg mineral (Mg hydroxide or carbonate in the case of olivine) or free silica (or a Si-rich mineral in the case of pyroxene) we can expect to find them at the place of the crime, but they are never where they should be. Actually, the phases that theoretically should accompany the hydrosilicates are missing in almost all cases. Why?

THE ALTERATION OF NICKEL-BEARING SULFIDES DURING THERMAL METAMORPHISM ON ORDINARY CHONDRITE PARENT BODIES.

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Introduction: Sulfurization of FeNi alloys under solar nebula conditions produces Ni-bearing sulfides [1,2]. These sulfides have several distinctive characteristics including pentlandite [(Fe,Ni)$_9$S$_8$] inclusions within monosulfide solid solution [mss, (Fe,Ni)$_{1-x}$S] crystals, increasing Ni content with distance from the remnant metal, multilayer structures, and oriented sulfide crystals. The extent to which some (or all) of these features are altered by thermal metamorphism is unknown, but important to quantify so we can distinguish nebular from parent-body processes in the meteorite record. We performed experimental simulations of dry thermal metamorphism of an ordinary chondrite parent body to determine the effect of this process on sulfide chemistry and morphology.

Experimental Method: The starting material of the thermal metamorphism experiments was composed of silicates with the normative mineralogy of LL chondrite silicates [3], filings from the Canyon Diablo (CD) Fe meteorite, and Ni-bearing sulfides produced by gas-solid reaction between CD metal and H_2-H_2S gas [1]. These
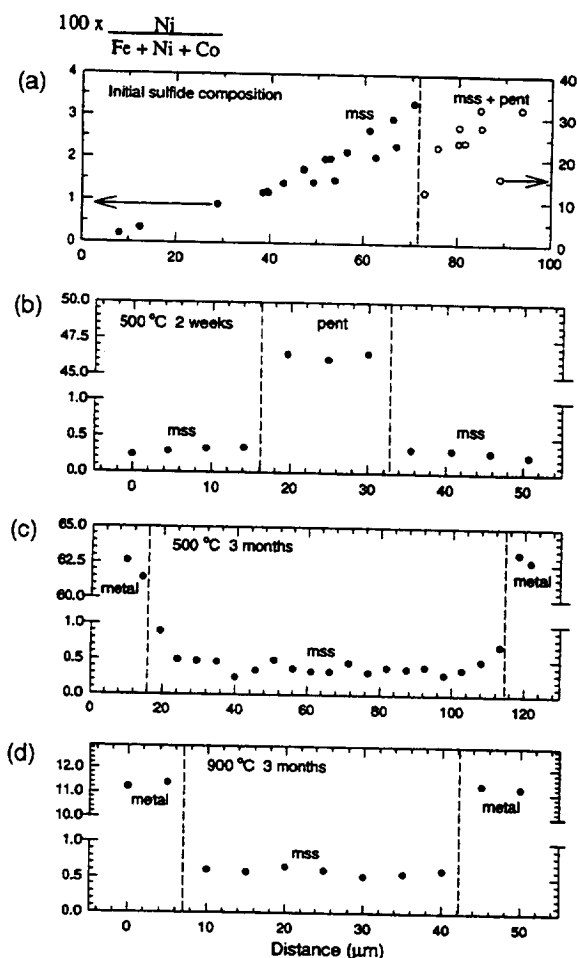
Fig. 1. Traverse across sulfide grains at different stages of reaction. Composition is given as atomic percent Ni (cations basis). **(a)** The initial sulfide composition. The concentration gradients are characteristic of sulfides formed under nebula conditions. **(b)** Heating for short times removes the concentration gradients leaving behind an equilibrated mss-pentlandite assemblage. **(c)** Longer duration heating produces $FeNi_2$ and Ni-poor troilite. **(d)** Taenite (~12% Ni) exsolves at higher temperatures.

components were mixed together in proportions similar to those in LL chondrites. The components were pressed into a pellet and heated in an evacuated, sealed silica tube at 500°C or 900°C for two weeks and three months.

Results: The Ni content of the starting sulfides is shown in Fig. 1a and the composition is plotted on a Fe-Ni-S diagram (wt%) in Fig. 2a. The sulfide is divided into two compositional regions. The region originally adjacent to metal is composed solely of mss (solid circles). The Ni content of this region varies from 0.2 to 3 atom% Ni. The outer region is composed of mss grains with pentlandite inclusions and is Ni-rich (10–30 atom% Ni). We compare these compositions to the heated assemblages. The extent of alteration varies with the temperature and duration of the experiment. These experiments produced three distinct results: (1) local equilibration of the sulfide grains, (2) limited S mobilization, and (3) extensive cation diffusion and S vapor transport. These are discussed in detail below.

Local equilibration. The experiments begin with metal and sulfide separated by a silicate matrix. After two weeks at 500°C, we observed a very limited extent of reaction. However, the Ni concentration gradient is gone and the mss and pentlandite are locally equilibrated. The compositional variation across a mss-pentlandite assemblage is given in Fig. 1b, and the bulk compositions are plotted in Fig. 2b.

Sulfur mobilization. After three months reaction at 500°C there was noticeable S mobilization. The system moves from local equilibrium toward global equilibrium by creating metal-sulfide assem-
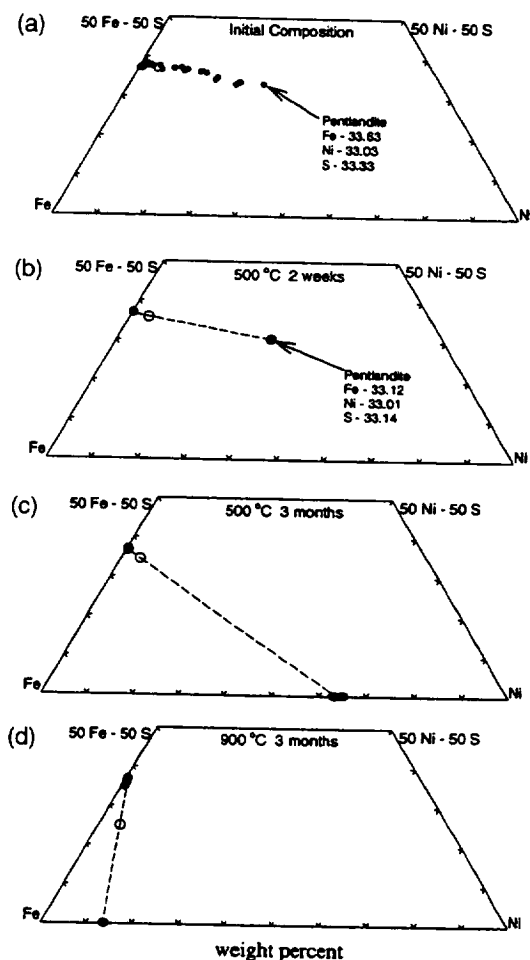
Fig. 2. The composition of experimental sulfides plotted on Fe-Ni-S ternary diagrams (wt%). Dashed lines connect equilibrium phases. The bulk composition of each assemblage is plotted as an open circle. The lever rule determines the relative abundance of each phase. **(a)** Composition of sulfide produced by sulfurization of an FeNi alloy. The sulfide is composed of both mss and pentlandite. **(b)** The sulfide composition after heating for two weeks at 500°C. The compositional variation is gone, and an mss-pentlandite equilibrium assemblage has formed. **(c)** A sulfide grain that was heated for three months at 500°C. $FeNi_2$ has exsolved from the sulfide leaving Ni-free sulfide. **(d)** A sulfide grain that was heated for three months at 900°C. The equilibrium metal composition has a much lower Ni content than at 500°C.

TABLE 1.   Partition coefficients.

Phases	Temperature (°C)	Ni	Co
mss-α	500	0.020	0.239
mss-γ'	500	0.007	0.068
mss-γ	900	0.027	0.130

blages from originally distal metal and sulfide grains. In order to establish this global equilibrium, the Ni-bearing sulfides release S_2 vapor resulting in metal precipitation at the sulfide edges. The Ni-content of this metal is determined by thermodynamic equilibrium between metal and sulfide. At 500°C $FeNi_2$ (γ') exsolved from the sulfide leaving behind troilite containing <0.5 atom% Ni. The compositional variation across such an assemblage is given in Fig. 1c, and the metal and sulfide compositions are plotted on an Fe-Ni-S ternary phase diagram in Fig. 2c. The dashed line in Fig. 2c indicates the tie-line between these two phases. A similar tie-line was suggested by [4]. The S released from the evaporating sulfides condenses as sulfide rims on isolated metal grains. Thus, these sulfides form by a gas-solid reaction between FeNi metal and S-bearing gas. This is similar to sulfide formation in the solar nebula. However, as the sulfide layers grow around the metal grains, they incorporate nearby silicates, a morphology unique to sulfides formed on a parent body.

Extensive transfer of material. Evidence of extensive S mobilization is observed after three months reaction at 900°C. Since $FeNi_2$ is not stable at 900°C, taenite containing ~12 atom% Ni exsolved from the sulfide (Figs. 1d,2d). The growth of sulfide layers on metal grains is widespread. Thin sulfide trails grew throughout the sample connecting initially separate metal-sulfide assemblages. Since Fe and Ni diffusion through sulfides is rapid, the network of sulfide trails allows for extensive cation movement. As a result, metal grains are nearly equilibrated throughout these sample.

Conclusions: Thermal metamorphism can alter sulfides that formed under solar nebula conditions. The extent of alteration varies with temperature and time. Initially, individual sulfide grains equilibrate, erasing Ni concentration gradients established during sulfide formation in the nebula. Longer heating times result in S loss and metal exsolution from the sulfides. $FeNi_2$ forms at 500°C and taenite with ~12% Ni forms at 900°C. The equilibrium relationships observed in the samples allow us to the determine partition coefficients for Ni and Co between mss and metal (Table 1).

References: [1] Lauretta et al. (1997) *LPS XXVII*, 783. [2] Lauretta et al. (1996) *Proc. NIPR Symp. Antarct. Meteorites, 9*, 97. [3] McSween and Bennett (1991) *Icarus, 90*, 107. [4] Blum et al. (1989) *GCA, 53*, 543.

NEBULAR AND PARENT-BODY PROCESSES IN CHONDRITES: LABILE TRACE ELEMENTS AS INDICATORS AND THERMOMETERS. M. E. Lipschutz, Department of Chemistry, Purdue University, West Lafayette IN 47907-1393, USA.

Obviously, all planetary samples (including chondrites) derive ultimately from material that condensed from the nebula so that at least some of their properties must record this primary process. Oxygen isotopic compositional data indicate that the various chondritic groups accreted from nebular material that varied isotopically, hence chemically, since it should have been easier for the nebula to be homogenized isotopically than chemically. Mineralogic and petrographic characteristics of chondrites indicate that many experienced extended, postaccretionary, heat-associated genetic episodes (e.g., thermal metamorphism, shock heating). Contents of thermally labile trace elements in them should reflect such secondary episodes provided that the heating events occurred under partly or totally open conditions. Here we review the evidence provided by thermally labile elements as to specific genetic processes important in the formation of the major chondrite groups.

From circumstantial evidence and experimental results obtained from extended heating of low-petrographic-grade chondrites under simulated parent-body conditions, certain trace elements are considered as moderately to highly labile [1]. These elements—which include Ga, Rb, Ag, Se, Cs, Te, Zn, Cd, Bi, Tl, and In (ordered by putative volatility during nebular condensation)—are mainly quantified by RNAA. These elements are volatilized from primitive chondrites heated over a wide temperature span, beginning at 400°C (for the most labile) to ≥1000°C for the least labile elements [1]. To the extent that these experiments approximate open-system parent-body processes, their results should enable us to identify materials that experienced such processing. In the absence of evidence of such secondary processing, compositional trends for such elements can be taken to be of nebular origin.

Carbonaceous chondrites provide the clearest samples to test whether parent-body processes altered compositions established by nebular processes. This is only possible because C1-normalized levels of labile trace elements are constant in most carbonaceous chondrites [2] and consistent with a two-component model similar to, but somewhat different from, that of Anders and co-workers [29]. Noble gas, petrographic, and Mössbauer data for three such chondrites support the conclusion, based upon data for mobile trace elements, that these were thermally metamorphosed in their parent bodies [4,5]. Spectral reflectance data for these three and artificially heated Murchison samples indicate that the surfaces of many C, G, B, and F asteroids contain a substantial complement of thermally metamorphosed materials excavated from their interiors [30,31].

Parent material(s) for L4–6 chondrites apparently condensed and accreted at temperatures lower than those that produced H4–6 chondrites. Primary contents of mobile trace elements in most L4–6 chondrites were altered by shock (Table 1). An accompanying report discusses the situation in H chondrites [32].

The situation for E3–6 chondrites is less clear. Since EH and EL chondrites differ in contents of major, refractory elements, it may be that contents of labile trace elements also reflect nebular processes [33]. However, contents of mobile trace elements could also reflect open-system, thermal metamorphism and differentiation in the parent body/bodies (Table 1).

References: [1] Lipschutz M. E. and Woolum D. S. (1988) in *Meteorites and the Early Solar System* (J. F. Kerridge and M. S. Matthews, eds.), pp. 462–487, Univ. of Arizona, Tucson. [2] Xiao X. and Lipschutz M. E. (1992) *JGR, 97*, 10197–10211. [3] Takeda H. et al. (1984) *EPSL, 71*, 329–339. [4] Paul R. L. and Lipschutz M. E. (1989) *Z. Naturf., 44a*, 979–987. [5] Paul R. L. and Lipschutz M. E. (1990) *Proc. NIPR Symp. Antarct. Meteorites, 3*, 80–95. [6] Ikramuddin M. and Lipschutz M. E. (1975) *GCA, 39*, 363–375.

TABLE 1.   Agents for establishing mobile trace-element contents in chondrites and relevant heating studies.

Chondrite Type	Heating Studies	Nebular Process(es)	Parent-Body Process(es)
C	[6–10]	61 C1–C6 [2]	Mobilization by thermal metamorphism in 1 C1, 2 C2 [4,5]
H	[11]	H4–6 [12–14]*	
L	[15]	unshocked L4–6 [?]	Mobilization by shock in most or all (?) L4–6 [16,17]*
E	[18,19]	E3 (?)	Mobilization and/or fractionation of FeS-Fe eutectic by thermal processes in E4–E6 [19,20]
Unequilibrated ordinary chondrites	[11,15]	H3, L3, LL3 [21]*	
H regolith breccias	[11]		Implantation of mobile trace elements in regolith [22–24]*
Rose City			Fractionation of metal (and sulfide?) [13]*
Y 74160 (LL7)	[15]		Mobilization (?) and fractionation of FeS-Fe eutectic by thermal process(es) [3]
Chondrules		[25]	
H inclusion in Barwell (L5–6)		[25]	Fractionation of FeS-Fe eutectic by shock (?) [26]
Igneous inclusions in ordinary chondrites			Fractionation of metal (and sulfide?) in inclusions within equilibrated H and L chondrites [27,28]

*Additional references cited in these papers.

[7] Matza S. D. and Lipschutz M. E. (1977) *Proc. LSC 8th*, pp. 161–176. [8] Matza S. D. and Lipschutz M. E. (1978) *GCA*, *42*, 1655–1667. [9] Herzog G. F. et al. (1979) *GCA*, *43*, 395–404. [10] Bart G. et al. (1980) *GCA*, *44*, 719–730. [11] Ikramuddin M. et al. (1977) *GCA*, *41*, 1247–1256. [12] Lingner D. W. et al. (1987) *GCA*, *51*, 727–739. [13] Wolf S. F. and Lipschutz M. E. (1995) *JGR*, *100*, 3335–3349. [14] Wolf S. F. et al. (1997) *JGR*, in press. [15] Ikramuddin M. et al. (1977) *GCA*, *41*, 393–401. [16] Walsh T. M. and Lipschutz M. E. (1982) *GCA*, *46*, 2491–2500. [17] Huston T. J. and Lipschutz M. E. (1984) *GCA*, *48*, 1319–1329. [18] Ikramuddin M. et al. (1976) *GCA*, *40*, 133–142. [19] Biswas S. et al. (1980) *GCA*, *44*, 2097–2110. [20] Binz C. M. et al. (1974) *GCA*, *38*, 1579–1606. [21] Binz C. M. et al. (1976) *GCA*, *40*, 59–71. [22] Bart G. and Lipschutz M. E. (1979) *GCA*, *43*, 1499–1504. [23] Xiao X. and Lipschutz M. E. (1991) *GCA*, *55*, 3407–3415. [24] Lipschutz M. E. et al. (1993) *Meteoritics*, *28*, 528–537. [25] Sears D. W. G. et al. (1995) *Meteoritics*, *30*, 169–181. [26] Hutchison R. et al. (1988) *EPSL*, *90*, 105–118. [27] Sack R. O. et al. (1994) *JGR*, *99*, 26029–26044. [28] Yolcubal I. et al. (1996) *JGR*, submitted. [29] Takahashi H. et al. (1978) *GCA*, *42*, 97–106. [30] Hiroi T. et al. (1993) *Science*, *261*, 1016–1018. [31] Hiroi T. et al. (1996) *Meteoritics & Planet. Sci.*, *31*, 321–327. [32] Wolf S. F. and Lipschutz M. E., this volume. [33] Keil K. (1989) *Meteoritics*, *24*, 195–208.

WHAT DO ENSTATITE METEORITES TELL US ABOUT THE SOLAR NEBULA?

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The highly reduced enstatite chondrites (EC) and achondrites (aubrites) are exotic, but important, meteorites. Enstatite chondrites comprise about 1–2% of all chondrites (carbonaceous chondrites are ~2–5%). The enstatite meteorites form three groups: (1) EH chondrites, typically metamorphic type 3 and 4; (2) EL chondrites where metamorphic types 5 and 6 are prominent; (3) aubrites, which are differentiated achondrites. EHs may provide more information about the nebula, ELs may record metamorphic parent-body processes, and aubrites give insights into metal-sulfide fractionation on a very reduced parent body. Here we focus on conditions required for ED formation in the solar nebula.

Larimer [1–3] showed that more-reducing conditions than in a solar gas are required to form Fe-free silicates, osbornite (TiN), Si-bearing Fe-Ni metal, and oldhamite (CaS). The redox state is given by the C/O ratio, which is 0.48 for a solar gas [4]. In a solar gas all C is in CO while O is about evenly divided into CO and H_2O and oxide condensation reactions such as $2\,Al\,(g) + 3\,H_2O = Al_2O_3\,(s) + 3\,H_2$ occur. Figure 1 shows major-element condensation at $P_{tot} = 10^{-3}$ bar as a function of C/O ratio, which was varied by decreasing the O abundance from solar. Initial condensates from a solar gas are corundum, hibonite, grossite, perovskite, melilite (shown by gehlenite), spinel, forsterite, and enstatite. Iron metal condensation is independent of C/O. Increasing C/O decreases $H_2O\,(g)$, and oxides only form at lower T when the reaction $CO + 3\,H_2 = H_2O$ supplies H_2O.

At C/O ~0.91 to ~0.95 osbornite forms instead of perovskite. Oxides of Al, Ca, and Si remain initial condensates because enough H_2O is still available. Interestingly, the relatively reduced CH chondrites contain osbornite and the oxides (e.g., grossite [5,6]) predicted for this intermediate C/O range.

At C/O > 0.95 TiC replaces TiN as an initial condensate; AlN and CaS replace Ca-Al oxides, and SiC replaces gehlenite. Graphite and cohenite (Fe_3C) condensation requires C/O > 1. If C/O is increased by increasing the C abundance TiN appears at C/O ~0.95 and TiC, AlN, and CaS form at C/O ~0.98.

The C/O range where ECs may have formed is constrained by their mineralogy. Graphite and Fe_3C are not very abundant indicating that C/O was ≤1 because graphite and Fe_3C require C/O > 1. The occurrence of CaS puts the lower bound at C/O ~0.95.

Larimer [2] noted that condensation predicts minerals not observed in ECs. These are TiC, AlN, and, to some extent, SiC. These initial condensates may be absent (or less abundant) because they continued to react with the gas at lower T. This idea is consistent with the high-volatile-element abundances in ECs [7]. At lower temperatures, TiC converts to TiN and AlN changes to albitic plagioclase.
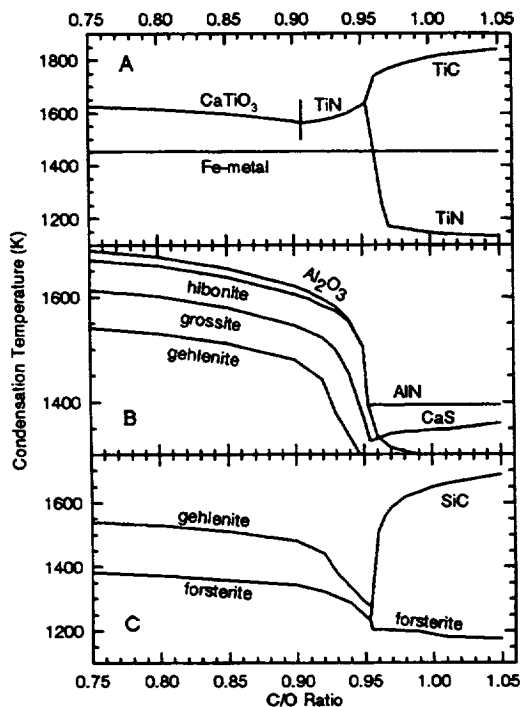
Fig. 1. Condensation temperatures for initial condensates as a function of C/O ratio at $P_{tot} = 10^{-3}$ bar.

The Ti-bearing troilite in enstatite meteorites may result from reactions like $TiC + 2 H_2S = TiS_2$ (in FeS) + CH_4 or $TiN + 2 H_2S = TiS_2$ (in FeS)+ $0.5 N_2 + 2 H_2$ at lower T. SiC forms at high T, but at C/O = 0.98, only ~20% Si is in SiC before all Si is consumed by forsterite and enstatite.

How were reducing conditions obtained in the solar nebula? Removal of O by oxide condensation increases C/O in the gas to ~0.57, but this is too low to produce reduced condensates, and the major elements are then already condensed. Injection of carbonaceous dust or removal of H_2O more plausibly increased the C/O ratio [1–3,8]. Isotopic variations in chondrites indicate that the solar nebula was not homogeneous. Higher abundances of presolar SiC in Qingzhen (EH3) than in Orgueil (CI) [9] may indicate that larger amounts of carbonaceous dust (which could raise the C/O ratio) were present in the EC-forming region. Drawbacks of dust addition are that (1) the C/O range where EC minerals form is very narrow (~0.98 to ~1), and (2) increasing C/O from solar to ~1 requires large amounts of carbonaceous dust. This dust probably contains SiC in ddition to other C-bearing phases. Thus, the Si abundance also increases and could account for the higher Si/Mg weight ratio in EHs (~1.5) than that in CI chondrites (~1.1). However, the Si/Fe ratio in EH and CI chondrites is very similar, which argues against Si enhancement but points to Mg fractionation.

If carbonaceous dust did not cause the reducing conditions, about half of the O had to be lost from the EC-forming region, possibly by H_2O ice condensation. Solar nebula models place H_2O ice condensation at 5.2 AU and beyond [10]. Early accretion of ice and rock may have caused a runaway accretion of Jupiter so that the jovian planets served as cold traps for H_2O ice [11,12]. A 440× solar

abundance of O (as H_2O) is required in Neptune to explain the observed CO concentration in its atmosphere [13]. Cold-trapping H_2O from the inner solar system would also explain how the reduced component postulated in the two-component accretion models for the terrestrial planets formed [14].

More modeling is needed to decide whether the reduced conditions were created by carbonaceous dust enrichment or H_2O removal, or by a combination of both.

References: [1] Larimer J. W. (1968) *GCA, 32,* 965. [2] Larimer J. W. (1975) *GCA, 39,* 389. [3] Larimer J. W. and Bartholomay M. (1979) *GCA, 43,* 1455. [4] Grevesse N. and Noels A. (1993) in *Origin and Evolution of the Elements* (N. Pranzos et al., eds.), pp. 15–25, Cambridge Univ. [5] Scott E. R. D. (1988) *EPSL, 91,* 1. [6] Bischoff A. et al. (1993) *GCA, 57,* 2631. [7] Larimer J. W. and Ganapathy R. (1987) *EPSL, 84,* 123. [8] Baedecker P. A. and Wasson J. T. (1975) *GCA, 39,* 735. [9] Huss G. R. and Lewis R. S. (1995) *GCA, 59,* 115. [10] Cameron A. G. W. (1995) *Meteoritics, 30,* 133. [11] Lissauer J. J. (1987) *Icarus, 69,* 249. [12] Stevenson D. J. and Lunin J. I. (1988) *Icarus, 75,* 146. [13] Lodders K. and Fegley B. (1994) *Icarus, 112,* 368. [14] Wänke H. (1981) *Philos. Trans. R. Soc. London, A303,* 287.

FRAGMENTAL AGGREGATION IN THE NEBULA: A BASIC NEBULAR PROCESS. G. E. Lofgren, Mail Code SN4, NASA Johnson Space Center, Houston TX 77058, USA (gary.e.lofgren@jsc.nasa.gov).

Summary: Fragmental and clastic aggregates have been identified in highly unequilibrated ordinary chondrites [1,2]. These aggregates are composed of pulverized chondrule debris including individual olivine and pyroxene crystal fragments, chondrule fragments, and, rarely, whole chondrules together with varying amounts of fine-grained nebular matrix material, troilite, and metallic Fe-Ni. These aggregates not only attest to extensive recycling as part of chondrule formation, but also suggest a process that affects chondrule compositional variations. The chondrule compositions are a function of random mixtures of these components in a manner similar to that described by Alexander [3]. Rims that are considered of nebular origin [4] enclose many of the aggregates, suggesting that they formed in the nebula. These aggregate particles may be unmelted or may show varying degrees of melting from incipient to extensive. Small degrees of melting produce coherent aggregates with clastic to granular textures. Larger degrees of melting produce igneous textures. Total or near total melting would produce melt droplet chondrules. The rims show different melting histories from the main aggregates suggesting multiple heating episodes. Thus these aggregates most likely are chondrule precursors. They form by processes similar to agglomeratic [5] and fine-grained type I Semarkona chondrules [6]. These findings support the existence of a solar nebula with a long and complicated history with many heating events and sufficient movement and density of particles to allow numerous collisions and comminution of chondrules and the subsequent aggregation of the generated debris followed by reheating and formation of new chondrules in repetitive cycles as suggested by [5,7]. As these aggregates approach larger dimensions, they are the beginning of nebular accretion and asteroid formation.
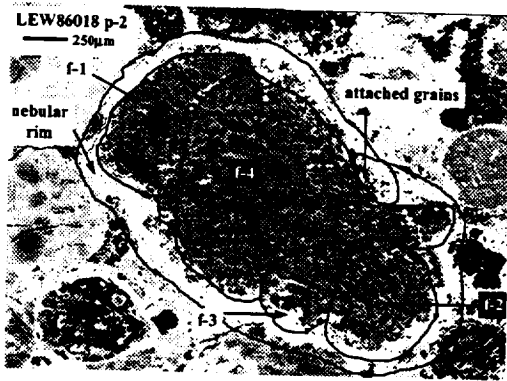
Fig. 1. Fragmental aggregate composed of BP chondrule fragments with attached pyroxene grains enclosed in a nebular rim.

