Workshop on Oxygen in Asteroids and Meteorites June 2-3, 2005 Hagstaff, Arizona

Workshop Program and Abstracts



LPI Contribution No. 1267

Workshop on

Oxygen in Asteroids and Meteorites

June 2–3, 2005 Flagstaff, Arizona

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Preface

This volume contains abstracts that have been accepted for presentation at the Workshop on Oxygen in Asteroids and Meteorites, June 2–3, 2005, Flagstaff, Arizona.

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Contents

Program	1
Constraints on the Detection of the Solar Nebula's Oxidation State Through Asteroid Observations	
P. A. Abell, M. J. Gaffey, and P. S. Hardersen	5
Oxidation/Reduction Processes in Primitive Achondrites G. K. Benedix and T. J. McCoy	6
Low-Temperature Chemical Processing on Asteroids P. A. Bland	7
On the Formation Location of Asteroids and Meteorites W. F. Bottke and D. Nesvorny	8
The Spectral Properties of Angritic Basalts T. H. Burbine and T. J. McCoy	9
Correlation Between Chemical and Oxygen Isotopic Compositions in Chondrites R. N. Clayton	10
Effect of In-Situ Aqueous Alteration on Thermal Model Heat Budgets B. A. Cohen and R. F. Coker	11
Oxidation-Reduction in Meteorites: The Case of High-Ni Irons C. M. Corrigan and T. J. McCoy	12
Ureilite Atmospherics: Coming up for 'Air' on a Parent Body J. S. Delaney	13
High Temperature Effects Including Oxygen Fugacity, in Pre-Planetary and Planetary Meteorites and Asteroids <i>J. S. Delaney</i>	14
Oxygen Isotopic Variation of Asteroidal Materials I. A. Franchi, R. C. Greenwood, L. Baker, and A. A. Morris	15
High-Temperature Chemical Processing on Asteroids: An Oxygen Isotope Perspective R. C. Greenwood and I. A. Franchi	16
Oxygen Isotopes and Origin of Opaque Assemblages from the Ningqiang Carbonaceous Chondrite	17
Water Distribution in the Asteroid Belt E. S. Howell, A. S. Rivkin, and F. Vilas	
Comparative Planetary Mineralogy: V Systematics in Planetary Pyroxenes and fO_2 Estimates for Basalts from Vesta	10
σ , μ , μ , μ , μ , σ , σ , τ , μ , μ , μ , σ , μ , σ	

Oxygen Fugacity Variations Within and Among Meteorite Parent Bodies D. S. Lauretta
Correlation of Oxidation State with Thermal Metamorphism in Ordinary Chondrites C. A. Marsh and D. S. Lauretta
Meteorite-Asteroid Links: Can They be Forged? T. J. McCoy and T. H. Burbine
Correlations of Δ^{17} O with Chemical Characteristics Among Chondrite Groups D. W. Mittlefehldt
Determining the Effects