Fig. 3. Clastic aggregate composed of angular to subrounded grains of olivine and pyroxene enclosed in a nebular rim.
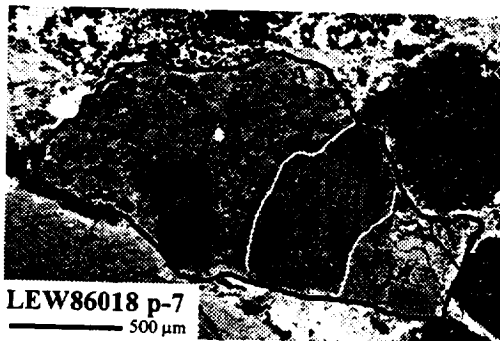
Fig. 2. Fragmental aggregate composed of clastic aggregates and BO and BP chondrule fragments.
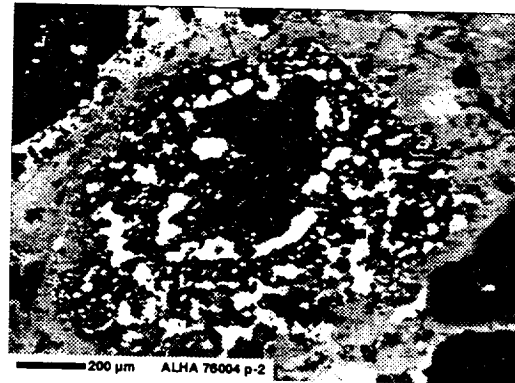
Fig. 4. Clastic aggregate composed of grains of olivine and minor pyroxene enclosed in a nebular rim. Abundant metal segregated toward outer rim of particle.

Particle Descriptions: The fragmental aggregate is the product of an important process in the nebula. It formed by accidental collisions of the six major components of nebular debris listed above and may or may not be enclosed in a clastic, metal/sulfide, or nebular rim. All fragments in the aggregate did not necessarily come together at the same time, consequently some of the fragments or groups of fragments may have acquired rim material before final aggregation. A fragmental aggregate composed of four chondrule fragments is show in Fig. 1. The largest fragment (f-4) is coarsely barred pyroxene and the other fragments are finer BP of similar composition . The boundaries between the fragments are sharp and free of debris. There are clastic pyroxenes of similar composition attached sporadically around the perimeter and the entire fragment is enclosed in a nebular rim of nebular matrix [4] mixed with sulfide. A more diverse fragmental aggregate is show in Fig. 2. It is composed of a clastic aggregate with a large olivine crystal (left), a BO fragment (center), and smaller olivine crystals and BP fragments (right). The clastic aggregate consists of anhedral to subhedral olivine and pyroxene grains with some angular faces and appears to have a clastic texture. The large olivine is distinctly more Mg rich. The BO fragment shows signs of partial melting prior to aggregation. The boundaries of the

large fragments are sharp and arcuate. There is no unequivocal nebular rim, but a partial rim is present.

Clastic aggregates are a subgroup of the fragmental aggregate. They are composed of crystal fragments, and chondrule fragments are rare. A coarse-grained aggregate, shown in Fig. 3, contains Mg-rich olivine and Fe-rich pyroxene with a large grain size variation. Crystals are subangular to subrounded. The pyroxenes are finer grained than olivine. Iron-rich grains tend to be in the outer part of the particle. There is rare sulfide in the particle and a sulfide-rich rim with some Fe metal and nebular matrix material. A much more metal-rich, clastic aggregate is shown in Fig. 4. It consists of a largely metal-free core of coarse, rounded olivines, Fo_{3-11}, surrounded by an outer zone of finer, more-angular olivines, richly interspersed with concentrations of metal and sulfide. The circumference of the particle is marked by an uneven distribution of finer pyroxene grains and a nebular rim encloses the whole particle. There is a group of fine-grained clastic aggregates that appear dark in plane light mostly because they are so fine grained. They usually have an irregular outline and may be metal rich or have a metal-rich rim. Some contain abundant rounded metal grains, some have none. Where partial melting occurs, subsequent overgrowths that develop upon cooling

give some of the crystals euhedral outlines. If there is partial melting, then the metal is usually spherical. With increased partial melting, the more rounded the particle the more the metal migrates outward. The particles described by [5,6] are included in this category, though some of the aggregate olivine particles of [5] may be coarser grained. Rims or partial rims are composed primarily of clastic olivine and pyroxene (angular crystals 5–20 μm), but also including Fe metal and sulfides—mostly troilite and other fine-grained rim or matrix-type debris. These rims may be partially melted and have slightly rounded to subrounded crystals or the crystals could have euhedral overgrowths and a glass or fine-grained mesostasis. With more extensive partial melting they would become the igneous rims described by [8].

Discussion: The processes documented here support existing models developed by [5–7] for aggregation of particles and multiple cycles of heating in the nebula. Further work is needed to determine the effects of these heating events on fine-grained, unmelted materials in order to distinguish them from parent-body heating associated with shock and other kinds of metamorphic heating. The processes that form these aggregates also suggest that the nebula must have a density of particles what would allow sufficient collisions to fragment chondrules to grain sizes of a few micrometers to tens of micrometers and the subsequent aggregation.

References: [1] Lofgren G. E. (1996) *Meteoritics & Planet. Sci., 31,* A81. [2] Lofgren G. E. (1997) *LPS XXVIII;* Russell P. and Lofgren G. E. (1997) *LPS XXVIII.* [3] Alexander C. M. O'D. (1994) *GCA, 58,* 3451–3467. [4] Metzler K. et al. (1992) *GCA, 56,* 2873–2897. [5] Weisberg M. K. and Prinz M. (1996) in *Chondrules and the Protoplanetary Disk* (R. H. Hewins et al., eds.), pp. 119–127, Cambridge Univ. [6] Hewins R. H. et al. (1996) *LPS XXVII,* 537–538. [7] Rubin A. and Krot A. (1996) in *Chondrules*

and the Protoplanetary Disk (R. H. Hewins et al., eds.), pp. 173–180, Cambridge Univ. [8] Krot A. and Wasson J. (1995) *GCA, 59,* 4951–4966.

PARENT-BODY METAMORPHISM OF CV3 CHONDRITES: COUNTERARGUMENTS BASED ON ACCRETIONARY RIMS AND CALCIUM-ALUMINUM-RICH INCLUSIONS.   G. J. MacPherson[1] and A. M. Davis[2], [1]Department of Mineral Sciences, U.S. Museum of Natural History, Smithsonian Institution, Washington DC 20560, USA (glenn@glennm.si.edu), [2]Enrico Fermi Institute, University of Chicago, Chicago IL 60637, USA (a-davis@uchicago.edu).

Krot and coworkers [1] proposed that many features of CV3 chondrites are the result of extensive metamorphism and metasomatism on the CV parent body, including the alkali-rich secondary mineralization in calcium-aluminum-rich inclusions (CAIs). Also, the distinctive platy olivine matrix in Allende and its kin was proposed to result from dehydration of former phyllosilicates. We argue that the model of [1] is too general in seeking to explain diverse features that in fact formed by a variety of processes in different locations, some of them nebular.

Prominent in Allende (and Vigarano and other CV3s) are dark accretionary rims around CAIs. The following features, summarized from the detailed study of [2], are salient: (1) the rims are layered, with the layers differing not only in mineral proportions and grain size but also in mineral compositions; (2) both within individual layers and from layer to layer, extreme disequilibrium mineral assemblages exist that could not have survived extensive high-temperature
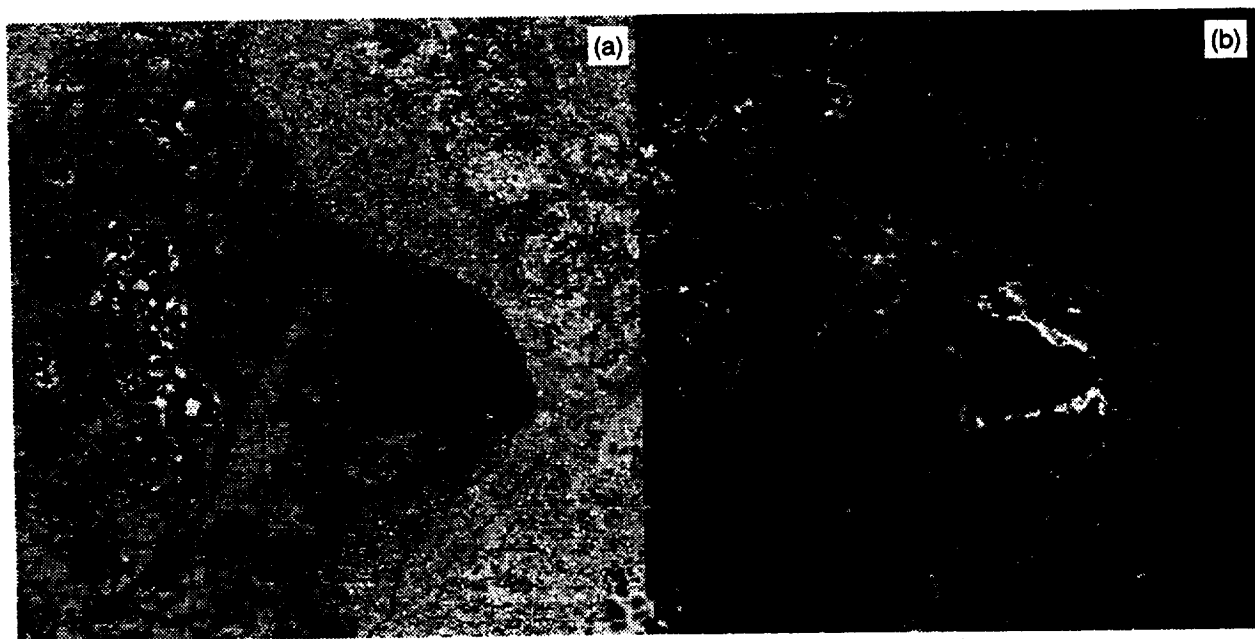
Fig. 1.   (a) Backscattered electron image and (b) Na X-ray map of a portion of an Allende fluffy type A inclusion, showing the distribution of nepheline and sodalite in the accretionary rim of the inclusion. The dark object filling the left of the images is the CAI; the accretionary rim is the uniformly fine-grained gray region just outside the CAI. Note that the inner part of the accretionary rim, nearest the CAI, does not contain Na-rich phases, only the outer portion.

parent-body metamorphism of the type proposed by [1], such as extensive compositional zoning (Fo_{56-94}) within olivine crystals that are <10–20 mm in size, and direct contact of diopside and hedenbergite crystals (the former *surrounds* the latter; [2, Fig. 9]) with no discernible compositional gradients at the point of contact; (3) the layers are highly porous, as are the meteorite matrixes; (4) olivine crystals in the accretionary rim layers have the same distinctive barrel- or lenslike shapes as olivine crystals in the meteorite matrixes; and (5) crystals in the rim layers and matrixes do not show growth interference textures. Many properties of the accretionary rim layers and the matrix in Allende are so similar that the two cannot have unrelated origins, and the properties of both are not compatible with either high-temperature metamorphism of originally anhydrous assemblages or with common formation from dehydration of phyllosilicates. Extensive high-temperature thermal metamorphism cannot explain the preservation of fine-scale mineral chemical zoning or the extreme disequilibrium assemblages within the rims; the dehydration model cannot explain the existence of fine-scale grain size and mineral chemical layering, the crystal chemical zoning or the disequilibrium mineral assemblages, the absence of crystalline intergrowths expected in an assemblage that purportedly grew in place, or the characteristic lensoid shapes of the olivines.

The term "alteration" in CV3 CAIs encompasses a wide range of mineral assemblages and petrographic settings that do not all necessarily have the same origin. The first stage of alteration in Allende CAIs was the replacement of Åk-rich melilite and anorthite with grossular monticellite and wollastonite. A study of such altered areas indicates that they inherit their refractory trace-element patterns from melilite, not fassaite and anorthite, and that no exchange of refractory elements with an external reservoir occurred during alteration [3]. Sodium and halogen infiltration was linked in a second alteration step, and led to the formation of nepheline and sodalite. This assemblage is common in the oxidized subgroup CV3 but sparse in the reduced subgroup. Melilite in type B CAIs commonly contains small but consistent amounts of Na in solid solution, which correlates positively with the åkermanite content of the melilite. This Na, unexpected in pristine high-temperature nebular condensates or their melted derivatives, apparently is the result of remelting of the inclusions following one or more periods of the alkali-rich secondary mineralization [4]. Nepheline and sodalite also occur in the accretionary rim structures described above. The dispersed grains are not uniformly distributed within the accretionary rims or in a general halo of Na-rich phases outside the CAIs but, rather, are confined to specific rim layers (Figs. 1a,b) where they do not appear to be replacing any minerals *in situ*. This stratigraphically controlled distribution suggests the Na-rich phases accreted as such and are not the products of parent-body metasomatism. Measurements of Al-Mg isotope compositions suggest that (1) formation of grossular in type B CAIs occurred >0.5 to >2.4 m.y. after initial CAI formation [3,5]; and (2) the CAI remelting episodes occurred as much as 2–3 m.y. after initial CAI formation [4]. The melting was almost certainly a nebular event, meaning that the alkali metasomatism must also have been nebular unless some mechanism is found for recycling individual CAIs from a parent body to the nebula and back again, possibly multiple times. A different "alteration" assemblage occurs in cavities within CAIs and includes whiskers of wollastonite [6]. The extreme length/width ratios of these crystals suggests growth from a vapor at low degrees of supersaturation, difficult to reconcile with parent-body metamorphism.

References: [1] Krot A. N. et al. (1995) *Meteoritics, 30,* 748–775. [2] MacPherson G. J. et al. (1985) *GCA, 49,* 2267–2279. [3] Davis A. M. et al. (1994) *LPS XXV,* 315–316. [4] MacPherson G. J. and Davis A. M. (1993) *GCA, 57,* 231–243. [5] Hutcheon I. D. and Newton R. C. (1981) *LPS XII,* 491–493. [6] Allen J. M. et al. (1978) *Proc. LPSC 9th,* 1209–1233.

EVAPORATION BEHAVIOR OF MINERALS AND SILICATE MELT IN VACUUM AND IN HYDROGEN GAS.

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Evaporation is one of the major phase transformations at low pressure of the solar nebula and stellar environments. Recent progress of well-controlled evaporation experiments and a theoretical approach have enabled us to recognize the evaporation processes. In the present study, kinetics of evaporation obtained from experiments are summarized with the link of theoretical consideration.

Experimental Work: In the kinetic theory of gas molecules, evaporation rate of a substance is related to its equilibrium vapor pressure, weight of the gas molecule, and temperature. Kinetics of the surface reaction, however, lowers the evaporation rate below that predicted from the equilibrium vapor pressure, which is shown by the evaporation coefficient. What should be studied in experiments are (1) the mode of evaporation, (2) evaporation rate, and (3) isotopic fractionation factor. These experimental results enable us to estimate the temperature and pressure history of the object, and particularly composition of the ambient gas.

Silicates. Mode of evaporation (congruent), evaporation rate in vacuum and H gas including temperature dependence, and isotopic fractionation factor have been studied for forsterite [1–3]. The mode of evaporation (incongruent) of enstatite is being studied [4], but little is know about kinetic behavior, particularly in the presence of H gas. The mode of evaporation, evaporation rate in vacuum and in H gas, and isotopic fractionation factor for SiO_2 in vacuum were studied [1,5]. Hibonite has been intensively studied in the relationship between CAIs [6,7]. Very limited work has been done for other silicates.

Sulfide. The mode of evaporation (incongruent) and evaporation rate of troilite in vacuum and H gas have been studied. Change of the dominant gas species is suggested for different H pressure conditions [8].

Silicate melt. Although many experiments have been carried out [9–12], the role of kinetics has not been fully evaluated. Dependence of a on melt composition and temperature has not been studied systematically. Melt of the SiO_2-MgO system has been fairly well studied, and dependence of the evaporation coefficient of Mg/Si on the bulk composition is suggested [13]. The evaporation of trace elements from silicate melt is quite different from that of major elements, which have a smaller kinetic barrier [14].

Application: Most minerals and silicate melt evaporate incongruently to cause chemical and isotopic fractionation. Two other kinetic processes play important roles when the chemical evolution of an object is considered. One is material transfer (diffusion) in the condensed phase [15,16]. Theoretical application of the possibility of isotopic fractionation was made [16]. The other is crystallization in silicate melt. Except for minerals that evaporate congruently, most minerals and silicate melt change the bulk composition due to partial

evaporation. It causes crystallization isothermally or even during heating [17]. Kinetics on the surface significantly control the evaporation rate and texture of the objects, which may be critical for the estimation of heating conditions of chondrules and CAIs [18].

References: [1] Hashimoto A. (1990) *Nature, 347,* 53. [2] Nagahara H. and Ozawa K. (1996) *GCA, 60,* 1445. [3] Davis A. et al. (1990) *Nature, 347,* 655. [4] Tachibana S. et al. (1997) *Proc. NIPR Symp. Antarct. Meteorites, 21,* 164. [5] Nagahara et al. (1993) *Meteoritics, 28,* 406. [6] Hashimoto A. (1991) *LPS XXII,* 529. [7] Floss C. et al. (1997) *LPS XXVIII.* [8] Tachibana S. and Tsuchiyama A. (1996) *Proc. NIPR Symp. Antarct. Meteorites, 21,* 164. [9] Hashimoto A. et al. (1983) *Geochem. J., 17,* 111. [11] Wang J. et al. (1994) *LPS XXV,* 1457 and 1459. [12] Floss C. et al. (1996) *GCA, 60,* 1975. [13] Nagahara H. and Ozawa K. (1996) *Proc. NIPR Symp. Antarct. Meteorites, 21,* 125. [14] Hashimoto A. (1988) *LPS XIX,* 459. [15] Wang J. et al. (1993) *LPS XXIV,* 1479. [16] Nagahara H. and Ozawa K. (1997) *LPS XXVIII.* [17] Nagahara H. and Ozawa K. (1996) *LPS XXVII.* [18] Ozawa K. and Nagahara H. (1997) *LPS XXVIII.*

RUBIDIUM-STRONTIUM ISOTOPIC SYSTEMATICS OF CHONDRULES FROM THE ANTARCTIC CV CHONDRITES YAMATO 86751 AND YAMATO 86009: ADDITIONAL EVIDENCE FOR LATE PARENT-BODY MODIFICATION.

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Chondrules and CAIs, as well as other components of the CV3 chondrites, were modified by different degrees of late-stage alteration processes [1]. Most Allende (CV) chondrules, as well as CAIs, also indicate Rb-Sr isotopic perturbation [2,3] caused by late open-system modification on the parent body at a significantly later time than 4.5 Ga. In order to clarify the time and nature of the event, we carried out combined Rb-Sr isotopic analyses and petrographic examination of the Allende chondrules [4]. Extending our Rb-Sr isotopic study of carbonaceous chondrites, we have carried out Rb-Sr analyses for the bulk samples and 11 chondrules from the two Antarctic CV chondrites Y 86751 (oxidized subgroup) [5] and Y 86009 (unclassified subgroup), and report the preliminary results compared with those of Allende.

Two BO chondrules with less Na-rich phases and one PO chondrule with more Na-rich phases were analyzed. As shown in Fig. 1a, all the Y 86751 data, including one bulk meteorite, plot closely on the 4.5-Ga reference line, indicating that the bulk meteorite and the chondrules have been in a closed system since their formation at 4.5 Ga. Note that a few Allende chondrules and the bulk meteorite show a similar isotopic feature, but the majority of chondrules show deviation from the 4.5-Ga line to a higher Rb/Sr ratio (Fig. 1a). Because data for Y 86751 are still limited, additional analyses may be required to confirm the observed feature for Y 86751.

Contrary to Y 86751, the Rb-Sr systems for Y 86009 chondrules, as well as the bulk meteorite, are extensively perturbed. Brief petrographic observations of chondrules suggest that Y 86009 chondrules carry more or less Na-rich alteration phases but their abundances appear to be much less than the Allende chondrules. In addition, we noted uncharacterized phases in a few chondrules (weathering prod-
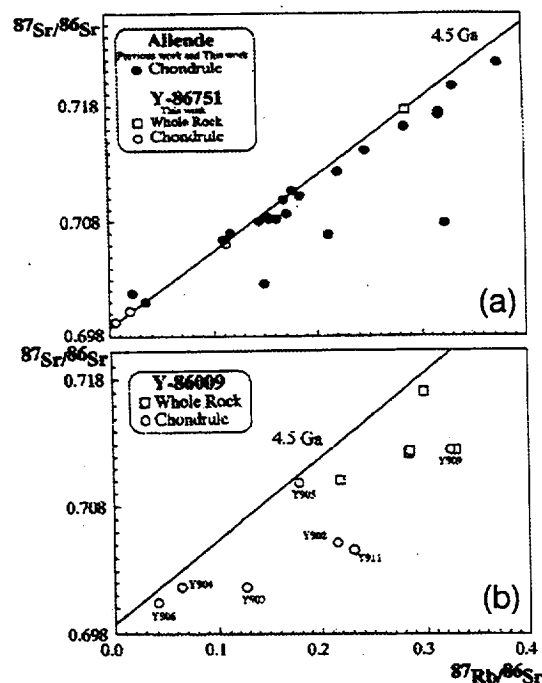
Fig. 1. Rubidium-strontium evolution diagram for the CV chondrites.

ucts?). So it is possible that the Rb-Sr system of the Y 86009 chondrules were affected by terrestrial weathering. However, the Antarctic weathering tends to leach out Rb and so to lower the ^{87}Rb/^{86}Sr ratio [6], which is not the case for the Y 86009 chondrules (see Fig. 1b). We therefore suggest that the chondrules were subjected to severe late-stage Rb-Sr isotopic perturbation on the parent body.

References: [1] Krot A. N. et al. (1995) *Meteoritics, 30,* 748–775. [2] Gray C. M. et al. (1973) *Icarus, 20,* 213–239. [3] Tatsumoto M. et al. (1976) *GCA, 40,* 617–634. [4] Nakamura N. et al. (1993) *Meteoritics, 28,* 407–408. [5] Murakami T. and Ikeda Y. (1994) *Meteoritics, 29,* 397–409. [6] Nishikawa Y. et al. (1990) *Mass Spectroscopy, 38,* 115–123.

EXPERIMENTAL STUDY ON FORMATION OF SECONDARY MINERALS IN CALCIUM-ALUMINUM-RICH INCLUSIONS IN CARBONACEOUS CHONDRITES.

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Introduction: Carbonaceous chondrites contain Ca-Al-rich inclusions (CAIs), which mainly consist of refractory minerals such as gehlenite, spinel, perovskite, and hibonite, which are predicted on the basis of thermodynamic calculations [1] to be the first phases formed from the early solar nebula. However, many CAIs contain secondary minerals such as nepheline, calcite, and phyllosilicates. The formation process of secondary minerals in CAIs is still controversial, whether they were produced by the reaction with the solar nebula [e.g., 2] or by aqueous alteration in parent bodies [e.g., 3].

We performed hydrothermal experiments on gehlenite, spinel, and diopside, which are common in CAIs in carbonaceous chondrites, to study aqueous alteration in parent bodies. Because the

discovery of thermally metamorphosed carbonaceous chondrites suggests that thermal metamorphism after aqueous alteration in parent bodies affects the mineral assemblage of CAIs, we also performed heating experiments on the products obtained by hydrothermal experiments to study subsequent thermal metamorphism after aqueous alteration.

Experimental: Hydrothermal experiments were performed for gehlenite, diopside, and spinel. The mixtures of gehlenite powder and Al_2O_3 and/or SiO_2 reagents were also prepared to study the effect of Al_2O_3 and/or SiO_2 on the aqueous alteration of gehlenite. Solutions with NaOH, Na_2CO_3, and HCl were used. The experiments were performed at 200°C for 7 days.

Heating experiments on hydrogrossular obtained by the hydrothermal experiments as starting materials were performed with an electric furnace at 400°, 500°, 600°, and 700°C for 24 hr. Thermal analyses including DTA (differential thermal analysis) and TG (thermogravimetric) were also performed to study the thermal metamorphism of hydrogrossular obtained by the hydrothermal experiments.

The mineral assemblage of run products was determined by using the X-ray powder diffraction (XRD) method.

Results and Discussion: Gehlenite was decomposed to hydrogrossular and acicular Ca-Si material (probably Ca-Si-hydrate) in a 1N NaOH solution. In a 1N Na_2CO_3 solution, gehlenite was decomposed to calcite and hydrosodalite. Calcite was euhedral and surrounded by the hydrosodalite matrix. This result is consistent with the texture of the CAIs often seen in CM chondrites [4] and can be interpreted as follows: Organic C in the matrix reacted with O_2 in fluid to generate CO_3^{2-} under the oxidizing condition. Gehlenite in CAIs was attacked by the CO_3^{2-}-rich fluid to generate Ca^{2+}-rich fluid enough to crystallize calcite.

Gehlenite was decomposed to amorphous Al-Si by leaching of Ca in a 1N HCl solution. This may be related to the formation of phyllosilicates in CAIs. Sodium-poor fluid may have produced phyllosilicates with calcite whereas Na-rich fluid in parent bodies may have generated hydrosodalite or other Na-Al-Si hydrate with calcite.

For the gehlenite-Al_2O_3 mixtures, the product was hydrogrossular. For the gehlenite-SiO_2 mixtures, the products were hydrogrossular and 11-Å tobermorite [$Ca_5(Si_6O_{18}H_2)$ $4H_2O$] for the 10:1 and 10:2 compositions. For the 10:4 composition, nepheline hydrate ($NaAlSiO_4$ $1/2H_2O$) was obtained in addition to tobermorite. For the 10:8 composition, analcime ($NaAlSi_2O_6$ H_2O) and tobermorite were obtained. The presence of tobermorite from this system suggests that Ca in tobermorite may be supplied by gehlenite because no CaO was added to the starting mixtures. As hydration proceeded, Ca, Al, and Si dissolved in the solution through decomposition of gehlenite to crystallize tobermorite. Analcime or nepheline hydrate may crystallize by the reaction of Al (dissolved from gehlenite), Si (supplied by starting material), and Na (supplied by solution) because Al is not added in the starting material of this system.

Neither diopside nor spinel were affected in all solutions with 1N HCl, NaOH, and Na_2CO_3. This result shows that both diopside and spinel are stronger than gehlenite against alteration under the hydrothermal conditions and is consistent with observation of CAIs [5].

The minerals closely related to secondary minerals observed in CAIs were obtained through hydrothermal experiments on gehlenite. This result suggests that several secondary minerals in CAIs were produced from gehlenite by aqueous alteration in parent bodies. However, anhydrous minerals such as wollastonite, nepheline, and grossular, which are found in CAIs, were not obtained by the hydro-

thermal experiments. One explanation for these anhydrous minerals is that secondary minerals in CAIs were produced by aqueous alteration and the subsequent mild thermal metamorphism in parent bodies.

In heating experiments, H_2O molecules in hydrogrossular decrease with increasing heating temperatures. The differential thermal curve for hydrogrossular gave one endothermic peak at about 500°C. A weight loss between 400° and 600°C in the thermogravimetric curve suggests that the endothermic peak in the differential thermal curve is due to dehydration of hydrogrossular.

On the basis of our experiments, the alteration processes are summarized as follows: Both Na- and Si-rich fluid was supplied by decomposition of matrix glassy materials. This fluid dissolved gehlenite to become rich in Al enough to crystallize nepheline hydrate and/or analcime. Under the oxidizing condition, organic C in parent bodies are expected to have reacted with O_2 in fluid to generate CO_3^{2-}, which reacted with Ca released from gehlenite to crystallize calcite. Under the reducing condition in parent bodies, gehlenite was dissolved by fluid to release Ca, Al, and Si from the surface into fluid. These ions crystallized hydrogrossular, and excess Ca and Si crystallized Ca-Si hydrate such as tobermorite. All hydrous minerals produced by aqueous alteration were dehydrated during the subsequent thermal metamorphism in parent bodies to be converted into anhydrous minerals.

References: [1] Grossman L. (1972) *GCA, 36,* 597–619. [2] Grossman L. and Steele I. M. (1976) *GCA, 40,* 149–155. [3] Greenwood R. C. et al. (1994) *GCA, 58,* 1913–1935. [4] MacPherson G. J. et al. (1983) *GCA, 47,* 823–839. [5] Tomeoka K. et al. (1992) *Meteoritics, 27,* 136–143.

IMPACT MELTING, METAL-SILICATE FRACTIONATION, AND VOLATILE-ELEMENT MOBILITY ON THE L-CHONDRITE PARENT BODY. M. D. Norman, GEMOC, School of Earth Sciences, Macquarie University, North Ryde NSW 2109, Australia (marc.norman@mq.edu.au).

"I think we'd all like to know what's in that rock."
—Agent Mulder

The L-chondrite parent body suffered a massive, possibly catastrophic, impact event about 500 m.y. ago [1–3]. We are investigating the petrologic and geochemical consequences of this event through studies of impact melt and host chondrite material preserved in Chico, a 105-g L chondrite. Chico is composed of ~60% impact melt that intrudes the host chondrite as a dike, and may represent a complex of dikes injected into the wall or floor of the crater during the 500-m.y. event [2].

The host chondrite is shocked to stage S6, and contains pockets of silicate melt and veins of shock-mobilized metal. Chondrules are highly deformed, and are fractured and terminated in sharp contact with the dike. The melt rock is clast poor, and consists primarily of fine-grained, randomly oriented, euhedral olivines and pyroxenes in a matrix of interstitial glass. Metallic globules up to 2 cm in diameter are concentrated along the center of the dike. Their orientation is suggestive of flow differentiation and implies an early stage of metal-silicate immiscibility. Melt textures are present within these globules, which contain Fe-Ni metal, troilite, and schreibersite [2]. Very small (<1–5 μm diameter) pinpoints of metal commonly adhere to the

surfaces of olivine grains, demonstrating imperfect segregation of metal from silicate during the melting.

Variable K/Ca and depletions of Cs, Cd, Bi, Tl, and In in the Chico impact melt relative to the host chondrite have led to suggestions that volatile elements may also have been mobilized during the impact event [2,4].

Chico thus provides a natural laboratory in which to study element partitioning and fractionation caused by metal-silicate segregation and volatile-element mobility during a large impact event on a chondritic parent body. Depletion of volatile elements and fractionation of metal from silicate are characteristic features of the terrestrial planets and presumably many asteroids (e.g., the eucrite parent body), so, conceivably, similar processes on larger scales may have influenced the differentiation of planetesimals during the early history of the solar system.

To investigate the consequences of this impact event on the L-chondrite parent body, we have conducted an INAA study of Chico using samples from the same cores that were analyzed by [2].

Rare-earth-element patterns of the impact melt and the host chondrite are all consistent with an undifferentiated parent body and no large-scale crystal-liquid fractionation during the impact melting event (Fig. 1). Absolute concentrations of the REE in splits of the melt rock vary by about 30%, and are negatively correlated with siderophile elements such as Fe, Ni, and Ir (Fig. 2). Rare-earth-element contents of the host chondrite splits also range to relatively high values, and do not vary with the amount of metal.
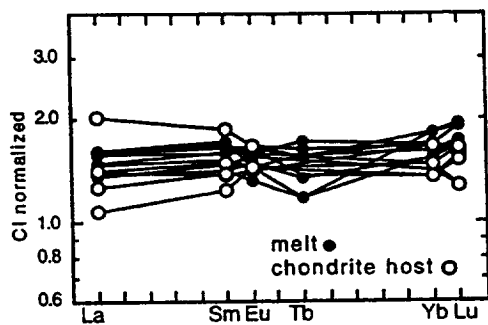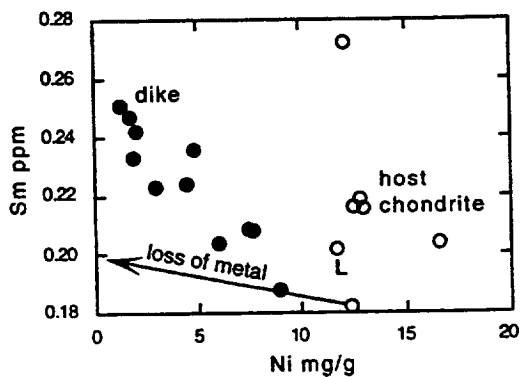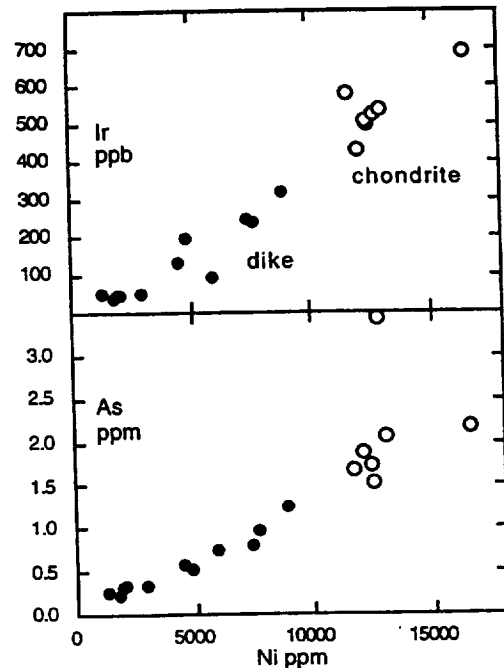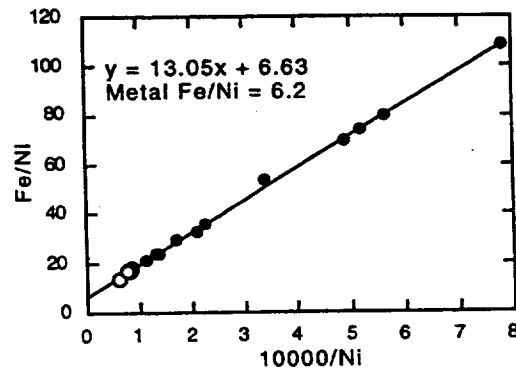

Fig. 3.

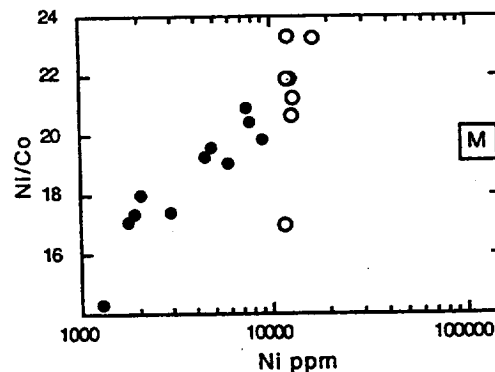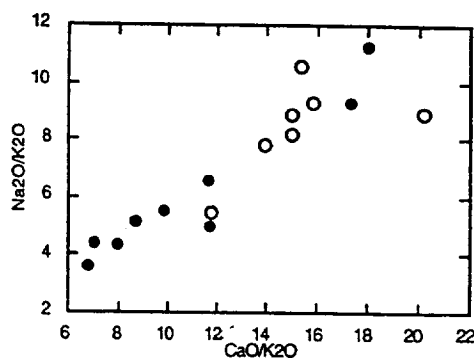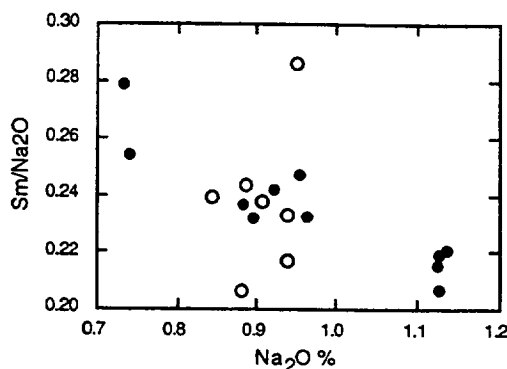Fig. 1.

Fig. 4.

Fig. 2.

Fig. 5.

Fig. 6.

Fig. 7.

Siderophile elements are strongly affected by the metal-silicate fractionation within the dike. Iron, Ni, Co, Ir, Au, As, and Se are progressively depleted in the melt relative to the host chondrite, and trend toward the composition of a metal fragment (M) separated from the dike (Figs. 2–4). Metal fractionation also drives the melt toward low Ni/Co and Ir/Au ratios (Fig. 5). Although Se is depleted in the melt, it was not detected in the metal globule and may have been lost due to weathering of sulfide.

The anticorrelation of REE and siderophile elements must reflect variable proportions of metal and silicate melt, but the melt arrays are too steep to be produced simply by removing metal from the chondrite host (Fig. 2). The dike appears to be overly enriched in incompatible lithophile elements, and the degree of this enrichment correlates with the degree of siderophile depletion. This may reflect migration of residual silicate melt within the dike, or addition of a metal-poor silicate melt component from the host chondrite. LREE variations in the host chondrite may also reflect variable amounts of a melt component.

Potassium and other volatile elements are depleted in the central portion of the dike [2,4], resulting in high Ca/K in some samples (Fig. 6). Most of the melt, however, appears to be enriched in K and have Ca/K lower than the host chondrite, implying possible volatile enrichment, although K may also have been added by the melt component responsible for enrichment of the REE.

Several samples of the dike have Na contents and Sm/Na ratios that cluster around the host chondrite values, while other samples

range to both higher and lower values (Fig. 7). Melting or crystallization of the melt should not fractionate these elements (as long as plagioclase is not involved), so the variations in alkali element content and Sm/Na in the dike may be indicating redistribution of alkalies. Sodium contents lower than those of the host chondrite almost certainly reflect volatile loss as this is difficult to achieve either by melting or by crystallization.

Within the dike there is a general correspondence between the degree of siderophile element depletion, REE enrichment, and alkali element enrichment, suggesting that the processes of metal extraction, melt migration, and volatile-element mobility were physically linked during this impact event in the L-chondrite parent body.

References: [1] Haack et al. (1996) *Icarus, 119*, 182–191. [2] Bogard et al. (1995) *GCA, 59*, 1383–1399. [3] Nakamura et al. (1990) *Nature, 345*, 51–53. [4] Yolcubal et al. (1997) *JGR Planets*, submitted.

FORMATION OF SINGLE-DOMAIN IRON PARTICLES: IMPLICATIONS FOR THE NEBULA.

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There is ample evidence in the meteorite record documenting significant episodes of vaporization and recondensation of refractory material. Under the H-rich conditions prevalent in the primitive solar nebula, one would expect some fraction of the Fe in such vapors to condense as metal. Even in the absence of H, Fe-metal particles can be formed, as has been shown to occur when chondritic starting materials are heated rapidly in vacuum in a solar furnace [1]. *In situ* oxidation-reduction couples can be formed in hot chondritic materials that could be responsible for the production of microscopic metal particles found in the dusty olivine grains occurring in some chondrules [2–4] as well as for the metal blobs found at the surfaces of some chondrules [5]. Given the meteoritic and experimental evidence suggesting the widespread formation of Fe-metal particles in the solar nebula we began a series of experiments to examine the fate of such particles.

Initial experiments [6] were carried out in the presence of a high magnetic field and we reported the rapid formation of enormous, weblike structures resulting from the magnetically induced coagulation of Fe dipoles. The structure of the individual strands was quite similar to the structure of electrostatically coagulated insulating particles studied on USML 1 and 2 by Marshall and Freund [7] and consisted of head-to-tail aggregates of thousands of individual particles linked into very long strings that became cross-linked through coagulation while suspended in the ambient gas. Subsequent work demonstrated that the individual coagulation cross section for magnetic dipoles should be several orders of magnitude greater than the geometric cross section of the grains [8] and argued that a small percentage of magnetic Fe dipoles formed together with insulating silicate grains could serve as a catalyst for the rapid accretion of all the particulates present in the region. Additional experiments carried out to examine the conditions necessary to form magnetic dipoles revealed one very intriguing fact: Magnetic particles could be formed in the absence of a strong magnetic field [9]. In fact, it may be possible to form one class of magnetic particles in the complete absence of

magnetic fields since single-domain grains are, by definition, more thermodynamically stable when the Fe atoms are magnetically aligned than when they are randomly oriented [10].

Our previous studies indicated that the particles produced in our experiments are magnetically hard (the degree and direction of magnetization is highly stable). Unfortunately these grains were produced in relatively strong magnetic fields and were most likely multidomain particles. Single-magnetic-domain Fe grains only occur within a very narrow size range; smaller grains are super paramagnetic and respond rapidly to changing magnetic fields whereas larger grains contain multiple domains and require a strong magnetic field to align them into a single dipole. By controlling the concentration of Fe vapor available for nucleation in our system we can exercise some degree of control over the resultant grain size distribution and have observed that the conditions likely to produce the smallest and largest particles do not show evidence for magnetically induced coagulation, whereas at intermediate particle size such coagulation occurs. We will present magnetic hysteresis loops for various grain size distributions in order to prove the presence of superparamagnetic, single-domain and multidomain grains in our various samples and to delineate the experimentally determined size range for each magnetic phase. We will discuss the implications of these results for observations of modern protostellar disks and will discuss possible morphological evidence in meteorite matrix that could be used to test for the formation and presence of magnetically coagulated grains in the primitive solar nebula.

References: [1] King E. (1983) in *Chondrules and Their Origins* (E. A. King, ed.), pp. 180–187, LPI, Houston. [2] Fredrikson K. et al. (1969) in *Meteorite Research* (P. M. Millman, ed.), pp. 155–165, Reidel, Dordrecht. [3] Nagahara H. (1981) *Nature, 292*, 135–136. [4] Rambaldi E. (1981) *Nature, 293*, 558–561. [5] Grossman J. (1988) in *Meteorites and the Early Solar System* (J. F. Kerridge and M. S. Mathews, eds.), pp. 680–696, Univ. of Arizona, Tucson. [6] Nuth J. A. et al. (1994) *Icarus, 107*, 155–163. [7] Marshall J. R. and Freund F. (1996) *LPS XXVII*, 811. [8] Nuth J. A. and Wilkinson G. M. (1996) *Icarus, 117*, 431–434. [9] Withey P. A. and Nuth J. A. (1996) *LPS XXVII*, 1449–1450. [10] Butler R. F. and Bannerjee S. K. (1975) *JGR, 80*, 252–259.

OXYGEN-FUGACITY INDICATORS IN CARBONACEOUS CHONDRITES: PARENT-BODY ALTERATION OR HIGH-TEMPERATURE NEBULAR OXIDATION?

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Type 3 carbonaceous chondrites (CC) are considered as the best candidates for the identification of primitive components formed by gas-solid reaction in a nebular environment, primarily because of the rarity of H_2O-bearing phases and the lack of thermal metamorphism. That the lack of hydrous phases is indicative of the presence of primary nebular mineral assemblages has been recently challenged [1–3]. It has been proposed that Allende and other type 3 CCs have experienced extensive hydrous alteration but that later dehydration has removed volatile constituents and produced fayalitic olivine with inclusions of pentlandite and Cr-spinel and other secondary minerals in CAIs and chondrules (sodalite, nepheline, andradite, etc.).

Characteristic features of the alteration, whether of nebular or parent-body origin, are described below.

1. The extent of the alteration is different for different meteorites, but even individual meteorites were nonuniformly affected. The boundary between the Allende AF inclusion, considered to be almost completely altered by [3], and normal Allende is very sharp [3,4]. In addition, although fayalitic rims around forsteritic olivine are ubiquitous in Allende, occasionally olivine grains with discontinuous rims are found, which excludes alteration in the present environment [5]. In Y 86751 (CV3) there are chondrules with fayalitic rims and chondrules without rims [6], implying that alteration must have occurred before the final assemblage of brecciated fragments or the aggregation of components of nebular origin.

2. The relationship between the various processes collectively termed alteration is unclear. Rim formation alone may require more than one process [7].

3. The steep compositional gradient between forsteritic and fayalitic olivine provides a constraint to the last alteration process in time-temperature space. This process occurred under conditions that would not allow significant volume diffusion [8,5].

4. Type 2 and 3 CCs have locally retained accretionary structures in the form of rims around chondrules, minerals, and lithic fragments [9,10]. Accretionary rims are still present in AF [4].

5. The bulk chemical changes produced by alteration processes are minor or even absent. There is no evidence in type 2 and 3 CCs for large-scale redistribution of elements by fluid phases on a centimeter scale, except for unusually high abundances of Na, Cl, Br, Au, As, and Sb in Allende AF [11].

It thus can be concluded that the last alteration event in CV chondrites that produced the fayalitic rims with extremely steep FeO-gradients either occurred at low temperatures with variable and limited H_2O-rock interaction in local compartments of the parent body and subsequent short heating or at high temperatures by fast reaction with an oxidizing gas phase and rapid cooling. Both processes are characterized by low ^{16}O [12]. However, there is no simple relationship between $\delta^{17}O$ and the extent of alteration. Type 3 meteorites of the reduced subgroup have higher $\delta^{17}O$ but show less alteration [13]. It appears, in summary, that even if some of the mineralogical changes in type 3 CCs are the result of the hydration/dehydration mechanism, the extent is limited. Many of the mineralogical and mineral chemical phenomena in these meteorites require oxidizing conditions at high temperatures. In the following, arguments for gas-solid reactions at high temperatures and oxidizing conditions is given. Such conditions are not predicted for the canonical solar nebula, they would require addition of O from vaporized material.

There is evidence for oxidizing conditions in Ca,Al-rich inclusions at high temperatures as recorded by trace elements such as W, Mo, and Ce (see summary [14]). Refractory metal alloys in CAIs are oxidized and sulfurized. This requires extensive elemental redistribution, i.e., solid-state diffusion during or after oxidation [15].

Formation of fayalitic halos (~50 μm) in forsteritic olivines requires solid-state diffusion and thus high temperatures. This event must have preceded formation of fayalitic rims with sharp transitions. Less steep FeO gradients in olivine, often observed, also involve significant volume diffusion and must have formed earlier and at high temperatures [5].

Dohmen et al. [16] have experimentally demonstrated that rim formation with the release of gaseous Mg occurs readily on forsterite grains given high temperatures and appropriate O fugacities. The presence of metallic Fe is sufficient to trigger this reaction; physical

contact with forsterite is not required. The ease with which this reaction occurs is surprising and suggests that formation of fayalitic olivine at high temperatures is a common process. This applies equally to the replacement of enstatite by olivine through reaction with FeO.

Fine-grained spinel-rich inclusion of oxidized CV meteorites show simultaneous enrichment in FeO, CoO, Ga_2O_3, and ZnO [17]. In the highly altered Allende AF these elements have normal bulk Allende abundances. Their incorporation into spinel is readily explained by gas-solid reaction, as has been experimentally demonstrated for FeO, CoO, and NiO [15].

The conclusion is that low-temperature alteration, if present in type 3 CCs, is of limited extent and that there is abundant evidence for high-temperature oxidation of primary mineral assemblages. A chaotic solar nebula, variable in f_{O_2} but uniform in chemical composition, is required. This is achieved by the addition of various fractions of volatilized chondritic material.

References: [1] Krot A. N. (1995) *Meteoritics, 30,* 748. [2] Krot A. N. (1997) *Meteoritics & Planet. Sci., 32,* 31. [3] Kojima T. and Tomeoka K. (1996) *GCA, 60,* 2657. [4] Kurat G. et al. (1989) *Z. Naturforsch., 44a,* 988. [5] Weinbruch S. et al. (1990) *Meteoritics, 25,* 115. [6] Murakami T. and Ikeda Y. (1994) *Meteoritics, 29,* 397. [7] Brearley A. J. (1996) *Meteoritics & Planet. Sci., 31,* A21. [8] Hua X. et al. (1988) *GCA, 52,* 1389. [9] MacPherson et al. (1985) *GCA, 49,* 2267. [10] Metzler K. et al. (1992) *GCA, 56,* 2873. [11] Palme H. et al. (1989) *Z. Naturforsch., 44a,* 1005. [12] Weinbruch S. et al. (1993) *GCA, 57,* 2649. [13] Clayton R. N. and Mayeda T. K. (1996) *Meteoritics & Planet. Sci., 31,* A30. [14] Rubin A. E. (1988) in *Meteorites and the Early Solar System* (J. F. Kerridge and M. S. Matthews, eds.), p. 488, Univ. of Arizona, Tucson. [15] Palme H. et al. *GCA, 58,* 495. [16] Dohmen R., this volume. [17] Palme H. and Wark D. (1988) *LPS XIX,* 897.

THERMODYNAMIC MODELING OF AQUEOUS ALTERATION IN CV CHONDRITES.

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The CV carbonaceous chondrites are traditionally considered as rocks consisting of condensates formed in the nebula of the solar composition. The mineralogy and/or chemistry of some textural components of the CV chondrites, such as CAIs, chondrules, and grains of magnesian silicates, are similar to those predicted by equilibrium condensation models [e.g., 1,2]; thus, these components are thought to be primive nebular condensates that survived later stages of alteration in an oxidizing environment. The alteration has resulted in drastic increases in the Fe/Mg ratio in fine-grained matrix olivine and the Ni/Fe ratio in metal, and the formation of secondary minerals including garnets, clinopyroxenes, feldspathoids, phyllosilicates, and others. Petrographic observations indicate that the alteration has taken place on a local scale, i.e., CAIs, chondrules, metal grains, and matrix are replaced by different minerals. There is general agreement among meteoriticists that the secondary alteration was caused by metasomatism, which might have taken place either in the nebular or an asteroidal environment (see [3] for review). In this study we are testing an asteroidal hypothesis [3].

We assume that the primary, unaltered rock consisting of FeO-free silicates, metal, troilite, and accessory minerals has reacted with an aqueous solution that has altered the rock to a certain degree depending upon the water/rock ratio and the temperature of the alteration process. Subsequently, the aqueous solution was lost, and heating of the altered rock partially or completely dehydrated it. Our objective was to monitor changes in the mineralogy of rocks and the chemistry of aqueous solutions (fluids) in these processes.

Since the composition of the aqueous solution is unknown, we have based our estimate on a reasonable assumption that the solution was in equilibrium with the bulk rock or, at least, with the fine-grained matrix. We have chosen the bulk composition of the Allende CV3 chondrite [4] and the matrix composition of Kaba [5]. Calculations were done at 99°C and 150°C and W/R ratios ranging from 0.0001 to 0.5. We found that at W/R < 0.2, practically all H_2O is consumed by the reactions with the anhydrous rock. At W/R = 0.2, a completely altered rock contains ~1–3 wt% aqueous solution with high concentrations of Cl^-, Ca^{2+}, and Na^+ ions. At higher W/R ratios the aqueous solution becomes progressively diluted, with only minor or no changes in the mineralogy of the altered rock. At W/R < 0.2, H_2O reacts with the rock to form H_2 and H_2O-rich fluid, with the H_2O/H_2 ratio and minor contents of H_2S, CO_2, and CO increasing at higher W/R ratios. The reaction of H_2O with both the metal and C results in very high H_2 and CH_4 fugacities so the system must be open (i.e., lose H and methane) to allow H_2O-rock reactions to proceed.

Mineralogical changes during reactions between the H_2O and rock strongly depend upon the W/R ratio and the amounts of metal and C in the rock. If complete equilibrium is maintained, an addition of small amounts of H_2O at 100°C to the rock with the bulk composition of Allende results in a mineral assemblage of wollastonite, grossular, andradite, nepheline, melilite, Ca-olivine, sodalite, apatite, whitlockite, metal, troilite, and C. The first OH-bearing silicate, vesuvianite, appears in minor amounts at W/R as low as 0.001. Grossular disappears at W/R = 0.1. At W/R = 0.1, metal completely oxidizes to magnetite, and monticelite appears at the expense of Ca-olivine, wollastonite, and melilite. At W/R > 0.2, the mineral assemblage consisting of troilite, magnetite, andradite, and phyllosilicates coexists with aqueous solution.

To model H_2O-rock interaction on a local scale, we selected compositions of CAIs [6], chondrules [7], matrix [4], and metal and recalculated them on a FeO-deficient (mg# = 95) and Na, Cl, C, P, Na-free basis. Then we modeled reactions of these rocks and the bulk Allende with the aqueous solution (equilibrated with the Kaba matrix at 150°C and W/R = 0.2) at W/R ratios of 0.1, 1, and 10. At W/R = 0.1 the matrix would consist of metal, troilite, diopside, and olivine (Fa ~50) with minor amounts of spinel and pargacite. Chondrules would be altered to the assemblage of olivine (Fa ~50), diopside, serpentine, talc, clinochlore, troilite, and halite. The alteration of CAIs results in the appearance of Ca,Mg,Al-chlorites with minor amounts of hematite, calcite, and bassanite; no Na minerals are present. The reaction between metal grains and the aqueous solution results in partial replacement of metal by magnetite with trace amounts of magnesian olivine and halite; the latter crystallizes from the highly saline solution formed due to consumption of H_2O in reaction with the metal. At higher W/R values olivine and metal react with H_2O to produce serpentine and magnetite respectively.

Finally, we modeled the dehydration of altered mineral assemblages at various temperatures up to 600°C. At 300°C some amounts of Ca,Mg-amphibole and Na-phlogopite still remain in the bulk Allende along with forsterite (Fa ~50), diopside, troilite nepheline, spinel, and halite. At higher temperature the bulk mineralogy in-

cludes olivine (Fa ~40), diopside, troilite, anorthite, and spinel. No Na- and Cl-bearing minerals are present. Chondrules would consist of olivine (Fa~20), diopside, and ferroan spinel. CAIs would consist of melilite, spinel grossular, andradite, and traces of anhydrite. Anorthite and nepheline may be also present. Magnetite formed from metal during aqueous alteration should survive dehydration.

Our preliminary results suggest that neither aqueous solution nor fluid would supply Cl and Na to form nepheline and sodalite from volatile-free compositions. More calculations are in progress.

References: [1] Grossman L. (1972) *GCA, 36,* 579. [2] Wood J. A. and Hashimoto A. (1992) *GCA, 57,* 2377. [3] Krot A. N. et al. (1995) *Meteoritics, 30,* 748. [4] Jarosewich E. (1990) *Meteoritics, 25,* 323. [5] Scott E. R. D. et al. (1988) in *Meteorites and the Early Solar System* (J. F. Kerridge and M. S. Matthews, eds.), p. 718, Univ. of Arizona, Tucson. [6] McPherson G. J. et al. (1988) in *Meteorites and the Early Solar System* (J. F. Kerridge and M. S. Matthews, eds.), p. 746, Univ. of Arizona, Tucson. [7] McSween H. Y. Jr. et al. (1982) in *Chondrules and their Origins* (E. A. King, ed.), p. 195, LPI, Houston.

Fig. 1. Mg/Mg + Fe olivine vs. Mg/Mg + Fe orthopyroxene for Antarctic LL chondrites.

ANTARCTIC LL CHONDRITES. A. M. Reid, Department of Geosciences, University of Houston, Houston TX 77204-5503, USA.

Introduction: Among the ordinary chondrites the LL-group minerals have the compositional range that allows the best opportunity to both look at the intragroup variability in mineral compositions and also to determine the variation in mineral composition with petrographic type. Several excellent studies of the LL group [e.g., 1–5] have been restricted only by the relatively small number of samples available for study. The Antarctic collection contains a significant number of LL chondrites, though the majority are LL6s and there are very few LL4s. Silicate compositions have been determined for 28 LL chondrites from the Antarctic collection at NASA Johnson Space Center (JSC).

Analytical Techniques: Major silicate and oxide phases were analyzed by electron microprobe, using the Cameca SX100 at JSC. For each set of analyses the operating conditions were identical and the same standards were used. In addition, one of the most homogeneous LL chondrites was analyzed on separate occasions in order to monitor variation between runs. Table 1 shows the average composition and standard deviation for analyses of olivine, orthopyroxene, clinopyroxene, and spinel in the LL7 chondrite EET 92013. For elements present in amounts greater than 5 wt% the standard deviation on repeat analyses is less than 1.5% of the amount present.

Table 2 shows the average compositions determined for olivine and orthopyroxene in EET 92013,4 for runs on six separate days.

Results: Table 3 shows the average mineral compositions for the 28 Antarctic LL chondrites analyzed to date. Within each individual chondrite there is a remarkable homogeneity in both olivine and pyroxene composition. The total range in averaged olivine and orthopyroxene compositions is shown in Fig. 1, which can be interpreted as indicative of a progressive change in mineral compositions within the LL suite either over a range of bulk compositions, or over a range of redox/temperature conditions for essentially constant bulk meteorite compositions.

Using the Ca content of the orthopyroxene as a measure of metamorphic temperatures achieved, the more Fe-rich silicates record slightly higher temperatures. The mineral data fall approximately into two groups with minerals in LL4,5 chondrites more Mg-rich than the LL6,7s. Thus the more metamorphosed LL chondrites do tend to have more Fe in the silicates and more Ca in the orthopyroxene, consistent with the suggestion that the sequence LL4 to LL7 is one of progressive metamorphic grade and oxidation state [5]. In detail, however, the data are not wholly consistent with this model: While the orthopyroxene has lower Mg/Fe than the coexisting olivine, the Mg/Fe partitioning varies among the meteorites and does not correlate with the Fe content in the silicates. Using the preliminary petrographic classification of the Antarctic LL chondrites, there is not a consistent correlation between petrologic type and mineral compo-

TABLE 1.   Average mineral compositions in LL7 chondrite EET 92013,4.

	SiO$_2$	TiO$_2$	Al$_2$O$_3$	Cr$_2$O$_3$	FeO	MnO	MgO	CaO	Na$_2$O	Total
Olivine	36.94	0.01	0.01	0.02	27.50	0.47	34.59	0.02	0	99.61
n = 208	0.37	0.01	0.05	0.10	0.37	0.03	0.43	0.01	0.01	
Opx	54.40	0.19	0.17	0.12	16.38	0.47	26.92	0.88	0.01	99.56
n = 50	0.28	0.02	0.02	0.05	0.23	0.03	0.25	0.12	0.01	
Cpx	53.33	0.43	0.50	0.81	6.31	0.20	15.96	21.71	0.51	99.79
n = 17	0.32	0.02	0.02	0.05	0.25	0.02	0.16	0.29	0.03	
Spinel	0.05	3.86	5.82	54.31	32.49	0.05	1.73	0.03	0.01	98.37
n = 8	0.03	0.09	0.08	0.31	0.24	0.13	0.19	0.03	0.01	

Numbers in alternate rows are 1σ.

TABLE 2. Mineral compositions for LL chondrite EET 92013,4.

n	SiO$_2$	TiO$_2$	Al$_2$O$_3$	Cr$_2$O$_3$	FeO	MnO	MgO	CaO	Na$_2$O	Total
Olivine										
56	36.90	0.01	0.01	0.04	27.44	0.50	34.26	0.02	0	99.21
36	36.73	0.01	0.01	0.01	27.67	0.45	34.59	0.02	0	99.56
22	37.08	0.01	0.04	0.03	27.50	0.47	34.43	0.03	0	99.62
37	36.60	0.01	0.01	0.01	27.75	0.45	34.85	0.01	0	99.75
31	37.34	0.01	0.01	0.02	27.19	0.45	34.58	0.02	0	99.64
26	37.19	0.01	0.01	0.01	27.46	0.49	35.10	0.01	0	100.3
Orthopyroxene										
17	54.27	0.19	0.16	0.12	16.41	0.49	26.74	0.89	0.01	99.31
2	54.37	0.22	0.18	0.09	16.54	0.44	26.85	0.90	0.02	99.62
9	54.39	0.19	0.18	0.10	16.38	0.47	26.89	0.88	0.01	99.50
8	54.34	0.18	0.18	0.10	16.56	0.45	27.03	0.84	0.01	99.69
5	54.51	0.19	0.17	0.21	16.21	0.44	26.85	0.91	0.01	99.51
9	54.63	0.19	0.17	0.10	16.23	0.48	27.26	0.88	0.02	99.98

Each row is an average of analyses on a separate day.

TABLE 3. Average mineral compositions for Antarctic LL chondrites.

	SiO$_2$	TiO$_2$	Al$_2$O$_3$	Cr$_2$O$_3$	FeO	MnO	MgO	CaO	Na$_2$O	Total
Olivine	37.22	—	—	—	26.36	0.44	35.54	0.04	—	99.72
Opx	54.50	0.18	0.21	0.16	15.89	0.44	27.19	0.96	0.02	99.57
Cpx	53.15	0.41	0.67	0.84	6.28	0.20	16.40	21.01	0.53	99.52
Spinel	0.10	2.98	6.10	55.38	31.75	0.11	1.89	0.03	—	98.35

sitions (e.g., see Fig. 1). In order to provide a complete test of the model of progressively increasing grade and redox state within the Antarctic LL chondrite suite, and perhaps resolve some of the apparent inconsistencies, the preliminary classification as to metamorphic type will be reassessed, and the modal amounts of silicate, metal, and troilite will be determined as a check on the compositional range within the group.

References: [1] Fredriksson K. et al. (1968) in *Origin and Distribution of the Elements* (L. H. Ahrens, ed.), pp. 457–466, Pergamon. [2] Heyse J. V. (1978) *EPSL, 40,* 365–381. [3] McCoy T. J. et al. (1991) *GCA, 55,* 601–619. [4] McSween H. Y. and Patchen A. D. (1989) *Meteoritics, 24,* 219–226. [5] McSween H. Y. and Labotka T. C. (1993) *GCA, 57,* 1105–1114.

ALTERATION OF PRESOLAR DUST BASED ON TRANSMISSION ELECTRON MICROSCOPE/ANALYTICAL ELECTRON MICROSCOPE STUDIES OF CHONDRITIC INTERPLANETARY DUST PARTICLES AND NONEQUILIBRIUM SIMULATION EXPERIMENTS. F. J. M. Rietmeijer, F. Guofei, and J. M. Karner, Department of Earth and Planetary Sciences, University of New Mexico, Albuquerque NM 87131, USA.

Chondritic interplanetary dust particles (IDPs) collected in the lower stratosphere include porous (CP) to less porous chondritic filled (CF) aggregates and compact hydrated chondritic IDPs. Aggregate IDPs are typically dominated by anhydrous minerals, but they may contain small amounts of layer silicates, carbonates, and sulfates to indicate incipient aqueous alteration. Two important observations on the nature of CP and CF IDPs are (1) their morphologies, textures, and ultrafine-grained minerals and mineral assemblages are unique and not found in any conventional meteorite [1] and (2) their infrared spectra closely resemble those of the P and D outer-belt asteroids and comet nuclei [2]. Thus, they are associated with protoplanets containing the least-altered solar nebula dusts that are not sampled by conventional meteorites. Chondritic IDPs from short-period comets may include vestiges of presolar and interstellar dusts among their constituents. Anhydrous IDPs are classified as olivine- and pyroxene-rich CP, whereas CF IDPs and hydrated IDPs are classified as serpentine- and smectite-rich IDPs. These layer silicates are secondary phases due to postaccretion aqueous alteration, and at least part of this IDP classification scheme relies on secondary mineral properties.

The grain sizes of Mg,Fe olivines and Mg,Fe pyroxenes in the smallest recognizable textural units in CP and CF IDPs range from 2 nm to ~50 nm in diameter, occasionally up to ~500 nm. All IDPs enter the Earth's atmosphere at kilometer-per-second velocities and experience a brief (5–15 s) period of flash heating (up to ~1000°C). Based on nucleation and growth theory alone, a typical thermal profile of this event will be conducive to form these Mg,Fe silicates in an amorphous precursor. There is no proof that these ultrafine olivines and pyroxenes, or a fraction of them, formed in this manner. Their formation does not require a sustained thermal regime. It is possible that they are also secondary minerals.

Observations: CP and CF IDPs are typically made up of subcircular units between ~100 nm and ~500 nm in diameter. The first type of unit, "granular units (GUs)," consists of ultrafine-grained

Mg,Fe olivines, Mg,Fe pyroxenes, and Fe,Ni sulfides in an amorphous C and hydrocarbon matrix [3]. To these were added C-free "polyphase units (PUs)" of amorphous to holocrystalline, Ca,Al-bearing ferro-magnesiosilica materials. They include (1) coarse-grained PUs that consist of Mg,Fe olivine and Mg,Fe pyroxene (En,Fo = 0.75–1.0), Ca-bearing aluminosilica materials, and an Fe,Ni sulfide [4] and (2) ultrafine-grained PUs consisting of Mg,Fe olivines and Mg,Fe pyroxenes, plus Fe,Ni sulfides, Fe,Ni metals, or Fe oxides in an amorphous ferro-magnesiosilica matrix. The bulk compositions range from Mg/(Mg + Fe) (el. wt%) = 0.3 to 0.75 [4,5]. They were mislabeled "tar balls" [6], but are now known as GEMS [7]. They occur as S-bearing and S-free units. Sulfur may be lost during atmospheric entry heating [5]. Concentric circular 1.2-nm smectite lattice fringes may occur in ultrafine-grained PUs in addition to anhydrous minerals [5]. A third unit consists of low-atomic-number elements only. Although sheets of carbonaceous materials occur in CP and CF IDPs [8], there is still little evidence for discrete carbonaceous units that may fuse more readily than other units, including GEMS.

The chondritic IDPs are mixtures of these units plus micrometer-sized silicates and Fe,Ni sulfides [10]. None of the units is chondritic for all major elements. In a diagram Mg-Fe-Si (el. wt%) C-free units define two trends: (1) ultrafine-grained units along the Mg,Fe serpentine dehydroxylate, $(Mg,Fe)_3Si_2O_7$, line, and (2) coarse-grained units along the Mg-rich part of a smectite dehydroxylate line, $(Mg,Fe)_6Si_8O_{22}$. Two models to explain the petrological properties of C-free units are (1) preaccretion irradiation and amorphization of silicates and sulfides [7] and (2) closed-system crystallization and phase separation within isolated amorphous precursors [4,5]. The presence of typically nonchondritic amorphous materials as precursors to layer silicates, (rare) feldspars, and plagioclase that do not occur as discrete subspherical units in chondritic IDPs was already recognized [cf. 3]. These amorphous materials could be fragments of coarse-grained PUs.

The analytical and transmission electron microscope (AEM/TEM) data revealed two critical properties of the chondritic IDPs: (1) the common presence of amorphous materials with discrete Mg-Fe-Si ratios and Ca-bearing aluminosilica materials and (2) the ultrafine size of their constituent minerals. Both properties cause a high level of free energy that will be available during alteration. Our simulation studies constrain these properties assuming a critical role of nonequilibrium vapor phase condensation in the formation of amorphous materials. We note that amorphous silica and tridymite were prominent phases in the early stages of thermal annealing and hydration and that micrometer-sized silica grains occur in at least one CP IDP [3].

Experiments: We analyzed ultrathin sections of analog samples in the same manner as the IDPs. These analogs included vapor phase condensates (smokes) in the system MgO-Fe₂O₃-SiO₂ [10]. Binary smoke samples were produced in the Flow Condensation Apparatus at 500°C in an H₂ atmosphere at a pressure of ~80 torr. Silicon and O are introduced as SiH₄ and O₂. The starting materials for Fe silicates are liquid Fe(CO)₅ entrained in H gas fed through the liquid before mixing with SiH₄ and excess H₂ in a mixing bulb. This gas then flowed to an alumina furnace tube. Magnesium vapor is produced by heating solid Mg in a graphite crucible in the furnace tube. The mixed gases flow from the furnace (where some condensation occurs) to the cooler collection chamber wherein the remaining vapor condenses. Smokes are scraped from a collector plate located near the gas outlet of the appparatus. We also studied thermal
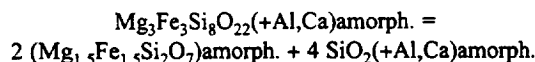
annealing of Mg,Fe,SiO and MgSiO smokes and the hydration of MgSiO smokes.

The condensation study showed that the compositions of the individual smoke grains coincide with metastable eutectic points in the binary equilibrium phase diagrams. The metastable eutectic points in the MgO-SiO₂ system match serpentine and smectite dehydroxylates. Eutectic points in the FeO-Fe₂O₃-SiO₂ system at Fe/(Fe + Si) (el. wt%) = 0.4 and 0.15 do not match Fe silicates. During thermal annealing *in vacuo* fayalite and ferrosilite (~20 nm in diameter) formed after 8 hr at 725°C in amorphous ferromagnesiosilica material. After 167 hr these grains were 100–200 nm. After 167 hr Mg vapor reacted with Fe oxide to magnesioferrite (MgFe2O₄) with local periclase condensation [11]. Forsterite + tridymite had reacted to thermodynamically stable enstatite after 30 hr annealing. In the initial stages of MgSiO smoke hydration, discrete amorphous silica globules formed in the smokes. Only regions that evolved stoichiometric Mg/Si ratios showed kerolite and/or saponite protophyllosilicates and associated Mg(OH)₂ [12].

Discussion: The bulk compositions of ultrafine-grained units plot along the serpentine dehydroxylate line. Its termination on the Mg-Si join of the ternary diagram is constrained by vapor phase condensation. Since Fe during FeSiO condensation was oxidized, we found no metastable eutectic points matching the Fe serpentine dehydroxylate composition (assuming it is allowed in the equilibrium phase diagram). Fayalite and ferrosilite and intermediate phases readily formed during thermal annealing *in vacuo*. This result supports that as long as the Fe oxidation remains in the FeO stability field, $Mg_3Si_2O_7$ condensate may evolve to its Fe end member within the limits of the equilibrium phase diagram, i.e., Mg/(Mg + Fe) ratio <0.85, which matches the highest ratios for pyroxenes and olivines in GEMS. The O fugacities of the environment wherein they evolved were characterized by wustite. Formation of either olivine or pyroxene will be a function of heating rate [13]. Once started, their formation is linked to local supersaturation and formation of an Fe,Ni phase.

The bulk compositions of coarse-grained PUs plot on lines connecting the metastable eutectic points on the Fe-Si join and the metastable smectite dehydroxylate eutectic on the Mg-Si join. This relationship supports that they condensed at more oxidizing conditions than GEMS. The subsequent crystallization and phase separation into Fe,Mg silicates and amorphous Ca-bearing aluminosilica materials proceeded in the FeO stability field.

The mineralogy of coarse-grained units is presented by two generic reactions

$$Mg_3Fe_3Si_8O_{22}(+Al,Ca)amorph. =$$
$$2\ (Mg_{1.5}Fe_{1.5}Si_2O_7)amorph. + 4\ SiO_2(+Al,Ca)amorph.$$

and

$$2\ (Mg_{1.5}Fe_{1.5}Si_2O_7)amorph. = MgFeSi_2O_6 + 2\ MgFeSiO_4$$
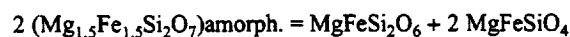
When the original composition was more Fe rich, the sulfides associated with these units formed by sulfidation according to

$$1.5\ Mg_2Fe_4Si_8O_{22}(+Al,Ca)amorph. + 3\ H_2S =$$
$$Mg_3Fe_3Si_8O_{22}(+Al,Ca)amorph. +$$
$$4\ SiO_2(+Al,Ca)amorph. + 3\ FeS + 3\ H_2O$$
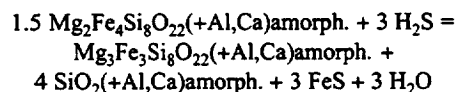
followed by either one or both of the above reactions. The units show

no evidence (yet) for hydration, but H_2O produced in this fashion could be used to form kaolinite, e.g.

$$(Al_2Si_2O_7) \text{ amorph.} + 2\ H_2O = Al_2Si_2O_5(OH)_4$$
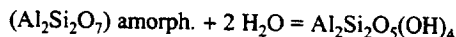
Similar reactions describe the mineralogical properties in GEMs that may contain saponite.

Conclusions: The C-free units are amorphous condensates that underwent thermal annealing in a closed system, but its timing is not constrained by the observations on IDPs. Sulfide formation requires an open system involving H_2S in the solar nebula and also causes incipient aqueous alteration. The data do not invalidate a model of preaccretion irradiation and amorphization, but this model does not account for the origin of preexisting silicates and sulfides.

The amorphous smoke grains that formed directly as solids from the vapor may be regarded as quenched liquids with metastable eutectic points probably at ~500°C. Subsequent thermal annealing and hydration at comparable temperatures promoted phase relations at metastable extensions of equilibrium phase boundaries. Under highly kinetically controlled conditions alternative metastable behavior is to be expected. Thus, alteration products in IDPs will be chaotic, largely unpredictable assemblages until the free energy has dropped to levels commensurate with their local environments.

References: [1] Mackinnon I. D. R. and Rietmeijer F. J. M. (1987) *Rev. Geophys., 25,* 1527. [2] Bradley J. P. et al. (1992) *Astrophys. J., 394,* 643. [3] Rietmeijer F. J. M. (1992) *Trends Mineral., 1,* 23. [4] Rietmeijer F. J. M. (1997*) LPS XXVIII,* 1173. [5] Rietmeijer F. J. M. (1996) *LPS XXVII,* 1073. [6] Bradley J. P. (1988) *GCA, 52,* 889. [7] Bradley J. P. (1994) *Science, 265,* 925. [8] Thomas K. L. et al. (1993) *GCA, 57,* 1551. [9] Rietmeijer F. J. M. (1997) *LPS XXVIII,* 1169. [10] Karner J. M. (1997) M.Sc. thesis, Univ. of New Mexico. [11] Fu G. and Rietmeijer F. J. M. (1994) *LPS XXV,* 493. [12] Rietmeijer F. J. M. (1996) *LPS XXVII,* 1069. [13] Rietmeijer F. J. M. (1996*) Meteoritics & Planet. Sci., 31,* A114.

CORRELATION OF WATER OF HYDRATION WITH DIAMETER IN THOLEN E-CLASS AND M-CLASS ASTEROIDS.

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Water and the OH radical, both in free and bound forms, have strong absorption features near 3 μm, observed on many asteroids since the late 1970s [1,2]. A knowledge of which asteroids are hydrated and where hydrated asteroids are located gives important insights into the conditions prevailing near the beginning of solar system history.

In 1988, Jones et al. discovered two M-class asteroids that had strong absorption features at 3 μm. A systematic survey of M asteroids was started in 1991, with the results through 1993 summarized in [3]. These results confirmed the existence of "wet M" asteroids,

and upset the interpretation of these objects as all being fragments of Fe-Ni cores. These observations led Rivkin [3] to split the "wet M" asteroids off to form a new asteroid class, the W class. The composition of the members of this class is as yet unknown, but may be partly similar to hydrated salts found in the veins of carbonaceous chondrites. Similarly, observations of hydrated E-class asteroids at 3 μm by [3] call into question the association between this asteroid class and the igneous, anhydrous aubrite meteorites [4].

Further studies of M asteroids undertaken in 1995 and 1996 give a total of 26 M-class asteroids observed. These data show a distinct size dependence with regard to the hydration state of M-class asteroids. 16 Psyche, which is anhydrous, is the only M-class asteroid surveyed that is >200 km. In the 65–200-km-diameter range, 12 asteroids have been observed: 8 hydrated, 3 anhydrous, and 1 uncertain. Of the 13 asteroids surveyed in the 0–65-km-diameter range, 2 are hydrated, 10 are anhydrous, and 1 is uncertain.

Although the E asteroids are much less common than M asteroids, and consequently only six of these elusive asteroids have been observed, a similar trend is recognizable. Four of the six E-class
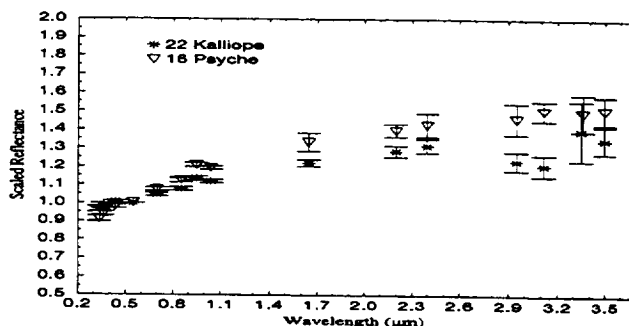
Fig. 1. 0.3–3.5-μm spectra of Tholen M-class asteroids, 16 Psyche and 21 Lutetia, normalized to 0.55 μm. Although these are the two largest asteroids classified as M by [7], they clearly have quite different hydration states. The 0.3–2.5-μm data for these asteroids are from [8,9], and the 1.25–3.5-μm data for the asteroids are from references as per Table 1.
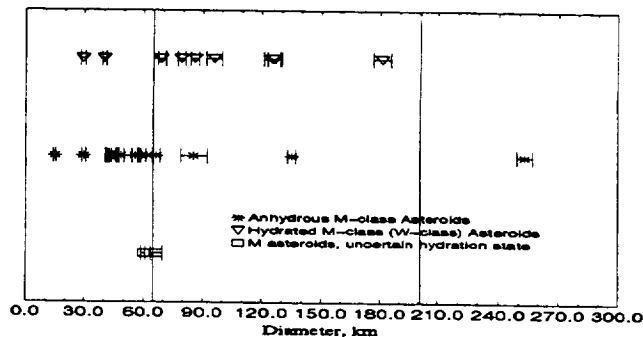
Fig. 2. Comparison of sizes of anhydrous M-class and hydrated M (W-class) asteroids. Vertical lines are drawn at 65 km and 200 km. Note that while most of the W-class asteroids are larger than 65 km in diameter, most M asteroids are smaller. This may be due to collisional properties or a primordial size distribution. The sizes are derived from IRAS [10].

TABLE 1.   Hydration states of E and M asteroids.

Asteroid	Hydrated?	Class	Reference
16 Psyche	No	M	[3,5,6]
21 Lutetia	Yes	W	[6]
22 Kalliope	Yes	W	[6]
55 Pandora	No?	MW	[3,5,6]
75 Eurydike	No	M	[3]
77 Frigga	Yes	W	[6]
92 Undina	Yes	W	[3,5]
110 Lydia	Yes	W	[6]
125 Liberatrix	No	M	[6]
129 Antigone	Yes	W	[6]
135 Hertha	Yes	W	[6]
136 Austria	Yes	W	[6]
161 Athor	No	M	[6]
184 Dejopeja	No	M	[6]
201 Penelope	Yes	W	[3]
216 Kleopatra	No	M	[3]
337 Devosa	No	M	[6]
359 Georgia	No	M	[6]
369 Aeria	Yes?	WM	[6]
497 Iva	No	M	[3]
572 Rebekka	No	M	[3]
771 Libera	Yes	W	[6]
785 Zwetana	No	M	[3,6]
796 Sarita	No	M	[3]
857 Glassenappia	No	M	[6]
44 Nysa	Yes	E	[3,6]
64 Angelina	Yes	E	[3,6]
214 Aschera	Yes	E	[6]
317 Roxane	Yes	E	[6]
620 Drakonia	No	E	[3]
2035 Stearns	No	E	[6]

We follow [3] in splitting hydrated M asteroids to the W class.

asteroids are observed to have a 3-μm water-of-hydration feature, while the other two are anhydrous. The two anhydrous E asteroids (620 Drakonia and 2035 Stearns) are the two smallest asteroids in the group observed, while the hydrated E asteroids are the largest in the spectral class.

We will present spectra of these asteroids and discuss the implications of this size dependence with regard to their possible origin and composition and how this relates to aqueous alteration and thermal history.

References: [1] Lebofsky (1978) *Mon. Not. R. Astron. Soc.,* *182,* 17. [2] Feierberg et al. (1985) *Icarus, 63,* 183. [3] Rivkin et al. (1995) *Icarus, 117,* 90. [4] Bell et al. (1989) in *Asteroids II,* Univ. of Arizon, Tucson. [5] Jones et al. (1990) *Icarus, 88,* 172. [6] Rivkin et al., this volume. [7] Tholen (1989) in *Asteroids II,* Univ. of Arizona, Tucson. [8] Zellner et al. (1985) *Icarus, 61,* 355. [9] Bell et al. (1988) *LPS XVIIII,* 57. [10] Tedesco et al. (1989) in *Asteroids II,* Univ. of Arizona, Tucson.

ALTERATION OF CALCIUM-ALUMINUM-RICH INCLUSIONS: TIMES AND PLACES. S. S. Russell and G. J. MacPherson, Department of Mineral Sciences, MRC NHB-119, U.S. Museum of Natural History, Smithsonian Institution, Washington DC 20560, USA (srussell@volcano.si.edu).

Calcium-aluminum-rich inclusions (CAIs) commonly contain a distinctive suite of secondary minerals. The chemical and isotopic compositions of these minerals can be used to constrain the site and timing of the alteration event. The style of alteration in CAIs is strongly dependent on the meteorite group in which they are found.

CV Meteorites: CAIs from the oxidized subgroup (e.g., Allende) show extensive signs of secondary alkali and Fe enrichment. The fine-grained secondary minerals (typically <10–20 mm) include nepheline, sodalite, monticellite, hedenbergite, andradite, and grossular; these typically embay primary minerals and fill cross-cutting veins within the CAIs. Some euhedral whiskers of wollastonite and nepheline are located within cavities. In addition, multilayered Wark-Lovering rim sequences on CAIs clearly postdate the CAI interior, and in that sense can be considered secondary. Fine-grained inclusions are typically more altered than coarser-grained ones: alteration in these inclusions consists of feldspathoid layers surrounding primary spinel. The temperature of melilite + anorthite breakdown to grossular + monticellite in type-B Allende CAIs has been estimated to be 668°C [1]. Hutcheon and Newton argued that the temperature must have remained around this value for a "prolonged period" to allow formation of large grossular grains, but the timing of the high-temperature alteration event was probably <~100,000 yr, otherwise Mg diffusion would ensure the CAI anorthite no longer retains a ^{26}Mg excess [2].

The location of the alkali-Fe alteration has been widely debated. Most workers believe the alteration took place in a nebular setting. The sequence of alteration is compatible with equilibration with a cooling, oxidized solar nebula gas [3]. Wark [4] argued for pre-accretionary alteration because of the presence of alkali-rich halos in the meteorite matrix surrounding some CAIs. Sodium mapping of Allende CAIs shows that the Na is enriched in accretionary rims, suggesting CAIs became alkali rich prior to incorporation in the parent body. Veins cross cutting CAIs typically do not extend into the meteorite matrix, indicating they did not form *in situ.* Euhedral wollastonite whiskers, nepheline needles, and grossular in CAI cavities are indicative of condensation from a vapor, and these grains probably formed in the nebula. An alternative viewpoint, championed by Krot et al., argues that the alteration of CV CAIs can be explained by a parent-body process of alteration by alkaline-rich fluids followed by dehydration [5]. This process is postulated to have affected the more oxidized CV meteorites, such as Allende, more than the other CVs, a conclusion also reached by some other studies [e.g., 6].

CO Meteorites: CAIs in CO3 chondrites have experienced considerable secondary alteration, both before and after accretion [7,8]. The presence of altered CAIs in unmetamorphosed CO3s indicates some events occurred in the nebula: formation of Wark-Lovering rims, melilite and anorthite breakdown, and Fe enrichment of spinels in hibonite-rich inclusions. In contrast, correlations between petrologic type of the host meteorite with Fe content and melilite breakdown in type A and spinel-pyroxene CAIs suggest some alteration occurred during parent body metamorphism [8]. Hibonite seems to be unaffected by the metamorphism experienced by CO3s.

CM Meteorites: CAIs in CM chondrites have suffered ubiquitous aqueous alteration. The CAI primary mineralogy has been altered to phyllosilicates (Fe serpentines and Mg serpentines) and tochilinite, calcite, and calcium sulphate. Secondary minerals typically occur in a layer immediately beneath the rim sequence. Some

CM CAIs have also suffered fragmentation and recrystallization. It is not clear what the phyllosilicate is replacing: anorthite is a possibility. Greenwood et al. [9] suggest that nebula processes caused fragmentation of CAIs, whereas aqueous alteration took place over a protracted period of time on the parent body. In contrast, [10] argued that the CAIs were not altered in the environment in which they are now found, and many are too fragile to have been moved to their current location by recycling in the regolith, so they favored formation of hydrous secondary minerals in a nebula environment.

CR Meteorites: CAIs in the CR chondrite Acfer 059 show no evidence of alteration [11], whereas inclusions in Renazzo and Al Rais contain some secondary calcite [12].

CH Meteorites: Some CAIs in the CH chondrite ALH 85085 show evidence of recrystallization due to reheating [13]. In contrast, inclusions from PCA 91467 and Acfer 182 appear unaltered [14].

Unequilibrated Ordinary Chondrites: CAIs in ordinary chondrites are rare. Unequilibrated-ordinary-chondrite CAIs are often rimmed, and secondary feld-spathoids are occasionally present. In one Semarkona CAI, melilite has been partially replaced by sodalite [15].

Conclusions: *Times.* While most CAIs are believed to have formed at around the same time, their alteration was an ongoing process that took place over several million years. Iodine-xenon dating suggests that the alteration took place up to >10 m.y. after initial CAI formation [16]. Aluminum-magnesium studies of grossular in CV CAIs also indicate formation >2.4 m.y. after CAI production [17], and a Al-Mg analysis of a recrystallized CAI from CH chondrite indicates a heating event >2 m.y. after CAI production [13]. Chemical exchange between anorthite and melilite in type B inclusions appears to have occurred >2–3 m.y. after CAI formation [18]. Similarly, sodalite in fine-grained CV inclusions is postulated to have formed after ^{26}Al decay, i.e., several million years after CAI formation [19]. In contrast, sodalite in a Semarkona (LL3.0) inclusion apparently formed very quickly after CAI formation [15].

Places. Many CAIs are pristine, but some underwent several heating events. The presence of altered plus pristine CAIs close together in some meteorites (e.g., CMs) suggests that some alteration occurred before they reached their current site in the parent body (although this may reflect postaccretionary brecciation). Many features of alteration appear to have occurred in the nebula. Wark-Lovering rims predate accretion into the present parent bodies. Some primary minerals exchanged with a nebula gas, and some secondary minerals condensed from a vapor. Sodalite in Semarkona [15] probably formed in the nebula, since ^{26}Al dating suggests it formed before the accretion of the asteroids. In contrast, the long time span of alteration suggested by I-Xe dating for Allende CAIs has been used to argue in favor of alteration in a parent body [16]. In addition to nebula processes, metamorphism in parent bodies tended to equilibrate CAIs with their host rock. Aqueous processing in some meteorites may have affected CAIs in parent bodies. The location of the event responsible for incorporation of alkalis into CAIs, however, is still highly contentious.

References: [1] Hutcheon and Newton (1981) *LPS XII*, 491–493. [2] LaTourette and Wasserburg (1997) *LPS XXVIII*, 781–782. [3] Hashimoto and Grossman (1987) *GCA, 51,* 1685–1704. [4] Wark (1981) *LPS XII*, 1145–1147. [5] Krot et al. (1995) *Meteoritics, 30,* 748–775. [6] McSween (1977) *GCA, 41,* 1777–1790. [7] Greenwood et al. (1992) *Meteoritics, 27,* 229. [8] Russell et al. (1997) *GCA,* submitted. [9] Greenwood et al. (1994) *GCA, 58,* 1913–1935. [10] MacPherson and Davis (1994) *GCA, 58,* 5599–5625. [11] Weber and Bischoff (1997) *Chem. Erde, 57,* 1–24. [12] Weisburg et al. (1993) *GCA, 57,* 1567–1586. [13] Kimura et al. (1993) *GCA, 57,* 2329–2360. [14] Weber et al. (1995) *LPS XXVI,* 1475–1476. [15] Russell et al. (1997) *LPS XXVIII,* 1209–1210. [16] Swindle et al. (1998) *GCA, 52,* 2215–2227. [17] Davis et al. (1994) *LPS XXV,* 315–316. [18] Podosek et al. (1991) *GCA, 55,* 1083–1110. [19] Brigham et al. (1986) *LPS XVII,* 85–86.

EVIDENCE FROM THE BOVEDY (L3) CHONDRITE FOR IMPACT-GENERATED CHONDRULES.

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Among the more unusual objects in the Irish meteorite Bovedy are two chondrules whose features suggest that they are the products of shock melting of preexisting rock. One of them is a millimeter-sized, composite object in which one half has the appearance of a cryptocrystalline pyroxenitic chondrule and the other half resembles a coarse-grained, lithic clast. The "chondrule" part has a distinctive blue-brown color, with radiating crystallites and a semicircular external outline. It contains a number of inclusions, up to 50 μm long, of irregularly shaped, birefringent, polycrystalline olivine. The "lithic" part comprises large grains of mosaicized olivine and low-Ca pyroxene. The two halves are interpreted as forming a single object because the boundary between them is intricately interdigitated. Delicate subparallel protrusions from the olivine resemble residual fingers of partially digested silicate in the blue-brown cryptocrystalline phase. The entire object is interpreted as a fragment of impact ejecta in which a small volume of shock-induced melt remained attached to a fragment of its precursor rock.

The second chondrule is also blue-brown in color, pyroxenitic in composition and cryptocrystalline. It is a 2-mm-long, arrow-head-shaped object whose scalloped margins testify to substantial squeezing in the parent body and indentation by neighboring chondrules. It contains conspicuous, colorless, weakly birefringent inclusions of pure silica. Some of the inclusions are elongate, about 30 μm wide, and gently curving, while others are globular with radial protrusions, resembling the shape of an amoeba. This chondrule is figured in [1], where it was incorrectly described as being glassy throughout. The chondrule is interpreted as a droplet of shock melt derived from a silica pyroxenite parent rock. The elongate inclusions suggest inheritance from crystals of tridymite in the precursor rock. The amoeba-shaped inclusions are interpreted as evidence of the coexistence of immiscible silica melt and pyroxenitic melt (consistent with phase chemistry in the silica-enstatite system). As it happens, a potential parent rock for the chondrule, an igneous-textured silica pyroxenite, has been found as a clast elsewhere in Bovedy [2]. This clast has a fractionated composition suggesting that it crystallized on a planetary body. This indirect evidence for early planetary bodies is clearly in keeping with the idea of collision and impact melting.

The recognition of impact-melt chondrules in Bovedy is of interest because it augments a growing body of evidence that some chondrules, at least, are not the products of flash melting of dust clumps in the solar nebula. For example, Sears [3] points to the presence of impact-produced chondrules on the Earth and the Moon. Kitamura and Tsuchiyama [4] show that relict grains in chondrules are far more intensely shocked than their coexisting phenocrysts, and they propose that the relics are survivors of impact melting. Hutchi-

son [5] has long advocated impact as a major force in chondrule production. Rubin [6], while not specifically addressing chondrule production, reports many examples of impact melting, some of which have since been shown to date back to the very early solar system [7].

If chondrules were produced by impact, then why are they so abundant in chondrites yet so rare on the Moon? A simple but unhelpful answer is that most chondrules must have been produced other than by impact. A more interesting speculation is that the efficiency of impact-melt production increases exponentially with temperature, such that a hot target (e.g., an early planetary body heated by short-lived radioactivity) would melt much more copiously than a cold one, such as the Moon. Furthermore, if the hot planetary body were internally molten or partially molten at the time of impact, the scope for abundant chondrule production would seem limitless.

References: [1] Hill H. G. M. (1993) *Meteoritics, 28*, 363. [2] Ruzicka A. et al. (1995) *Meteoritics, 30*, 57–70. [3] Sears D. et al. (1995) *Meteoritics, 30*, 577. [4] Kitamura M. and Tsuchiyama A. (1996) in *Chondrules and the Protoplanetary Disk* (R. H. Hewins et al., eds.), pp. 319–326, Cambridge Univ. [5] Hutchison (1996) in *Chondrules and the Protoplanetary Disk* (R. H. Hewins et al., eds.), pp. 311–318, Cambridge Univ. [6] Rubin A. E. (1985) *Rev. Geophys., 23*, 277–300. [7] McCoy T. J. et al. (1995) *GCA, 59*, 161–175.

ASTEROIDAL MODIFICATION OF C AND O CHONDRITES: MYTHS AND MODELS.

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Accurate models for asteroidal metamorphism and alteration are important for helping to distinguish products of asteroidal and nebular alteration in chondrites, understanding geological processes on chondritic asteroids, and relating chondrite groups to known asteroids. Here we review several ideas about alteration and metamorphism that appear to be oversimplified or incorrect, in order to help identify mineralogical and chemical features in chondrites that are truly products of solar nebular processes.

Aqueous Alteration and Thermal Metamorphism are Separate Processes: McSween's necessary modification of the Van Schmus-Wood sequence for petrologic types [1] has helped to promote the idea that metamorphism and alteration are entirely separate processes that operated in different asteroids. Metamorphism to meteoriticists is the process whereby parent bodies of type 3–6 chondrites were heated in the range 400°–1000°C, homogenizing and coarsening silicates by solid-state diffusion after fluids were largely removed [2]. Alteration is considered to be the process that operated on carbonaceous asteroids at low temperatures (0°–200°C) under conditions where H_2O was stable, producing hydrated minerals, salts, and certain other phases characteristic of CI and CM chondrites [3]. By this process, type-3-like material was converted to lower petrologic types [1]. Recent studies suggest that the two processes may be part of the same asteroidal heating process.

Studies of type 3 chondrites suggest that they commonly experienced both metamorphism and alteration in asteroids. In CV3 chondrites, fluid-assisted growth of new phases in asteroids dominates over simple diffusive equilibration of silicates: magnetite, fayalite, Ca-rich pyroxenes, nepheline, sodalite, grossular, etc., formed in

chondrules, matrixes, and CAIs [4,5]. Allende, which is relatively anhydrous, appears to have experienced extensive asteroidal alteration and dehydration [4,5]. In CO3 chondrites, type I and II chondrules have properties consistent with simple diffusive exchange with matrixes as in type 3.0–3.6 ordinary chondrites [6]. However, plagioclase-rich chondrules in Kainsaz and Lancé experienced metasomatic alteration [7]. The abundance of secondary nepheline in CAIs in CO3s correlates with petrologic subtype, also suggesting that alteration and metamorphism are closely linked [8]. Although CK4–6 chondrites are anhydrous and have chondrules that appear to have suffered only simple metamorphic equilibration, we find that chondrite matrixes have coarse fayalite grains, including some Allende-like laths, that appear to reflect alteration that may have caused S depletion.

Type 3 ordinary chondrites contain small amounts of phyllosilicates [9], carbides, magnetite [10], and metasomatized chondrules [11], which appear to reflect asteroidal alteration. Matrixes in Tieschitz, Bishunpur, and Chainpur have "dendritic" Fe-rich olivines [12] with textures suggestive of fluid-assisted metamorphism. Type 3–6 ordinary chondrites have variations in FeO concentrations in olivine and pyroxene, normative olivine/pyroxene ratios, and metal abundances consistent with fluid-assisted oxidation during metamorphism [13].

Chronologic constraints indicate that metamorphism and alteration both began less than 20 m.y. after CAI formation [14]. We infer that all chondritic asteroids experienced some degree of fluid-assisted metamorphism that was powered by a short-lived heat source, probably ^{26}Al, possibly electrical induction, but not impact heating [15]. Fluids were largely but not completely lost by 500°C because pressures were much lower than on Earth.

Chemical Fractionations Among Chondrites are all Nebular in Origin: Since the composition of CI chondrites, which is the most heavily altered group of chondrites, matches that of the solar photosphere and each chondrite group is held to be isochemical (except for a few volatiles) it is commonly asserted that chemical fractionations between chondrites must be nebular or terrestrial in origin. But there is much mineralogical and chemical evidence to suggest that fluid-assisted metamorphism did change the local bulk chemical composition of chondrites.

CI chondrites show concentrations of Al, Ca, Mg, and Ni that are more heterogeneous than those in, e.g., CO chondrites [16]. Alais has systematically lower Au and higher Sb concentrations than Orgueil [16]. In CM chondrites, Na, K, halogens, and H may have been mobilized during alteration [17,18]. In CV3 chondrites, oxidized and reduced subgroups have different Na, Mn, and Fe concentrations [4].

Compositions of chondritic components were also modified by fluid-assisted metamorphism. Chondrules and CAIs in CV3 chondrites suffered Fe-alkali-halogen metasomatism [4,5]. In LL3 chondrites, Semarkona, fine-grained chondrules were depleted in alkalies by aqueous alteration [11].

The apparent absence of chondrites that are enriched in volatiles above CI levels has been used to argue against volatile loss in asteroids as most volatiles would recondense in the cool outer parts of the asteroid [19], but their absence may reflect low inherent strength or resistance to impact lithification, as for martian meteorites. Volatiles may also have been lost explosively during metamorphism [20].

Heterogeneous Alteration Features are Characteristic of Nebular, not Asteroidal, Processes: Even in relatively homogeneous materials, fluids escape by being focused into distinct con-

duits. The best evidence for the extreme heterogeneity of asteroidal alteration is provided by the Bali CV3 chondrite. Unaltered regions with fresh chondrules and unaltered mesostases are found next to heavily altered veins in which chondrules are largely replaced by phyllosilicates [21]. The veins follow the foliation indicating asteroidal alteration [21]. Heterogeneous metamorphic and alteration features may result from impact brecciation after metamorphism. Thus chondrules that have been partly metamorphosed or altered and subsequently broken to reveal an unaltered surface are not evidence for nebular alteration and metamorphism.

A better understanding of asteroidal processing should lead to an improved system of classification that clearly identifies groups of chondrites from the same asteroid and the nature and extent of their asteroidal modification. The present scheme is fine for types 3–6 but type 1 and 2 mean only Ivuna-like and Murchison-like. A one-parameter scheme is clearly inadequate for low-grade asteroidal metamorphism as chondrules and matrix minerals did not equilibrate with the fluid below 600°C. The primary parameters used for classifying chondrites into groups, and chemical and O isotopic compositions, are not uniform within groups, for reasons that are poorly understood. These problems are illustrated by the difficulty in assigning a group or type to Acfer 094, which contains primitive FeO-poor matrix material, and is probably the least altered chondrite yet identified [22].

References: [1] McSween H. Y. Jr. (1979) *Rev. Geophys. Space Phys., 17,* 1069–1078. [2] McSween H. Y. Jr. et al. (1988) in *Meteorites and the Early Solar System* (J. F. Kerridge and M. S. Matthews, eds.), pp. 102–113, Univ. of Arizona, Tucson. [3] Zolensky M. and McSween H. Y. Jr. (1988) in *Meteorites and the Early Solar System* (J. F. Kerridge and M. S. Matthews, eds.), pp.114–143, Univ. of Arizona, Tucson. [4] Krot et al. (1995) *Meteoritics, 30,* 748–775. [5] Krot et al., this volume. [6] Scott E. R. D. and Jones R. H. (1990) *GCA, 54,* 2485–2502. [7] Jones R. H. and Hutcheon I. D. (1996) *Meteoritics & Planet. Sci., 31,* A67–A68. [8] Kojima T. et al. (1995) *Proc. NIPR Symp. Antarct. Meteorites, 8,* 79–96. [9] Hutchison R. H. et al. (1987) *GCA, 51,* 1875–1882. [10] Krot et al. (1997) *GCA, 61,* 219–237. [11] Grossman J. N. et al. (1997) *LPS XXVIII,* 481–482. [12] Alexander C. M. O'D. et al. (1989) *EPSL, 95,* 187–207. [13] McSween H. Y. Jr. and Labotka T. C. (1993) *GCA, 57,* 1105–1114. [14] Endress et al. (1996) *Nature, 379,* 701–703. [15] Keil K. et al. (1997) *Meteoritics & Planet. Sci.,* in press. [16] Kallemeyn G. W. and Wasson J. T. (1981) *GCA, 45,* 1217–1230. [17] Wolf et al. (1980) *GCA, 44,* 711–717. [18] Browning L. and Bourcier W. (1996) *Meteoritics & Planet. Sci., 31,* A22–A23. [19] Larimer J. W. and Anders E. (1967) *31,* 1239–1270. [20] L. Wilson, private communication. [21] Keller L. P. et al. (1994) *GCA, 24,* 5589–5598. [22] Greshake A. (1997) *GCA, 61,* 437–452.

NEBULAR OR PARENT-BODY ALTERATION OF CHONDRITIC MATERIAL: NEITHER OR BOTH?

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Most chondrite classes contain indications of alteration since the formation of their solid components. In some cases it is clear that the

alteration occurred after aggregation of the present meteorite materials, for example, recrystallization of the metal grains so that they interdigitate silicates. However, in most cases it is unclear where the alteration occurred and often the discussion centers on whether the locale was the "parent body" or the "nebula." If it appears that the alteration involved one of the reactants being in the gas phase, then it is usually assumed that the locale was the nebula. We have been exploring the idea that chondrules and chondrites formed in the regoliths of asteroid-sized bodies made dynamic by the passage of gases from the interior [1]. Figure 1 describes our proposal as it might apply to LL chondrites, but a similar situation applies to the other chondrite classes, except perhaps the CI and CM chondrites where metal is absent and bulk Fe/Si values are solar. The interior is assumed to be CI- or CM-like in its high volatile contents (10–20 wt% H_2O). Radioactive or impact heating causes the release of these volatiles and the larger components are temporarily suspended by the aerodynamic drag of the upward-flowing gases. Smaller particles like metal can be carried through the pore space to the surface, thereby creating a zone of material below the surface (the "LL chondrite region" in Fig. 1) in which there is an enrichment of chondrules and depletion of metal. The degree of separation of metal, and whether the metal particles rise to the surface or sink the bottom of the regolith, is determined by the relative force of gravity and aerodynamic drag. The scenario we propose seems to explain the size sorting of components, and the Fe/Si values characteristic of the major chondrite classes (qualitatively in all cases, quantitatively in some). It also provides a reasonable environment for the formation of chondrules by impact [2]. Here we point out that a dynamic regolith also provides a "planetary" environment for producing a great many alterations requiring a gas phase. In this sense it has elements of both nebula and planetary properties. Some points for discussion:

1. If chondrule rims ("accretionary rims") were produced by the recondensation of volatiles lost by chondrules [3,4], then the temporary atmosphere would be a reservoir to retain volatiles long enough for recondensation on chondrule surfaces without invoking unusually high gas and dust agglomerations in the nebula.

2. Formation of chondrules by impact into such a loosely consolidated regolith would readily explain why chondrules are so highly oxidized, why many cooled in an atmosphere rich in Na and
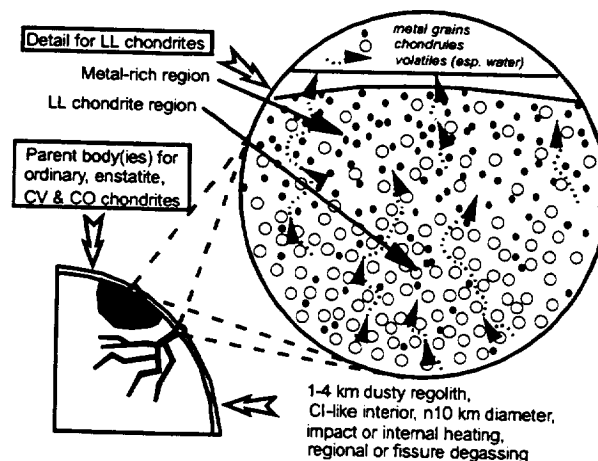

Fig. 1.

other volatiles, why cooling rates were so slow, and why chondrule densities were so high [2].

3. The gas causing the regolith to be dynamic will be largely H_2O (with minor CO_2), and thus a convenient O-bearing reservoir for isotopic exchange [5].

4. The dynamic regolith creates an environment in which a large number of liquid and gas phase reactions involving major, minor, and trace minerals occurred [e.g., 6,7].

5. The time interval between formation of first planetesimals and chondrules, which is very long by nebula standards (several million years [9]), is explained as the interval between formation of parent body and time at which impacts have sufficient energy for chondrule formation [8].

If accretion was of long duration (several million years), then the regolith dust layer would also be an accretionary layer and classical nebular and parent-body processes would be occurring simultaneously. However, whether the dynamic regolith idea has any merit or not, it does illustrate a need to consider environments other than the simple "nebula" and "parent-body" scenarios commonly discussed.

References: [1] Huang S. et al. (1996) *JGR, 101,* 29373. [2] Sears D. W. G. et al. (1995) *LPS XXVI,* 1263–1264. [3] Sears D. W. G. et al. (1993) *Meteoritics, 28,* 669. [4] Hewins R. H. (1991) *Proc. NIPR Symp. Antarct. Meteorites, 2,* 200. [5] Clayton et al. (1983) in *Chondrules and Their Origins* (E. A. King, ed.), p. 37, LPI, Houston. [7] Hutchison R. et al. (1989) *GCA, 51,* 1875. [8] Krot A. N. et al. (1997) *GCA, 61,* 219. [9] Podosek F. A. and Cassen P. (1994) *Meteoritics, 29,* 6.

EVOLVED GAS ANALYSIS: A TECHNIQUE TO STUDY COSMIC ALTERATION OF CHONDRITES? Th. Stelzner and K. Heide, Institut für Geowissenschaften, Friedrich-Schiller-Universität, 07749 Jena, Germany.

Evolved gas analysis has been used to compare the terrestrial alteration of ordinary chondrites with the modification features in three carbonaceous chondrites (Orgueil, Murchison, and Allende).

The interpretation of the evolved gas analysis curves can be complicated due to the often unknown and complex reaction mechanisms or due to the lack of suitable reference substances. For example, particle size or crystallinity of Fe-oxyhydroxides were found to be important factors affecting the release temperature of H_2O [1]. Furthermore, sample-generated O can lead to redox reactions like the oxidation of graphite or carbides (unpublished data).

Falls of ordinary chondrites usually release only very small amounts of volatiles, whereas weathering leads to significant mineralogical changes reflected by the evolved gas analysis curves (Fig. 1).

From the carbonaceous chondrites Orgueil (CI) and Murchison (CM) large amounts of volatiles are evolved (Fig. 2), which can be attributed to products probably formed by aqueous alteration on the parent body [e.g., 2,3].

The following features distinguish the evolved gas analysis curves of Orgueil and Murchison from those of strongly weathered ordinary chondrites: (1) Water release continues to higher temperatures and is probably related to the dehydroxylation of phyllosilicates present in the meteorites (e.g., saponite, serpentine); (2) the release of CO_2 and CO between ~100°C and 700°C indicates that much higher amounts of carbonates were formed; (3) and Orgueil liberates relatively high amounts of SO_2 due to the decomposition of sulfates.

The evolved gas analysis curves of Allende (CV3) are comparable to those of unweathered ordinary chondrites. However, the multistage release of substantial amounts of CO_2 from Allende and of CO from all carbonaceous chondrites above ~700°C have to be related to the oxidation of C-containing phases like graphite, carbides, and diamonds.
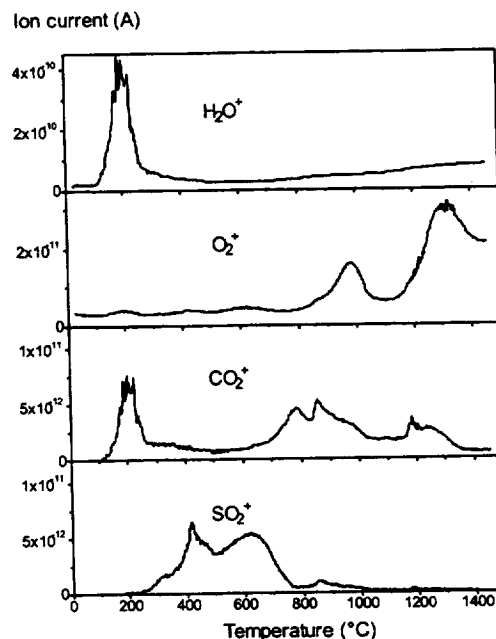

Fig. 1. Evolved gas analysis curves upon heating the strongly weathered H5 chondrite Acfer 212 under vacuum conditions.
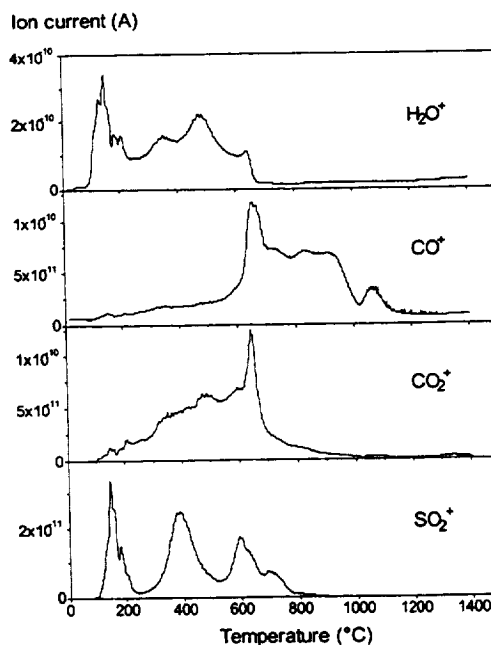

Fig. 2. Evolved gas analysis curves upon heating Orgueil under vacuum conditions.

Conclusions: There are distinct features in the gas release profiles of the investigated carbonaceous chondrites differing from the profiles of weathered ordinary chondrites. Some of the peaks cannot simply be explained by the decomposition of alteration phases identified in these meteorites by means of electron microscopic techniques [i.e., 2,3]. A further investigation of the mineral phases and assemblages responsible for these effects should help to improve the understanding of the chemical and thermal history of carbonaceous chondrites.

References: [1] Stelzner Th. and Heide K. (1996) *Meteoritics & Planet. Sci., 31,* 249–254. [2] Tomeoka K. and Buseck P. R. (1988) *GCA, 52,* 1627–1640. [3] Zolensky M. et al. (1993) *GCA, 57,* 3123–3148.

VOLATILE-ELEMENT ENRICHMENTS IN INTERPLANETARY DUST DUE TO NEBULAR PROCESSES?

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Introduction: Interplanetary dust particles (IDPs) potentially allow us to investigate the most pristine solar system bodies, comets and asteroids. Therefore, they should be predestined to provide information on nebular processes. Many stratospheric IDPs are richer in volatile elements than CI chondrites (cf. compilation by Arndt et al. [1]) while the abundances of major elements usually are chondritic. Attempts to explain the enrichments range from postulating a new type of volatile-rich chondritelike matter [2] to invoking atmospheric contamination processes [3]. Before far-reaching conclusions on nebular processes can be drawn, stratospheric processes, contamination during capture and handling, and artifacts from various selection effects or from analytical techniques and even from numerical data treatment have to be excluded.

Contamination: After the probable importance of stratospheric contamination processes was emphasized based on plausibility reasoning [3], the first direct experimental evidence for contamination—at least for Br, the element with the highest enrichment, up to $10^3 \times$ CI—were Br-salt nanocrystals attached to IDP W7029E5 [4] and a halogen-rich exterior rim of IDP L2006G1 found with time-of-flight secondary ion mass spectrometry (TOF-SIMS) [5]. The distributions of secondary halogen ions emitted from a section of this IDP upon sputtering with primary Ga$^+$ ions (Fig. 1) reveal an outer ring structure for F, Cl, and also Br, though the latter image is disturbed by rather high background. Assuming a spherical particle, 20 µm in diameter, and a continuous 1.5-µm-thick surface layer, this layer represents ≈28 vol% of the IDP. This estimate is an upper limit but illustrates the influence that surface contamination might have on bulk chemistry.

To test more directly for surface contamination, we analyzed the original surfaces of stratospheric particles with TOF-SIMS. A major analytical problem results from residual silicone oil from IDP collection and handling that often cannot be completely removed, even not by extensive hexane rinsing. Nevertheless, we unequivocally detected F, Cl, and Br on the very surfaces of six particles: one Fe,NiS-rich IDP (U2071H9), four Al$_2$O$_3$ spheres (rocket exhaust), and one Ca-rich particle of unknown origin. Extensive sputtering reduced and finally removed the halogens from the Al$_2$O$_3$ surfaces, unambiguous proof of a contamination surface layer.

Arndt et al. [6,7] studied experimentally the question of when contamination occurred by exposing IDP analogs on a capture flag to the stratosphere. Bromine was measured with PIXE before and after flight. Bromine concentrations before exposure were below detection limit, while after exposure significant Br signals were detected. The stratospheric air column passed by the collector even quantitatively accounts for the Br contamination.

Another source of contamination observed in our TOF-SIMS study was surface-correlated Be resulting from SEM EDS analysis performed on Be substrates. After such analyses, some particles tend to stick to the substrate and carry Be after they were removed.

For other elements, no unambiguous evidence for or against contamination is available so far.

Selection Effects: Stratospheric IDPs are subject to selection processes. Thus, the collected particles only roughly represent the near-Earth dust population. The first and maybe most severe selection is caused by the stratosphere itself, more precisely by atmospheric entry heating. Large and high-velocity particles do not survive entry into the atmosphere and thus smaller and slower particles are overrepresented [8].

Human selection also occurs, prevailing in most studies, in that mostly only "chondritic-looking" (black and fluffy) particles are picked from the collector flags [9] and only particles preclassified from SEM EDS analysis as "cosmic" are further investigated. The latter classification is mainly based on major-element composition. This strong bias might be the main reason for the observation that cosmic particles are usually chondritic.

Analytical Techniques and Data Treatment: To measure trace-element concentrations in IDPs very often approaches the limits of detection of most analytical techniques. Therefore, the average concentrations of trace elements are prone to be overestimated since element abundances below detection limits are typically not considered.

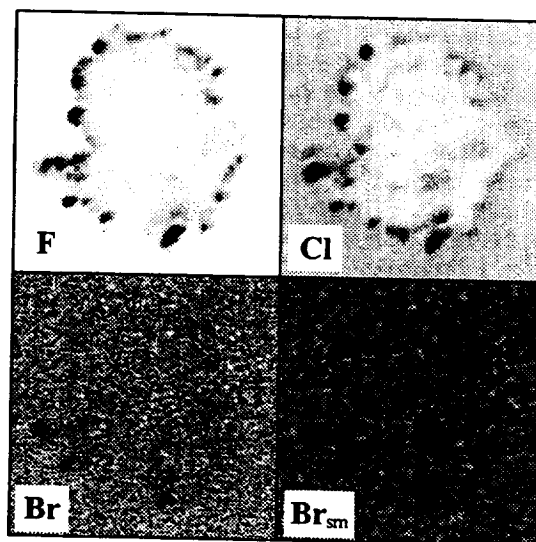Fig. 1. Lateral distribution of negatively charged secondary F, Cl, and Br ions respectively from IDP L2006G1. The three elements are clearly correlated. Field of view is 30 × 30 µm²; high intensity is shown as black. Since the background of Br is relatively high, we also show a smoothed Br image (Br$_{sm}$). In this section the halogens occur in a 1.5-µm-thick rim surrounding the 20-µm (diameter)-sized particle.

The calculation of averages is itself also a problem. The general question is: What does an average tell us if individual IDPs have individual and different parent bodies? Certainly, one does this exercise in order to search for large-scale similarities. But, strictu sensu, only the mean composition of particles that demonstrably— by whatever means—are related to each other provides information on the chemical composition of their precursor. However, no criteria to demonstrate a relationship have so far been developed.

Most trace-element abundances are only known as element ratios relative to a major element, Fe [1]. Low Fe can therefore feign high trace-element contents, and elements anticorrelated with Fe are over-estimated. However, by discussing element groups as done by Arndt et al. [1] this effect is minimized.

Another question is: Which type of average, e.g., geometric or arithmetic, most reliably reproduces the original parent-body composition? If all particles had the same mass and Fe concentration, the arithmetic average would be the best choice. If absolute atom numbers were available for all individual IDPs and if all selection effects were neglected, then the summed atom numbers would represent the parent-body composition [10]. However, in the doable case, i.e., with the existing limited dataset, the geometric averages are appropriate [1]. One also has to keep in mind that within individual IDPs the trace-element distributions are largely variable and reflect chemical inhomogeneity on a micrometer scale [1,11].

Discussion: Since trace-element abundances are available for only 89 stratospheric particles, the reliability of any conclusion from average compositions has to be closely scrutinized [1]. If not all IDPs have the same parent body, averaging can be instrumental in detecting features common to all IDPs, like contamination, or to define groups of IDPs that reflect large-scale chemical differences of the source regions.

Chlorine and Br enrichments have already been attributed to atmospheric contamination processes. Arsenic, Rb, and Zr were detected in only a few IDPs since their limits of detection are close to the chondritic values. Thus, the significance of the enrichments remains questionable [1]. The other elements that are enriched, at least in chemically defined subgroups of the whole IDP set—P, Cu, Ga, Ge, Se, and Zn—show distributions over ~1 or 2 orders of magnitude that include the respective chondritic values. Geometric averages yield enrichment factors of about 2 for these elements that appear to be significant, possibly questionable for Ge.

Sulfur and Ca, on the other hand, are significantly depleted in almost all IDPs and only a few particles with enrichments have been found [1]. Sulfur depletion by atmospheric entry heating has been proposed [12]. In CI chondrites, the best available analog to chondritic IDP parent bodies, Ca occurs as carbonate. Therefore, Ca depletion may result from two effects: First, during disruption of the parent bodies carbonate-rich grains are released that might be too large to survive atmospheric entry. Second, if individual carbonates survive they would probably be discarded as terrestrial contamination since their composition is far from CI-like. Similar selection effects can produce apparent enrichments as well as depletions for other elements.

Conclusions: Since little is known about the actual host phase of most trace elements even in CI chondrites, far reaching conclusions on enrichments in IDPs cannot be drawn. Selection effects during break-up of the parent body, capture by the Earth and by the collector, as well as particle picking in the laboratory, may strongly bias the sample assemblage. Nevertheless, since most IDPs are

chemically remarkably similar to CI chondrites they most probably represent an adequate sample of primitive solar system material and even the only available sample of comets.

References: [1] Arndt P. et al. (1996) *Meteoritics & Planet. Sci., 31,* 817–833. [2] Flynn G. J. and Sutton S. R. (1992) *LPS XXIII,* 373–374. [3] Jessberger E. K. et al. (1992) *EPSL, 112,* 91–99. [4] Rietmeijer F. J. M. (1993) *JGR, 98,* E7409–E7414. [5] Stephan T. et al. (1994) *LPS XXV,* 1341–1342. [6] Arndt P. et al. (1996) *Meteoritics & Planet. Sci., 31,* A8. [7] Arndt P., personal communication. [8] Love S. G. and Brownlee D. E. (1994) *Meteoritics, 29,* 69–70. [9] Warren J. L., personal communication. [10] Jessberger E. K. et al. (1988) *Nature, 332,* 691–695. [11] Stephan T. et al. (1994) *EPSL, 128,* 453–467. [12] Flynn G. J. et al. (1993) *LPS XXIV,* 497–498.

DO IODINE-XENON AGES TELL US ANYTHING ABOUT THE SITE OF SECONDARY ALTERATION?

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The first extinct radionuclide for which evidence was discovered in meteorites was ^{129}I, which has a 16-m.y. halflife and decays to ^{129}Xe. Since the $^{129}I/^{127}I$ should vary with time because of decay, the I-Xe system is potentially a sensitive chronometer. "I-Xe ages" ($^{129}I/^{127}I$ ratios) have been determined in nearly 200 samples from more than 80 meteorites [1]. Although I-Xe ages were originally envisioned as "formation ages," the data never quite made sense because the range in ages was larger than expected in the solar nebula, and there were few correlations with bulk properties. On the other hand, if I-Xe ages are interpreted as secondary ages, not only do the "ages" make sense, but they can tell us something about the timing and location of secondary processing. What they seem to tell us is that much of the processing that the I-Xe ages record occurred on parent bodies.

There are several reasons to think that I-Xe ages are primarily dating secondary parent-body events on a parent body:

1. The range in apparent ages is nearly 50 m.y. for chondrules from the unequilibrated ordinary chondrite Chainpur [2], and at least 10 m.y. for various objects from CV3 Allende [1,3,4]. Two dark inclusions from Efremovka give apparent ages that differ by about 6 ± 2 m.y. [5]. These all seem too long to be reflecting nebular timescales.

2. In studies of whole-rock LL chondrites [6] and of individual chondrules from Chainpur [2] and Tieschitz [7] (and, to a lesser extent, Semarkona [8]), the $^{129}I/^{127}I$ at the time of I-Xe closure is anticorrelated with the $^{129}Xe/^{132}Xe$ ratio, analogous to the evolution with time of Sr or Nd isotopes. Not only does this imply that these objects evolved in a closed system, but we can estimate the I/Xe ratio of that closed system, and it is roughly chondritic, rather than solar.

3. In Allende, the bulk of the I resides in sodalite [9], which is clearly a secondary alteration product. Iodine-xenon studies of objects from Allende have frequently shown highly variable ages within a single object [e.g., 3], almost always showing earlier apparent ages at higher extraction temperatures, as would be expected in a system where a series of events (or even a continuous cooling) caused the I-Xe system in different phases to be set (or reset) at different times. With rare exceptions, no I-Xe ages in Allende are within 5 m.y. of the oldest measured I-Xe ages [1,3,4]. The variability suggests that most,

or all, of what we are seeing is alteration, and the range in ages suggests that it occurred on a parent body.

The most reasonable alternative to the idea that I-Xe ages are dating secondary events is to presume that I-Xe "ages" are really reflecting inhomogeneity in the $^{129}I/^{127}I$ ratio in the solar nebula. Although this is possible, it seems unlikely, both because there is no obvious source for the inhomogeneous I (note that interstellar grains do not seem to have ^{129}I anomalies) and because the anticorrelation of $^{129}I/^{127}I$ and $^{129}Xe/^{132}Xe$ is difficult to explain in the context of nebular inhomogeneity.

This doesn't necessarily mean that there wasn't any secondary alteration in the nebula, but it does strongly suggest that at least some alteration, particularly that involving sodalite in Allende, occurred on parent bodies, rather than in the nebula. The process that introduced volatiles into the dark inclusions in Efremovka (which have much more I and Xe than chondrules or CAIs so far analyzed) also appears to have been a parent-body process.

References: [1] Podosek F. A. and Swindle T. D. (1988) in *Meteorites and the Early Solar System* (J. F. Kerridge and M. S. Matthews, eds.), pp. 1127–1146, Univ. of Arizona, Tucson. [2] Swindle T. D. et al. (1991) *GCA, 55,* 861–880. [3] Swindle T. D. et al. (1988) *GCA, 52,* 2215–2227. [4] Nichols R. H. Jr. et al. (1990) *LPS XXI,* 879–880. [5] Krot A. et al. (1997) *LPS XXVIII,* 769–770. [6] Bernatowicz T. J. et al. (1988) *GCA, 52,* 1113–1121. [7] Nichols R. H. Jr. et al. (1991) *LPS XXII,* 975–976. [8] Swindle T. D. et al. (1991) *GCA, 55,* 3723–3734. [9] Kirschbaum C. (1988) *GCA, 52,* 679–699.

AQUEOUS ALTERATION AND DEHYDRATION PROCESSES IN THE CARBONACEOUS CHONDRITES.

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CI and CM Chondrites: Aqueous alteration is an extremely important process for understanding the formation history of carbonaceous chondrites. CI and CM chondrites, in particular, consist largely of hydrous phyllosilicates and show abundant evidence of aqueous alteration. Where the alteration occurred has long been the subject of controversy. Many recent authors suggest that it occurred in the meteorite parent bodies [e.g., 1–6], although some believe that most of it completed before accretion [e.g., 7]. The most convincing evidence for postaccretional aqueous alteration is probably the presence of veins of sulfates, carbonates, and phyllosilicates [8–10]. The textures suggest that these vein-forming minerals were formed during impact brecciation and leaching events on the regoliths of their parent bodies. Isotopic studies show that at least some of this alteration took place very early after the formation of the parent bodies [11].

Recently, a growing number of CI and CM chondrites mainly from Antarctica have been found to show evidence that they experienced thermal dehydration after aqueous alteration [e.g., 12–14]. In contrast to the normal CI and CM chondrites, they contain abundant fine grains of Fe-rich olivine and Fe-(Ni) sulfides in close association with phyllosilicates in the matrixes. The phyllosilicates show disordered structures characteristic of intermediate states in transition to olivine [13]. The Fe-rich olivines commonly show fibrous morphology, suggesting that they formed by dehydration of phyllosilicates [12,13]. Trace elements in these meteorites are systemati-

cally depleted in the order of increasing volatility [15]. From the mineralogy and trace-element chemistry, they are likely to have been heated to 600°–700°C. Of particular interest is that the metamorphosed CM chondrites show O isotopic compositions distinct from the normal CM chondrites but close to the CI chondrites [16].

CV Chondrites: Evidence from Dark Inclusions: Type 3 carbonaceous chondrites (CV3 and CO3) contain little or no hydrous minerals and have been widely believed to have escaped major degrees of aqueous alteration. However, there is growing evidence that the bulk of the CV3 chondrites were involved in various degrees of aqueous alteration [e.g., 17–21], and it has recently been suggested that some dark inclusions (DIs) in CV3 chondrites were once affected by extensive aqueous alteration [22–25].

Dark inclusions are lithic clasts that range widely in texture from one end member being composed of chondrules and CAIs embedded in a matrix to the other end member consisting mostly of fine grains of homogeneous Fe-rich olivine [26]. Previously they have been proposed to be primary aggregates of condensates from the solar nebula [e.g., 27]. However, a completely opposing interpretation has emerged from recent studies of some DIs [22–25]. Many of the fine-grained type of DIs were found to contain numerous rounded to oval-shaped inclusions in matrixes. The textures suggest that they are pseudomorphs after chondrules and CAIs. Veins filled with fibrous olivine grains were also found to be abundant in the DIs; some veins penetrate several chondrule pseudomorphs, providing strong evidence for aqueous alteration after accretion [26]. Nevertheless, no hydrous phase indicative of aqueous alteration was found from the DIs. This apparent paradox could be resolved by invoking that these DIs have undergone thermal dehydration after aqueous alteration [22–25]. The DIs indeed contain abundant Fe-rich olivine grains with characteristic fibrous morphology similar to phyllosilicates [24,25]. The size distribution of chondrule pseudomorphs and the abundance of CAI pseudomorphs in some DIs suggest that they may have been formerly lithic clasts of chondritic material, most likely to be the host CV chondrites [24], although other DIs may have been derived from other precursors [28].

Parent Bodies: CI and CM parent bodies are regarded to have accreted initially as mixtures of anhydrous silicates and ice [29]. Ice/rock ratios in these parent bodies would have been very high as suggested by the O isotopic study [30]. In the process of parent-body growth, heating must have occurred, and aqueous alteration began by reaction between anhydrous silicates and H_2O derived from melting ice. The presence of veins of sulfates, carbonates, and phyllosilicates suggests that the aqueous alteration occurred in regoliths, and was contemporaneous with the period of regolith gardening. If this hypothesis is valid, the heat to melt ice may have been supplied *in situ* by shock impacts on the regoliths, although the heat may also have been supplied by the decay of radionuclides from the internal regions of the parent bodies. Because of the low gravity in such small bodies, the water would have been gradually lost by sublimation and vaporization. If the heat source continued to operate, the H_2O would have finally run out, then dehydration and thermal transformation of hydrous phases should have begun.

If the suggestion that the precursors of DIs are the host CV chondrites is correct, the following implications would be possible. The CV parent body should also have been once involved in extensive aqueous alteration and subsequent thermal metamorphism. As DIs were incorporated as clasts and show abundant evidence of vein mineralization, aqueous alteration may have occurred in the regolith

like CI and CM parent bodies. However, it may not have been so pervasive as in the CI and CM parent bodies; it probably occurred locally in the parent body where both H_2O and heat were available. Thus, CV materials located where H_2O could not have penetrated remained unaltered. Dark inclusions may represent the materials that existed in the location where H_2O was originally abundant but later ran out, while most of the existing CV chondrites may have come from a relatively dry, unmetamorphosed place. Therefore, the heterogeneity in alteration condition may reflect the heterogeneous distribution of ice and rock at the initial state of the CV parent body.

References: [1] McSween (1979) *GCA, 43,* 1761. [2] Bunch and Chang (1980) *GCA, 44,* 1543. [3] Barber (1981) *GCA, 45,* 945. [4] Tomeoka and Buseck (1985) *GCA, 49,* 2149. [5] Brearley (1995) *GCA, 59,* 2291. [6] Browning et al. (1996) *GCA, 60,* 2621. [7] Metzler et al. (1992) *GCA, 56,* 2873. [8] Richardson (1978) *Meteoritics, 13,* 141. [9] Tomeoka (1990) *Nature, 345,* 138. [10] Lee (1993) *Meteoritics, 28,* 53. [11] Endress et al. (1996) *Nature, 379,* 701. [12] Tomeoka et al. (1989) *Proc. NIPR Symp., 2,* 36. [13] Akai (1990) *Proc. NIPR Symp., 3,* 55. [14] Ikeda (1992) *Proc. NIPR Symp., 5,* 49. [15] Paul and Lipschutz (1989) *Z. Naturforsch., 44a,* 979. [16] Clayton and Mayeda (1989) *LPS XX,* 169. [17] Tomeoka and Buseck (1990) *GCA, 54,* 1745. [18] Keller and Buseck (1990) *GCA, 54,* 2113. [19] Keller et al. (1994) *GCA, 58,* 5589. [20] Lee et al. (1996) *Meteoritics & Planet. Sci., 31,* 477. [21] Brearley (1997) *LPS XXVIII.* [22] Kojima et al. (1993) *Meteoritics, 28,* 649. [23] Krot et al. (1995) *Meteoritics, 30,* 748. [24] Kojima and Tomeoka (1996) *GCA, 60,* 2651. [25] Krot et al. (1997) *Meteoritics & Planet. Sci., 32,* 31. [26] Johnson et al. (1990) *GCA, 54,* 819. [27] Kurat et al. (1989) *Z. Naturforsch., 44a,* 988. [28] Weisberg et al. (1996) *LPS XXVII,* 1407. [29] Grimm and McSween (1988) *Icarus, 82,* 244. [30] Clayton and Mayeda (1984) *EPSL, 67,* 151.

MANGANESE-CHROMIUM SYSTEMATICS IN SULFIDES OF UNEQUILIBRATED ENSTATITE CHONDRITES: PARENT-BODY VS. NEBULAR PROCESSING AND IMPLICATIONS FOR ACCRETION TIMES.

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We recently reported the results of an ion microprobe study of Mn-Cr systematics in individual sulfide grains of unequilibrated enstatite chondrites (UECs) [1]. In that study, we measured Mn/Cr ratios and Cr isotopes in sphalerite (ZnS) and alabandite (MnS) grains of four EL3 chondrites (MAC 88136, MAC 88180, MAC 88184, and EET 90299) and sphalerite and niningerite (MgS) grains of five EH3–4 chondrites (Indarch, Qingzhen, Kota Kota, Y 69001, and Y 74370). The main findings from this investigation are summarized as follows: (1) Sulfide grains analyzed in four of the nine UECs (MAC 88136, MAC 88180, MAC 88184, and Indarch) have clear ^{53}Cr excesses. (2) These excesses can be extremely large, with $\delta^{53}Cr/^{52}Cr$ ranging up to ~18,400‰, the largest ^{53}Cr excess measured so far. Additionally, in some grains, these excesses in ^{53}Cr correlate well with the Mn/Cr ratios (see Figs. 1 and 2 for sphalerites
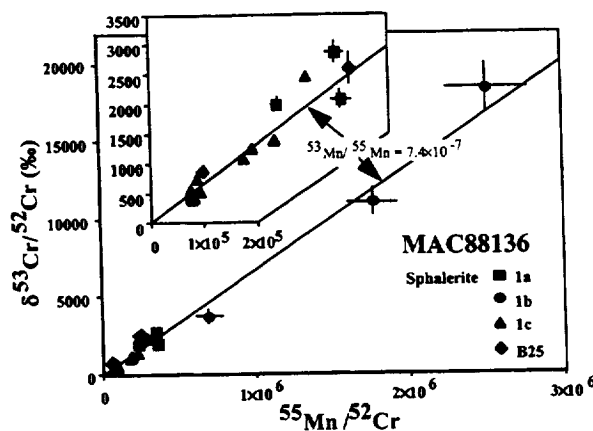

Fig. 1. Manganese-chromium evolution diagram for isolated sphalerite grains, sphalerite #1 (spots a, b, and c) and #B25 in MAC 88136 (EL3). The data are consistent with an inferred $^{53}Mn/^{55}Mn$ ratio of (7.4 ± 0.3) × 10^{-7}. Errors plotted are ±1σ.

in MAC 88136 and Indarch) and are thus most likely produced by *in situ* decay of live ^{53}Mn. (3) In the four meteorites with ^{53}Cr excesses, there are variations in the inferred $^{53}Mn/^{55}Mn$ ratios between different sulfide grains within the same meteorite. Furthermore, within some individual grains, data points scatter and do not lie on a single isochron. These variations are explained by diffusional redistribution of Mn and/or Cr after partial or complete decay of ^{53}Mn. (4) Although no strict chronological significance can be ascribed to the differences in inferred $^{53}Mn/^{55}Mn$ ratios in sulfides of the four meteorites that have ^{53}Cr excesses, limited time constraints may be obtained. Specifically, our data indicate that the $^{53}Mn/^{55}Mn$ ratio in sulfides in the EL3 chondrites was (7.4 ± 0.3) × 10^{-7} at the time of isotopic closure, while the minimum inferred value for sulfides in the Indarch meteorite at the time of isotopic closure was (1.7 ± 0.3) ×
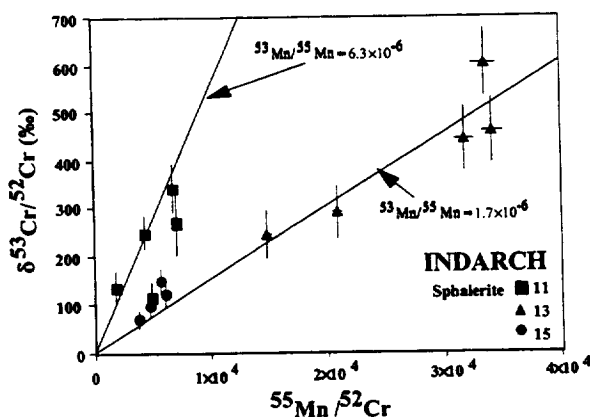

Fig. 2. Data for sphalerite #13 and #15 in Indarch (EH4) are consistent with an inferred $^{53}Mn/^{55}Mn$ ratio of (1.7 ± 0.3) × 10^{-6}, while those for sphalerite #11 appear to be disturbed, with five of the six data points plotting along a line (within 2σ) corresponding to a $^{53}Mn/^{55}Mn$ ratio of 6.3 × 10^{-6}. Errors plotted are ±1σ.

10^{-6}. This further implies that the time of last isotopic equilibration of sulfides in the EH meteorite Indarch preceded that of sulfides in the EL chondrites by at least ~3 m.y.

Although it is clear that diffusive reequilibration has indeed affected the Mn-Cr systematics of the sulfide grains in both EH and EL, we did not ascribe a parent-body or nebular environment for this subsequent processing. However, if the disturbance in the Mn-Cr systematics can be attributed to a specific environment (nebular or parent-body), it would have important implications for the time of condensation of the sulfides and/or accretion of the EH and EL chondrite parent bodies. Therefore, we consider here some plausible scenarios for the environments that may have affected the Mn-Cr systematics in sulfides in these EH and EL chondrites, and their possible implication for the relative accretion times of the EH and EL parent bodies.

In the case of the Indarch EH4 chondrite, it has been previously suggested that the sulfides equilibrated at temperatures in excess of 1000°C, and may even have undergone partial melting [2–4]. This event is generally believed to have occurred "postaccretion" on the EH parent body. It most likely marked the time of last isotopic equilibration for this meteorite. Therefore, it is at this time that the $^{53}Mn/^{55}Mn$ ratio in the sulfides in this meteorite was at least (1.7 ± 0.3) × 10^{-6}. This value may, thus, be regarded as the lower limit on the $^{53}Mn/^{55}Mn$ ratio in Indarch sulfides at the time of accretion. Regarding the isotopic closure of sulfides in the EL chondrites, when the $^{53}Mn/^{55}Mn$ ratio was (7.4 ± 0.3) × 10^{-7}, there are three possibilities, i.e., that it occurred at the time of (1) condensation of the sulfides in the nebula, (2) accretion of the EL parent body, or (3) "postaccretion" metamorphism at a later (unknown) stage. In either of the first two cases, the accretion time for the EH parent body would have to precede that for the EL parent body by at least ~3 m.y. However, in case (3), it is not possible to make any inferences regarding the accretion times of the EH and EL parent bodies. It should be noted that of the three possibilities, the first one is most likely since major- and minor-element zonation patterns preserved in the sulfides in these EL3 chondrites suggest equilibration during cooling in a nebular environment [5,6]. Therefore, it seems most likely that the time of accretion of the EH parent body preceded that of the EL parent body by at least ~3 Ma.

Finally, it should be noted that the above comparisons between EH and EL chondrites are only valid if ^{53}Mn was homogeneously distributed in the region where the enstatite chondrites formed. Recent work [7] suggests that this may indeed be the case.

References: [1] Wadhwa M. et al. (1997) *Meteoritics & Planet. Sci., 32,* 281. [2] Mason B. (1966) *GCA, 30,* 23. [3] Hohenberg C. M. et al. (1967) *Science, 156,* 233. [4] Birck J.-L. and Allègre C. J. (1988) *Nature, 331,* 579. [5] Lin Y. T. et al. (1991) *LPS XXII,* 811. [6] El Goresy A. et al. (1992) *LPS XXIII,* 331. [7] Lugmair G. W. and Shukolyukov A. (1997) *LPS XXVIII,* 851.

CONDITIONS FOR FORMING CALCIUM-ALUMINUM-RICH-INCLUSION RIM LAYERS: PRELIMINARY EXPERIMENTS.

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Similar "Wark-Lovering" rim layers are present on virtually all types of coarse-grained Ca,Al inclusions (CAIs) in CV chondrites.

The aim of this work is to discover the temperature and duration of the nebular processes that created these rim layers (of spinel + perovskite, melilite, and pyroxene).

It was established 10 years ago [1–3] that rims formed in two stages: (1) flash heating of the outer layer of the CAI, leaving a refractory residue that is (2) metamorphosed by diffusion of Mg, Si, and O from the nebula to produce rims. This work will study step (2).

Flash Heating: Flash heating [4] volatilized much of the outer 100–400 μm of each CAI to leave a residue with concentrations of very refractory trace elements 2–8× higher than in the CAI. In order to produce refractory enrichments of 2–8×, the most volatile one half to seven eighths (i.e., 50–87%) of the outer CAI material was volatilized. The two most volatile major components (30–42% of CAIs) are MgO and SiO$_2$. Hence, all Mg and Si must have been volatilized. The next most volatile component, CaO, comprises 20–40% of CAIs. Hence, from one half to most of the Ca must also have been removed in the 50–87% volatilized matter. The residues would thus have been predominantly Al$_2$O$_3$ with lesser amounts of CaO and TiO$_2$. The residue corresponding to a rim:CAI refractory enrichment of approximately 2.3× has a composition [5] of 77.4% Al$_2$O$_3$, 20.0% CaO, and 2.6% TiO$_2$. Synthetic material of this composition, consisting of CaAl$_4$O$_7$ (grossite) with minor CaTiO$_3$ (perovskite) was used to represent the "rim residue" in the experiments below.

Metamorphism: Rims on CAIs typically contain about 16% MgO and 20% SiO$_2$ that diffused into the cooling residue from the nebular gas. The Mg:Si atom ratio in rims is on average ~1.2, close to the 1.1 ratio of nebular gas in the pressure-temperature interval after most Ca and Al had condensed and before major Mg and Si condensation. Magnesium, Si, and O each diffused into the refrac-

Fig. 1.

tory residue, with different chemical potentials at each depth, leading to formation of specific mineral layers [6].

Experiments: The aim is to find temperatures and diffusion times that produce rim layers. This preliminary work used a polished $MgSiO_3$ plate to supply Mg and Si in approximately the correct proportions to the polished surface of the synthesized "rim residue." So far, the following three diffusion couples have been heated in air, and analyzed by SEM: (1) 5 hr at 1400°C, (2) 18 hr at 1225°C (see Fig. 1), (3) 4 hr at 1300°C.

Why can a solid source be substituted for nebular gas? The assumption is that the governing process in forming rims is the rate of diffusion and reaction in the refractory residue, and thus the means of supplying Mg and Si is, to first order, not important. The conditions (time and temperature) for producing CAI rim layers can then be found in laboratory diffusion experiments.

Results: Experiment A did not produce rim layers, only a reaction zone 65 μm wide. Experiment B produced the rimlike layers in Fig. 1, with the following similarities to those in CAIs: (1) Parallel layers with thicknesses of 4–7 μm and total width of 45 μm; (2) same order of italicized phases: *hibonite, spinel,* plagioclase, forsterite, and silica, *diopsidic pyroxene.* In experiment C, 10% more MgO was mixed with the enstatite to reduce excessive silica, resulting in *gehlenitic melilite* replacing the plagioclase, as in CAI rims. The chief difference so far from CAI rims is the siliceous forsterite layer below the diopside. It also seems that Ca is too high. New experiments with lower CaO (12%) and a source with 1.1:1 Mg:Si atom ratio are underway. These early results suggest that rim formation could have required times of about 20 hr at about 1200°C.

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References: [1] Boynton W. V. and Wark D. A. (1985) *Meteoritics, 20,* 613–614. [2] Boynton W. V. and Wark D. A. (1987) *LPS XVIII,* 117–118. [3] Wark D. A. et al. (1988) *LPS XIX,* 1230–1231. [4] Boynton W. V. (1988) *Meteoritics, 23,* 254. [5] Hashimoto A. (1983) *Geochim. J., 17,* 111–145. [6] Ruzicka A. and Boynton W. V. (1995) *Meteoritics, 30,* 570.

OXYGEN FUGACITY IN THE SOLAR NEBULA.
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A major early success of cosmochemical modeling was the recognition that the constituents of chondrites are readily understood by sequential condensation in a cooling gas of cosmic (=solar) composition, tempered by the metastable survival of some high-temperature phases. Of particular importance is Fe, which prefers metallic bonds at high nebular temperatures (>1000 K) and bonds to O and S at low (<700 K) temperatures. Redox conditions in a canonical nebula (one with a solar composition) are controlled (buffered) by the abundance of gaseous H_2 and H_2O. The currently accepted canonical pH_2/pH_2O is 1500, and is relatively insensitive to nebular temperature. Thus, both the formation of Fe-Ni and its later corrosion by H_2O (and H_2S) are readily understood in terms of plausible processes in a canonical nebula.

Already two decades ago a few researchers began to try to model some features of chondrites by condensation from noncanonical nebulae [1]. About 12 years ago there was an upsurge in the development of such models stimulated by several petrographic and cosmochemical observations that seemed to require nebular redox conditions orders of magnitude greater than present under canonical conditions. A large fraction of these observations involved late-formed deposits of oxidized Fe, especially fayalite, and many were made on the Allende CV chondrite. Two papers were particularly influential: (1) Fegley and Palme [2] observed that, in many refractory inclusions, Mo and W are depleted relative to other siderophiles having similar volatilities, and that W and Mo are much more volatile under oxidizing conditions whereas other siderophiles are scarcely affected; and (2) Peck and Wood [3] observed that ferrous olivine rims the common forsteritic olivine in Allende and that the minor-element (Al, Cr, Ti) contents are too high to allow exsolution from forsterite. Other studies that developed these themes are Hua et al. [4], Rubin et al. [5], Palme and Fegley [6], Weinbruch et al. [7], and Matsunami et al. [8]; the latter two showed that MnO and FeO were well correlated in much of the fayalite, inconsistent with condensation from a canonical nebula but roughly consistent with formation under oxidizing conditions.

Typical pH_2/pH_2O ratios in these nebular models are 10, i.e., >100× lower than in a canonical nebula. The common approach to explaining such extreme conditions is to assume that (1) the nebula was originally canonical; (2) dust settled to the midplane and was evaporated there by an unknown heat source, the O from the oxides being largely converted to H_2O; and (3) grain (and, in some models, chondrule) condensation occurred before the turbulence led to remixing with the nebular gas outside the midplane.

The pendulum began to swing the other way. Blum et al. [9] showed that many CV opaque assemblages are best understood as asteroidal alteration products. Although Palme and Fegley [6] had reported that chromite condensed earlier than Fe-Ni under oxidizing conditions and thus the high Cr content of fayalitic materials was an indication of such conditions, new calculations by Krot et al. [10] showed that chromite condensation behavior was essentially independent of redox conditions. They also noted that those refractory inclusions that formed as a result of heating during infall into the nebula might retain their original redox state, in which case the depletions of Mo and W would not be indicative of nebulawide conditions. Wasson and Krot [11] showed that high-Fa olivine associated with silica in UOC probably formed by aqueous alteration on the parent bodies; Fe_2SiO_4 formed when Fe diffused from the surrounding matrix to the silica. The high Mn contents of these grains are readily understood if Mn condensed from the nebula as tiny, unstable grains that dissolved during aqueous alteration, the Mn diffusing to a suitable growing host such as fayalite. This model can also explain the MnO-FeO correlations observed by Weinbruch et al. [7] and Matsunami et al. [8].

Krot et al. [12] carried out an extensive review of CV alteration products and showed that they are pervasive, i.e., in chondrules, refractory inclusions, matrix, and metal. Their view was that the alteration, whether involving formation of phyllosilicates, Fe-alkali-halogen metasomatism, or oxidation/sulfidation of metal was best understood by low-temperature processes in the asteroidal parent body, as originally suggested for CV chondrites by Housley and Cirlin [13], and widely accepted for CM and CI chondrites since the work of Bunch and Chang [14] and Kerridge et al. [15].

There are two reasons it is easier to oxidize metal or aqueously alter other phases in the parent bodies than in the solar nebula. The

pH_2/pH_2O ratios are much lower in parent bodies, causing the stability fields of alteration phases to extend to higher temperatures, and H_2O pressures are much higher, leading to higher reaction rates. At a nebular pressure of 10^{-5} atm pH_2O is only 7×10^{-9} atm; because H_2O was probably the dominant volatile in asteroids, its pressure could be as high as the overburden pressure, which reaches 1 atm at a depth of 1 km in a chondritic asteroid having a radius of 50 km.

In summary, the evidence for highly oxidizing conditions in the solar nebula is weak. Although there is evidence (e.g., Mo depletions) for the formation of refractory inclusions under oxidizing conditions, those formed during infall heating could have been internally buffered. Other observations, mostly involving fayalite or magnetite, seem better understood in terms of aqueous alteration on the parent bodies.

There is no need to continue to invoke implausible events to flash evaporate nebular solids in the midplane (and to prevent the resulting gases from mixing with the other nebular gas). The more important global question now is whether the H_2O in the chondritic parent bodies condensed as ice or as hydrated silicates.

References: [1] Herndon J. M. and Suess H. E. (1977) *GCA, 41,* 233. [2] Fegley B. and Palme H. (1985) *EPSL, 72,* 311. [3] Peck J. A. and Wood J. A. (1987) *GCA, 51,* 1503. [4] Hua X. et al. (1988) *GCA, 52,* 1389. [5] Rubin A. E. et al. (1988) in *Meteorites and the Early Solar System* (J. F. Kerridge and M. S. Matthews, eds.), p. 488. [6] Palme H. and Fegley B. (1990) *EPSL, 101,* 180. [7] Weinbruch S. et al. (1990) *Meteoritics, 25,* 115. [8] Matsunami S. et al. (1990) *Proc. NIPR Symp. Antarct. Meteorites, 3,* 147. [9] Blum J. D. et al., *GCA, 53,* 483. [10] Krot A. N. et al. (1993) *EPSL, 119,* 569. [11] Wasson J. T. and Krot A. N. (1994) *EPSL, 122,* 403. [12] Krot A. N. et al. (1995) *Meteoritics, 30,* 748. [13] Housley R. M. and Cirlin E. H. (1983) in *Chondrules and Their Origins* (E. A. King, ed.), p. 145, LPI, Houston. [14] Bunch T. and Chang S. (1980) *GCA, 44,* 1543. [15] Kerridge J. F. (1979) *EPSL, 43,* 359.

REFRACTORY FORSTERITE IN CARBONACEOUS CHONDRITES: AN UNALTERED CONDENSATE FROM THE SOLAR NEBULA.

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The origin of chondrite components such as matrix, inclusions, chondrules, or isolated mineral grains is frequently obscured by alteration processes on parent bodies and/or in the solar nebula. In order to better understand the nature of these alteration processes and to quantify the extent they have influenced chondrites, attempts are made to identify pristine (unaltered) material.

Iron-poor (FeO <1 wt%) olivine enriched in refractory elements Ca, Al, and Ti (hereafter called refractory forsterite) is frequently encountered in carbonaceous and in ordinary chondrites [e.g., 1,2]. Refractory forsterite occurs as isolated grains in the matrix and within chondrules and is readily identified by its blue cathodo-luminescence. At present, two contrasting formation models are discussed for these olivine grains: (1) condensation from the solar nebula [e.g., 1,2], and (2) crystallization from chondrule melts [e.g., 3]. Here, we provide additional evidence for distinguishing between the two models.

We have studied 10 samples from the Allende meteorite containing a major fraction of refractory forsterite. The samples included two isolated olivine grains (IOG), one chondrule, and seven chondrule fragments. Bulk samples were analyzed by instrumental neutron activation analysis (INAA). Polished sections of the samples were studied by scanning electron microscopy (SEM), electron probe microanalysis (EPMA), and secondary ion mass spectrometry (SIMS). Preliminary INAA results are found in [4].

All samples contain approximately chondritic abundances of the refractory lithophile elements Al, Ca, Sc, V, and the rare earth elements (REE). Comparison between INAA and SIMS reveals that the REE, except Eu, reside predominantly in olivine. Refractory lithophile elements (RLE) are slightly volatility fractionated. In the two IOG, which consist almost entirely of refractory forsterite, RLE contents were found to decrease with increasing volatility, while in the chondrule sample a complementary pattern was observed, suggesting an origin by condensation. The abundance of Yb within this sequence reflects oxidizing conditions. This is supported by the comparatively high Mo contents (0.3–2.4 ppm).

The high abundances of RLE in olivine would either require very high bulk RLE contents or an unrealistically high degree of fractional crystallization to achieve the enrichment. Therefore, refractory forsterite occurring in chondrules has to be considered a relict phase that survived the chondrule-forming process.

Refractory forsterite has very low Mn (30–40 ppm) and Ni (1.2–1.7 ppm) contents. The low Mn concentrations also indicate that these grains did not form by igneous processes from precursors of Allende chondrule composition. Experimental olivine/melt partition coefficients (see [5,6] and references therein) would require melts with Mn contents below 100 ppm to produce the observed Mn concentrations in refractory forsterite. Chondrules with such low Mn contents are not observed in Allende or in any other carbonaceous chondrite [7,8].

In summary, an origin of refractory forsterite by condensation in the solar nebula is supported by the high concentrations of RLE, the volatility-dependent fractionation of RLE, and the low concentrations of Mn. In addition, refractory forsterite is enriched in [16]O compared to chondrules, which also excludes an igneous origin [9]. Refractory forsterites, thus, seem to represent unaltered condensates from the solar nebula. The lack of an Yb anomaly and the high Mo concentrations suggest oxidizing conditions during condensation of the forsterite grains analyzed here. This is not in contradiction with the low FeO content. Forsteritic olivine is the first Mg silicate to condense, even at comparatively high O fugacities [10].

References: [1] Steele I. M. (1986) *GCA, 50,* 1379–1395. [2] Steele I. M. (1988) in *Meteorites and the Early Solar System* (J. F. Kerridge and M. S. Matthews, eds.), pp. 808–818, Univ. of Arizona, Tucson. [3] Jones R. H. (1992) *GCA, 56,* 467–482. [4] Palme H. et al. (1986) *LPS XVII,* 640–641. [5] Colson R. O. et al. (1988) *GCA, 52,* 539–553. [6] Snyder D. A. and Carmichael I. S. E. (1992) *GCA, 56,* 303–318. [7] Rubin A. E. and Wasson J. T. (1987) *GCA, 51,* 1923–1937. [8] Palme H. et al. (1992) *LPS XXIII,* 1021–1022. [9] Weinbruch S. et al. (1993) *GCA, 57,* 2649–2661. [10] Palme H. and Fegley B. (1990) *EPSL, 101,* 180–195.

FAYALITIC OLIVINE IN CV3 CHONDRITE MATRIX AND DARK INCLUSIONS: A NEBULAR ORIGIN.

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Introduction: Olivines with compositions of $Fa_{>35}$ (dubbed fayalitic olivine) in the matrix, chondrule rims, and dark inclusions (DIs) have been at the heart of the nebular vs. parent-body formation controversy for components in CV3 and other chondrites. The "nebularists" have argued for processes of vaporization, condensation, oxidation, and/or metasomatism in a nebular setting to explain the unusual petrologic, compositional, and isotopic characteristics of the fayalitic olivine [1-7], while the "asteroidists" have evoked parent-body Fe-Mg exchange and, more recently, hydration/dehydration processes [8-11]. Here we summarize our petrologic data and observations on the occurrences of fayalitic olivines in matrix and DIs of CV3 chondrites, and discuss their origin.

Matrix: CV3 matrix is a porous aggregate and fayalitic olivine is the major component, generally making up >80 vol%. It ranges in morphology from platy and lath-shaped to anhedral crystals, generally <5 μm in size. Fluffy clusters of irregular olivine <1 μm in size are also present in matrix. The ratio of platy to irregular crystals varies widely among CV3 chondrites, with platy and lath-shaped crystals being dominant in some (e.g., Allende, Axtell, and Mokoia) and rare to absent in others (e.g., Vigarano). Despite morphological variations and compositional ranges, all fayalitic olivines in CV3 chondrites have a roughly similar, near-solar Fe/Mn ratio (Fig. 1). Chondrule olivines have different Fe/Mn ratios, and the coarser-grained (up to 100 μm) near-pure fayalites [12], found in some CV3 chondrites, have still different Fe/Mn ratios with a negative trend. Fayalitic olivines with similar morphologies (platy and lath-shaped crystals) and compositions are also present in the matrix of some unequilibrated ordinary chondrites (e.g., Krymka, Chainpur, and Bishunpur), occurring as single crystals, in clusters, and as epitaxial overgrowths on forsterite substrates [13].

Dark Inclusions (DIs): Dark inclusions are lithic fragments with complex histories that clearly predate their incorporation into their host chondrites. They are texturally diverse and display a range from chondrule- (and inclusion-)rich varieties to chondrule-free matrixlike material. Fayalitic olivines are the major component and are petrologically similar to that in host CV3 matrix, suggesting a similar origin. In addition, fayalitic olivines in some DIs are topotactic (structurally controlled) replacements of preexisting chondrule olivines, resulting in chondrule pseudomorphs. A remarkable DI in the Ningqiang CV3-related chondrite is petrologically and O isotopically similar to DIs in CV3 chondrites, but the fayalitic olivine grains are rimmed by amorphous olivine of the same composition [14,15].

Discussion and Conclusions: The parent-body heating/dehydration model for the formation of the fayalitic olivines has considerable uncertainties: (1) There is no direct evidence linking fayalitic olivines to precursor phyllosilicates. In known dehydrated chondrites, such as Belgica 7904 and Y 793321, a phase intermediate between phyllosilicate and olivine occurs [16], but no such phase has been found in Allende matrix or DIs. (2) Dehydration of phyllosilicates cannot explain the wide range of morphologies of the fayalitic olivines in the matrix and DIs and is inconsistent with the epitaxial growth of platy olivine. (3) In some CV3 chondrites the fayalitic olivines clearly predate the formation of the hydrous phases [e.g.,

17]. (4) Fayalitic olivines in CV3 chondrite matrix and DIs show a range of compositions (Fig. 1), suggesting they were not in contact at temperatures high enough to initiate equilibration. Many fayalitic olivines are zoned and have forsteritic cores, indicating direct replacement by fayalitic olivine without an intermediate (hydrous phyllosilicate) stage. Additionally, zoning and heterogeneity on such a fine scale could not survive a metamorphic heating event (>500°C) [e.g., 16] great enough to completely dehydrate phyllosilicates and transform them to olivines. (5) Dehydration reactions of serpentine-rich phyllosilicates produce enstatite and/or free silica (in addition to olivine), and neither of these phases are present in the matrix or DIs. (6) A Ningqiang DI that is compositionally and O isotopically similar to the Allende DIs has amorphous olivine rims that formed by irradiation damage in the nebula [15], indicating a primitive nebular origin for the fayalitic olivine in this case, and suggesting the same for fayalitic olivine in other CV3 chondrite DIs. (7) Allende chondrules contain unaltered primary glassy mesostasis [18]. Chondrule mesostasis would not survive parent-body hydration without becoming hydrated and would become devitrified at the metamorphic temperatures necessary to completely dehydrate the matrix and form fayalitic olivines. (8) Oxygen isotopic compositions of Allende matrix argue for little or no hydration [19].

One petrologic argument against a nebular model is that the fayalitic olivine contains numerous inclusions of pentlandite, oxides, and spinels that, in some cases, are rimmed by poorly graphitized C [20]; this presents an obstacle for a condensation model since it requires formation of hydrocarbons, at very low temperatures, prior to growth of the olivine. The chondrule pseudomorphs in some DIs could be used to support a parent-body dehydration model [e.g., 9], but a condensation model for the fayalitic olivine in these chondrules has also been proposed [6,7] and topotactic growth of fayalitic olivine in the nebula may also be possible. On balance, we favor a nebular model and propose that the fayalitic olivine formed by vaporization of chondritic dust to produce a fayalite-rich vapor, followed by recondensation of fayalitic olivine. Vaporization of olivine, with the exception of pure endmember compositions, is incongruent and therefore heating of forsteritic olivine to its vaporous produces a fayalite-rich vapor [21,22]. Magnesium-rich pyroxene will also evaporate incongruently to form olivine and a Si-rich
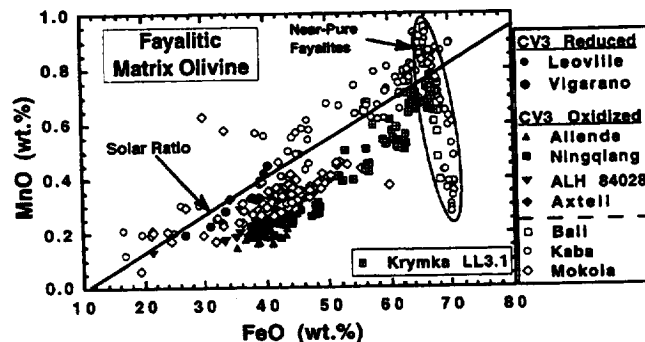

Fig. 1. FeO vs. MnO (wt%) for fayalitic olivine in CV3 and Krymka LL3.1 chondrite matrix. Matrix olivines in these chondrites have a similar, near-solar FeO/MnO ratio. The coarser-grained near-pure fayalites in Bali and Kaba have a different FeO/MnO ratio and a negative trend.

gas [23]. This event may have been concurrent with chondrule formation and the heating of some dust to its vaporous may have been a consequence of the same heating mechanisms that were responsible for the melting of nebular dust to form chondrules.

References: [1] Peck and Wood (1987) *GCA, 51*, 1503–1510. [2] Hua et al. (1988) *GCA, 52*, 1389–1408. [3] Weinbruch et al. (1990) *Meteoritics, 25*, 115–125. [4] Weinbruch et al. (1993) *GCA, 57*, 2649–2661. [5] Murakami and Ikeda (1994) *Meteoritics, 29*, 397–409. [6] Kurat et al. (1989) *Z. Naturforsch., 44a*, 988–1004. [7] Palme et al. (1989)*Z. Naturforsch., 44a*, 1005–1014. [8] Housley and Cirlin (1983) in *Chondrules and Their Origins* (E. A. King, ed.), pp. 145–161, LPI, Houston. [9] Kojima and Tomeoka (1995) *GCA, 60*, 2651–2666. [10] Krot et al. (1995) *Meteoritics, 30*, 748–775. [11] Krot et al. (1997) *Meteoritics & Planet. Sci., 32*, 31–49. [12] Hua and Buseck (1995) *GCA, 59*, 563–578. [13] Weisberg et al. (1997) *Meteoritics & Planet. Sci., 32*, in press. [14] Weisberg et al. (1996) *Meteoritics & Planet. Sci., 31*, A150–A151. [15] Zolensky et al. (1997) *LPS XXVIII*, 1629–1630. [16] Akai (1988) *GCA, 52*, 1593–1599. [17] Keller et al. (1994) *GCA, 58*, 5589–5598. [18] Ikeda and Kimura (1995) *Proc. NIPR Symp. Antarct. Meteorites, 8*, 97–122. [19] Clayton et al. (1997) *LPS XVIII*, 239–240. [20] Brearley and Prinz (1996) *LPS XXVII*, 161–162. [21] Nagahara and Kushiro (1987) *EPSL, 85*, 537–547. [22] Nagahara et al. (1988) *Nature, 331*, 516–518. [23] Mysen and Kushiro (1988) *Am. Mineral., 73*, 1–19.

VOLATILE TRACE-ELEMENT COMPOSITION AND SHOCK IN EQUILIBRATED H CHONDRITES.

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Shock loading and breccia formation can be fundamental processes in meteorite genesis [1]. Shock can affect many chemical and physical properties used to decipher meteorite history [2]. For example, volatile-trace-element (VTE) contents of mildly shocked L chondrites are significantly lower than in strongly shocked ones [3]. The assumption that this trend also holds for H chondrites, has colored interpretations of the relationships between VTE contents, and the thermal history of H chondrites and structure of the H chondrite parent body. In this study, we explore whether VTE contents of equilibrated H chondrites reflect shock metamorphism and brecciation.

Volatile-trace-element compositional data exist for 90 H chondrite falls: The complete dataset includes Co, Se, Rb, Cs, Te, Bi, Ag, In, Tl, Zn, and Cd (listed in increasing order of mobility) [4–6]. We use shock facies data [7] to classify samples as either mildly shocked (facies a–c) or strongly shocked (facies d–f). Our database contains 43 mildly shocked (<22 GPa) and 12 strongly shocked (>22 GPa) samples. Classification of samples as brecciated or unbrecciated is based on published observations [8]. Our database includes 70 unbrecciated and 15 brecciated samples. We use univariate statistical techniques (Student's t-test) and the multivariate statistical techniques of linear discriminant analysis (LDA) and logistic regression (LR) to compare VTE contents in these two pairs of meteorite suites, thus testing the null hypothesis and establishing that any observed compositional differences are the result of shock or brecciation. We also use bootstrap randomization-simulation (RS) statis-

tical techniques to calculate model-independent significance levels for both univariate and multivariate comparisons [9].

Results of univariate comparisons between unbrecciated and brecciated equilibrated H chondrites and between mildly and strongly shocked ones indicate that using VTEs, the mildly shocked suite of equilibrated H chondrites is indistinguishable from the strongly shocked one. Comparisons using Student's t-test reveal that none of the 11 VTE contents differ at the <0.05 significance level. Only one element, Ag, differs at <0.10, with mean Ag contents being higher in the strongly shocked suite of samples. We attribute this to chance. Results of multivariate comparisons between the mildly and strongly shocked suites based on all 11 VTEs using LDA and LR give model-dependent significance levels of 0.2466 and 0.0491 respectively. The value for LR, however, increases to 0.320 when a model-independent value is calculated; hence, we find no evidence for a shock-dependent, VTE compositional difference in H chondrites. These results strongly contrast with the results for analogous comparisons in L chondrites.

Comparisons between unbrecciated and brecciated suites indicate that these two suites are also indistinguishable using VTE contents. Using Student's t-test, one element of the 11, Zn, differs at the <0.05 significance level and an additional element, Cs, differs at the <0.10 level; means for both are higher in the brecciated suite. Multivariate LDA and LR comparisons between unbrecciated and brecciated suites using all 11 VTEs give model-dependent significance levels of 0.2549 and 0.0772 respectively. The LR value, however, increases to 0.131 when a model-independent value is calculated; hence, we find no evidence for a brecciation-dependent, compositional difference in H chondrites.

In principle, differences in the VTE contents of mildly and strongly shocked, and brecciated and unbrecciated equilibrated H chondrites might be obscured by other factors, e.g., a relationship involving VTE content and petrographic type [10]. To minimize this possibility, we repeated these comparisons using only H5 chondrites. Multivariate LDA and LR comparisons of mildly and strongly shocked suites of H5 chondrites using all 11 VTEs gave model-dependent significance levels of 0.0406 and 0.0022 respectively. However, these increase to 0.455 and 0.103, respectively, when model-independent comparisons are made for H5 chondrites. Multivariate LDA and LR comparisons of unbrecciated and brecciated H5 chondrite suites using all 11 VTEs give model-dependent significance levels of 0.1990 and 0.0069 respectively. The value for LR, however, increases to 0.270 when the model-independent RS technique is used. Thus, for H5 chondrite suites, neither shock nor brecciation has apparently been important in establishing VTE contents. To examine whether we are using too many elements in our comparisons for the size of the existing database we can reduce the number of elements seriatim, using mobility, as described elsewhere [5,9]. No matter how few elements we used, we found no evidence for a shock-dependent difference in VTE contents.

The postaccretionary shock and brecciation histories of parent bodies of equilibrated H and L chondrites obviously differ. In addition, parent materials of equilibrated H chondrites seem to have condensed and accreted at temperatures higher than those existing when L chondrite parent material formed. All ordinary chondrites were not created equal.

References: [1] Stöffler D et al. (1991) *GCA, 55*, 3845–3867. [2] Stöffler D. et al. (1988) in *Meteorites and the Early Solar System* (J. F. Kerridge and M. S. Matthews, eds.), pp. 165–202, Univ.

of Arizona, Tucson. [3] Huston T. J. and Lipschutz M. E. (1984) *GCA, 48,* 1319–1329. [4] Lingner D. W. et al. (1987)*GCA, 51,* 727–739. [5] Dodd R. T. et al. (1994) *JGR Planets, 98,* 15105–15118. [6] Wolf S. F. and Lipschutz M. E. (1997) *JGR Planets,* in press. [7] Dodd R. T. and Jarosewich E. (1979) *ESPL, 44,* 335–340. [8] Graham A. L. et al. (1985) *Catalogue of Meteorites,* 460 pp. [9] Wolf S. F. and Lipschutz M. E. (1995) in *Advances in Analytical Geochemistry, Vol. 2,* 241–281. [10] Wolf S. F. and Lipschutz M. E. (1993) *Meteoritics, 28,* 460–461.

A UNIQUE CHONDRULE CONSISTING OF FORSTERITE AND CLEAR GLASS GROUNDMASS WITH COMPOSITIONAL ZONING IN ORDINARY CHONDRITES.

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A unique chondrule is recognized in type 3 ordinary chondrites (OCs); while type 3 OCs contain many chondrules, one in particular is conspicuous for its unique texture. This chondrule consists of mostly euhedral olivine grains, with some drop-shaped Fe-Ni metals in a clear-glass groundmass, which is rimmed by orthopyroxenes. The glass groundmass consists of a transparent core with a pale-brown colored mantle-rim. The composition of glass shows typical zoning of Si, Al, Ca, Na, K, Fe, and Mg. Below are some results of our petrographical and chemical study of this unique chondrule.

The ordinary chondrite, shown in Fig. 1, is unequilibrated, classified as belonging to the L group because of its chemicals, minerals, and mineral compositions. It consists of many chondrules, chondrule fragments containing olivine and pyroxenes, Fe-Ni metals, troilite, and matrixes. The olivine compositions range from $Fe_{0.6}$ to $Fe_{30.7}$, whereas the orthopyroxenes range from $Fs_{1.4}$ to $Fs_{24.3}$ with pigeonite $En_{87.5}Fs_{7.2}Wo_{5.3}$. Various types of chondrules, e.g., granular, porphyritic, poikilitic, crystalline, and radial pyroxene, are present. The

Fig. 1.

unique chondrule, clearly distinguished by its texture, minerals, and mineral composition, lies within these chondrules.

The unique chondrule is ~2 mm in diameter, surrounded by a thin rim of pyroxene. Olivine is present as two types: (1) a prism-like shape with enriched euhedral in the core and (2) granular to porphyritic occurrences in the mantle to the rim. Both types of olivine have an identical composition of forsterite ($Fo_{99.5}Fa_{0.5}$), corresponding to those of an enstatite chondrite. Although the orthopyroxenes found in the rim share an almost uniform composition of enstatite ($En_{97-99}Fs_{0.5-2}Wo_{0.5-1.5}$), they show no similarities to those found in the enstatite chondrite. The olivine compositions and the pyroxenes are both quite different from those of other chondrules, and also differ from the matrix of olivine and pyroxene grains in the host rock.

The glass compositions of the chondrule groundmass are also unique, showing typical compositional zoning. Aluminum, Mg, and Ca are enriched at the core, but Si, Fe, Na, and K are poor. Calcium oxide is over 15% in the core, but decreased to 9% at the mantle rim. On the other hand, Na_2O is near 0% in the core, but increased to 7% at the mantle rim.

In this chondrule, phenocrysts (olivine and orthopyroxene) are characterized by their uniform compositions, but those of the glass groundmass show remarkable compositional variation (chemical zoning); they are different from those of the host rock. It is reasonable to consider the features of this chondrule as one of the unique characteristics of chondritic meteorites.

THE HISTORY OF METAL AND SULFIDES IN CHONDRITES.

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Introduction: Opaque minerals offer a unique approach to disentangling nebular from asteroidal effects in meteorites. Sulfur will be mobilized in every heating/cooling episode, whether nebular or asteroidal, but, unlike any other volatile element, its resulting distribution is easily documented in the reflected light microscope. Iron-nickel sulfurization/desulfurization happened several times in the history of chondrites and several generations of sulfides and metal can potentially be identified: nebular condensates, chondrule melts, postchondrule formation condensates, parent-body products.

First Condensation of Opaque Minerals: *Metal.* Grossman and Olsen [1] and Kelly and Larimer [2] described the condensation of Ni and Fe, but this early metal may not have survived subsequent S and O condensation. Phosphorus, Cr, and Si in metal in carbonaceous chondrites result from chondrule formation [3], not condensation (see below). Remnant condensate metal might be found in fine-grained matrix [4].

Sulfides. Sulfur condensation by reaction of H_2S with an Fe-Ni alloy was studied experimentally by [5–7] who showed that the Ni-bearing sulfides pentlandite and monosulfide solide solution (mss) would be produced under nebular conditions and suggested that sulfides in Alais [8] may be nebular condensates [5]. The absence of significant Ni in most sulfides in chondrites can be explained by subsequent chondrule formation and thermal metamorphism (see below). Apart from Alais, Ni-bearing sulfide also occurs in primitive
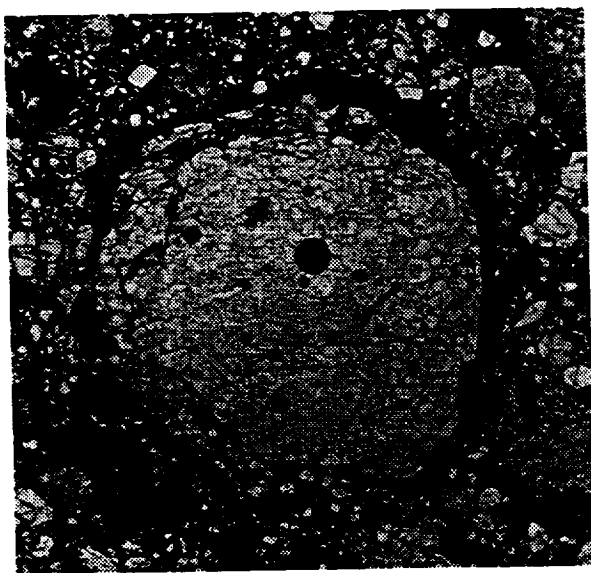
matrix [4] and is widespread in the finest-grained (least melted) "protoporphyritic" chondrules of Semarkona [9,10]. These chondrules contain little or no metal, showing that when chondrule precursors were assembled, metal sulfurization was essentially complete.

Magnetite. The condensation of magnetite is only predicted in restricted conditions [11]. Though systematically present in the finest chondrules of Semarkona, it probably results from parent-body alteration [12].

Chondrule Formation: The sequence of events during chondrule formation can be reconstructed by looking at a sequence of porphyritic chondrules with increasing grain sizes, from the finest grained (least melted and closest to their precursors) to the coarsest ones (efficiently melted) [10]. The opaque assemblages and their textures along this sequence match run products along a temperature gradient in a solar furnace [13].

Melting and breakdown of sulfides. The abundant sulfides in the finest chondrules of Semarkona (up to 14 wt% S) are interstitial to the silicates, as in the coolest region of solar furnace charges [13], in which the silicates have experienced very little melting [10]. With increasing melting, sulfides start breaking down and metal starts appearing, exhibiting typical melt textures with the remaining sulfides [13]. Such textures are found in the "intermediate" region of our solar furnace charges and throughout the grain-size sequence in type II (FeO-rich) chondrules. They are restricted to the "cryptoporphyritic" ones in type Is (FeO-poor), where bulk S contents rapidly decrease with increasing grain size [10]. We interpret this as volatile loss, as documented by systematic experiments [10,13] with sulfide-bearing chondrule analogs.

Regeneration of metal. Iron reduced from chondrule silicates occurs in "dusty" olivine grains [e.g., 14] as experimentally reproduced, for example, by [15]. In ordinary chondrites, however, chondrule metal is not the product of reduction [16] but mostly of desulfurization [13]. Metal is rare in type II sulfide-bearing chondrules. Its abundance gradually increases along the type I grain-size sequence as more and more extensive S loss has taken place: Blebs are absent in proto-, appear in crypto-, and become abundant in microporphyritic type I chondrules (but may be partly altered to carbides and magnetites [12]). As the silicate grain size further increases, Fe loss from chondrules is observed. The metal grains become coarser, like the silicates, and are distributed closer to the surface of the chondrules. Eventually, no metal is left inside the chondrules, whose surfaces become ornamented with metal grains that occur as a continuous layer or only a few massive grains. It is easy to form similar metal grains by desulfurization in chondrule analogs. Surface grains and crown grains all have a very uniform composition for a given chondrule, and their contents of Cr and Si yield f_{O_2} matching those based on Fe contents of the chondrule silicates [3]. Metal is thus regenerated by desulfurization during chondrule formation, and its composition is established by equilibration with the silicate melt [3]. Large matrix metal grains (often with fine-grained silicate rims) or "metallic chondrules" [17] were lost by chondrules [3].

Sulfur recondensation. Sulfur lost from chondrules recondenses on cooling, and metal crowns ornamenting the chondrule surfaces and metallic chondrules are readily available sites. Thus, much metal regenerated by chondrule formation will be sulfurized again during chondrule cooling. Sulfides in opaque encasements around chondrules and in large "opaque chondrules" account for roughly 90% of Semarkona's S, and metal and sulfide are almost always intimately associated [18], as in Allende [19]. These sulfides match the predictions of [5–7] for nebular condensates. In addition to mss, several Ni-bearing sulfides are found: pentlandite in Semarkona, but also heazlewoodite in Allende. They are associated with awaruite [19,20]. There are no Ni and S concentration gradients in the sulfides, however, which have undergone thermal equilibration throughout the rock (see below).

Parent-Body Processes: *Aqueous alteration.* Low-temperature aqueous alteration on carbonaceous chondrite parent bodies was pervasive and complex, particularly when thermal metamorphism also occurred [21,22]. This process produced tochilinite, sulfates, and ferrihydrite from nebular metal and sulfides [21,22]. However, pyrrhotite may be precipitated as a result of olivine dissolution [23] and tochilinite may break down to give sulfide on heating [22]. Limited aqueous alteration on ordinary chondrites resulted in the formation of carbide and magnetite in the opaque assemblages [12], but the dominant secondary process was dry thermal metamorphism.

Thermal metamorphism. 1. Thermal equilibration: The Ni content of the troilite in the most primitive chondrites is below detection and that of the pentlandite is homogeneous all through a given meteorite. We attribute this to parent-body equilibration, after [24], and determine temperatures of 230°C for Semarkona and 335°C for Allende [20]. A similar equilibration of the sulfide composition is displayed by the gentler reheating experiments of [25].

2. Sulfur migration: As shown by [25], the Ni-bearing sulfides eventually decompose into Ni-rich metal (FeNi$_2$) and troilite [25], which produces associations similar to those found in the most primitive chondrites. Sulfur mobilization remained very limited in these meteorites, but it became more extensive as metamorphism progressed from 3.1 to 3.5: the previously sulfide-free metal blebs of type I chondrules contain increasing quantities of troilite [18]. This is in agreement with the experiments of [25] that show that sulfide layers grow on the isolated metal grains of the starting assemblages. Natural opaque assemblages also change: By 3.1, pentlandite and awaruite disappear, and (apart from the relict kamacite) the Ni-bearing phase found in the opaque associations is taenite. A similar change is observed in the short high-temperature experiments of [25].

3. Sulfur redistribution: By 3.7, a redistribution of the S becomes apparent [18]. The sulfide grains tend to connect, and their original distribution becomes a little blurry. In particular, opaque encasements around adjoining chondrules tend to merge. This effect is observed more clearly in experimental charges in which metal and sulfides were initially separated: thin sulfide trails grow throughout the samples and eventually connect separate metal-sulfide assemblages [25]. The establishment of a connected sulfide network throughout the parent bodies allows extensive cation movement [25], which explains why metal compositions equilibrate from 3.5 to 4 and zoned taenites first appear by 3.8 [18].

4. Recrystallization: Between 3.8 and 5, metal and sulfide grains tend to separate, and adjacent metal grains coalesce, eliminating silicate inclusions [18]. This reduces surface free energy. Metal coarsening is reversed at type 6 by chondrule recrystallization, yielding separate interstitial/polygonal metal and sulfide grains evenly dispersed throughout the rock [18].

Impact Shock: The results of varying degrees of impact on opaque minerals in ordinary chondrites are summarized in [26].

Conclusions: Chondrites contain two successive generations of sulfides (pre- and postchondrule formation) and at least one of

metal (formed in chondrules). New generations of these minerals form on parent bodies.

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References: [1] Grossman and Olsen (1974) *GCA, 38,* 173. [2] Kelly and Larimer (1977) *GCA, 41,* 93. [3] Zanda et al. (1994) *Science, 265,* 1846. [4] Greshake (1997) *GCA, 6,* 437. [5] Lauretta et al.(1997) *LPS XXVIII,* 783. [6] Lauretta et al. (1996) *Icarus, 122,* 288. [7] Lauretta et al. (1996) *Proc. NIPR Symp. Antarct. Meteorites, 9,* 97. [8] Kerridge et al. (1979) *EPSL, 43,* 359. [9] Zanda et al. (1996) *LPS XXVII,* 1485. [10] Hewins et al. (1997) *Proc. NIPR Symp. Antarct. Meteorites, 10,* submitted. [11] Wood and Hashimoto (1993) *GCA, 57,* 2377. [12] Krot et al. (1997) *GCA, 61,* 219. [13] Zanda et al. (1997) *GCA,* submitted. [14] Nagahara (1981) *Nature, 292,* 135. [15] Connolly et al. (1994) *Nature, 371,* 136. [16] Alexander (1996) in *Chondrules and the Protoplanetary Disk* (R. H. Hewins et al., eds.), p. 233, Cambridge Univ. [17] Bevan and Axon (1980) *EPSL, 47,* 353. [18] Bourot-Denise et al., this volume. [19] Haggerty and McMahon (1979) *Proc. LPSC 10th,* 851. [20] Zanda et al. (1995) *Meteoritics, 30,* 605. [21] Zolensky and McSween (1988) in *Meteorites and the Early Solar System* (J. F. Kerridge and M. S. Matthews, eds.), p. 114, Univ. of Arizona. [22] Tomeoka et al. (1989) *Proc. NIPR Symp. Antarct. Meteorites, 2,* 55. [23] Browning et al. (1994) *Meteoritics, 29,* 450. [24] Blum et al. (1989) *GCA, 53,* 543. [25] Lauretta et al., this volume. [26] Bennett and McSween (1996) *Meteoritics & Planet. Sci., 31,* 255.

AQUEOUS ALTERATION OF CARBONACEOUS CHONDRITES: EVIDENCE FOR ASTEROIDAL ALTERATION.

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Introduction: The primary reactions involved in chemical alteration are oxidation, hydrolysis, and carbonation. Here we are concerned with the action of the second process, i.e., aqueous alteration. Aqueous alteration may occur over a very wide range of temperatures and pressures, including temperatures below 0°C. There are two primary reasons for studying these reactions. First we wish to better understand the overall history of chondritic materials. Second, aqueous reactions promote chemical redistribution, changes in petrologic relationships and isotopic fractionation, and can complicate thermoluminescence (TL) patterns [1], rendering uncertain the metamorphic grade if this is determined by TL. There are several possible major sources of H_2O available for aqueous alteration reactions in the early solar system. Water vapor would have been available for reactions in the primitive solar nebula and, in the absence of evidence for the direct condensation of hydrous minerals in the nebula, it is possible that these phases could have formed via the hydration (and reconstructive transformation) of preexisting anhydrous silicates. However, this scenario cannot account for all aqueous and related phases observed in meteorites.

In this abstract we describe the evidence for aqueous alteration observed within carbonaceous chondrites requiring an asteroidal (or other parent-body) setting. This evidence is of several types. First we have the presence of specific minerals unlikely to have formed from anything other than an aqueous fluid in an asteroidal environment. Secondly, we have textural evidence of the transport of mineralizing fluids after asteroidal accretion. Finally, we have pseudomorphs of anhydrous phases after hydrous ones.

Mineral Products of Aqueous Alteration: The mineralogical products of aqueous alteration most commonly encountered within primitive extraterrestrial materials include phyllosilicates, hydroxides, tochilinites, sulfates, oxides, and carbonates. Most of these alteration products are matrix phases, although alteration of larger components (e.g., chondrules, aggregates, and inclusions) also figure prominently. For many of these phases asteroidal origin is preferred because the conditions for growth would have been kinetically inhibited in the canonical solar nebula. For example, the fCO_2 necessary to stabilize carbonates was unlikely to be attained in the solar nebula [2], as was the fH_2O for phyllosilicates [3], not to mention hydrous sulfates.

Type 3 Chondrites: The least-equilibrated chondrites contain limited, though significant, direct evidence of aqueous alteration. Matrix, chondrules, and CAIs in the CV3 chondrites Kaba, Bali, Grosnaja, and Mokoia contain considerable amounts of phyllosilicates, principally smectites and micas, while these phases are also present in trace amounts in Allende and Vigarano [4]. These meteorites also contain feldspathoids (nepheline and sodalite) of proposed metasomatic origin. The alteration phases found in CV3 chondrites is grossly similar to that in the unequilibrated ordinary chondrites.

Recent work on CO3 chondrites has revealed minor amounts of serpentine associated with ferrihydrite, of probable asteroidal origin [5], replacing matrix olivine. However, Brearley used the immature protophyllosilicates found in ALHA 77307 to argue that some alteration had occurred to CO3s in the nebula [6]. The nature and origin of this and other poorly crystallized materials in chondrite matrix deserves much more work.

Type 2 Chondrites: The products of aqueous alteration are ubiquitously present in the CM2 and CR2 chondrites, in amounts far greater than within the type 3s, and in all components (matrix, phenocrysts, chondrules, CAIs). These minerals include abundant serpentines (with extremely variable compositions and structures), smectites (rare in the CM2s, abundant in the CR2s), clinochlore, Mg-Fe sulfates, tochilinite, tochilinite-serpentine intergrowths, and carbonates [7–9]. Abundant evidence of replacement reactions are evident, including olivine and glass being replaced by serpentine, metal and sulfides being replaced by tochilinite, and Fe-rich serpentine being replaced by Mg-rich serpentine [8–10].

Carbonates (calcite and dolomite), and lesser sulfates, intimately intergrown with matrix phyllosilicates and tochilinite have been notably reported in Murchison, Nogoya, Cold Bokkeveld, Nawapali, and Cochabamba [11–14].

The occurrence of aragonite in Cochabamba [12] is particularly interesting because of its metastability with respect to calcite. Armstrong et al. [2] report calcite intimately intergrown with hibonite in the core of a large CAI, and argue that its presence is best explained by aqueous alteration on (in?) a planetary body during which O isotopic exchange may have occurred.

The organic compounds found within CM2s [15,16] are believed to have processed during asteroidal evoution, with the present compounds being produced by aqueous and hydrothermal activity. More work on organics will probably be shortly forthcoming.

Type 1 Chondrites: The CI1 and CM1 chondrites are composed almost entirely of secondary phases, with the bulk being

phyllosilicate consisting of intergrown serpentine and saponite. Pyrrhotite is the major accessory phase, and it is present in pseudohexagonal plates and acicular crustals. The acicular pyrrhotites in Kaidun CM1 carry thick mantles of phyllosilicate not found anywhere else [17].

Magnetite is another mineral whose presence in chondrites is a potentially important indicator of the conditions of aqueous alteration, although this is the subject of considerable debate requiring additional work. The morphologies of magnetite in C1s (as well as most C2s and C3s, something not generally appreciated) include framboids, spherulites, and plaquettes, delicate structures that experimental work indicates may have crystallized from gels or aqueous solutions [18]). Many magnetite framboids are arranged into a closest-packing relationship that is difficult to reconcile with a nebular origin. In Kaidun magnetite framboids are clearly replacing pyrrhotite *in situ*, clearly requiring an asteroidal origin [17].

The CI1 chondrites frequently display crosscutting veins of Na-, Ca-, and Mg-sulfates (epsomite, hexahydrite, gypsum, and blodite) [19–21]. Younger carbonate veins can be observed to cut the sulfates in some cases. In the CM1 chondrites the carbonate veins only are present [22].

Studies of CIs (Orgueil) have revealed the presence of alkanes, aromatic hydrocarbons, aliphatic carboxylic acids, purines, pyrimidines, amino acids [23], and insoluble aliphatic and aromatic/olefinic structures [15], all taken to have formed from aqueous solutions.

Textural Evidence for Asteroidal Alteration: Aqueous alteration within meteorite parent bodies is required by the common occurrence of alteration minerals with the following special textures: (1) Mineral grains bridging chondrules, aggregates, and phenocrysts with matrix—for example tochilinite appearing at the interface between fractured chondrule grains and matrix in Mighei [8]; (2) veins bridging chondrules, aggregates, and phenocrysts with matrix — for example, serpentine-sulfide veins between chondrules, chondrule rims, and matrix in CM2 chondrites [24], carbonate veins in CM1 chondrites and the CR2 chondrite Al Rais, and sulfate/carbonate veins in CI1 chondrites [21]; (3) secondary phases being distributed throughout most, or all, constituents of a meteorite, often with near-identical composition everywhere (for example framboidal magnetite and "saponite" in Allende) [25]; (4) displaying relict chemical

zoning or correlations within matrix and altered chondrules and aggregates (the bulk compositional trends reported for CMs by McSween [26] for example); and (5) lining fractures and filling cracks—as calcite does in a Murchison CAI [2].

Pseudomorphs After Secondary Minerals and Textures: We have recently recognized that many chondrites hitherto considered to have experienced a free and easy life have actually been thoroughly aqueously altered, but with most evidence erased by subsequent thermal metamorphism, as discussed in more detail by Krot. In the CV3 chondrites there are inclusions of platy, defect-ridden, inclusion-bearing, fayalitic olivine, in obvious pseudomorphic replacement of phyllosilicates that had, in turn, replaced primitive chondrules, CAIs and matrix [27–29]. There are even pseudomorphs after veins crisscrossing large areas. The suggestion has been made that the host CV3s themselves have been similarly altered.

References: [1] Sears et al. (1980) *Nature, 287,* 791–795. [2] Armstrong et al. (1982) *GCA, 46,* 575–596. [3] Prinn and Fegley (1987) *Annu. Rev. Earth Planet. Sci., 15,* 171–212. [4] Krot et al. (1995) *Meteoritics, 30,* 748–775. [5] Keller and Buseck (1990) *GCA, 54,* 1155–1163. [6] Brearley (1993) *GCA, 57,* 1521–1550. [7] Barber (1985) *Clay Minerals, 20,* 415–454. [8] Tomeoka and Buseck (1985) *GCA, 49,* 2149–2163. [9] Zolensky et al. (1993) *GCA, 57,* 3123–3148. [10] Browning et al. (1996) *GCA, 60,* 2621–2633. [11] Fuchs et al. (1973) *Smithson. Contrib. Earth Sci., 10,* 39 pp. [12] Muller et al. (1979) *TMPM, 26,* 293–304. [13] Bunch and Chang (1980) *GCA, 44,* 543–1577. [14] Barber (1981) *GCA, 45,* 945–970. [15] Cronin (1987) *LPI Report 87,* p. 10. [16] Peltzer et al. (1984) *Adv. Space Res., 4,* 69–74. [17] Zolensky et al. (1996) *Meteoritics & Planet. Sci., 31,* 484–493. [18] Kerridge and Bunch (1979) in *Asteroids,* pp. 745–764. [19] Bostrom and Fredriksson (1966) *Smithson. Misc. Coll., 15,* 1–39. [20] Richardson (1978) *Meteoritics, 13,* 141–159. [21] Fredriksson and Kerridge (1988) *Meteoritics, 23,* 35–44. [22] Zolensky et al. (1997) *GCA,* in press. [23] Hayatsu and Anders (1981) *Topics in Current Chemistry, 99,* 1–37. [24] Browning and Keil (1997) *LPS XXVIII,* 163–164. [25] Tomeoka and Buseck (1982) *Nature, 299,* 326–327. [26] McSween (1979) *GCA, 43,* 1761–1770. [27] Akai (1988) *GCA, 52,* 1593–1599. [28] Kojima et al. (1993) *Meteoritics, 28,* 649–658. [29] Krot et al. (1995) *Meteoritics, 30,* 748–776.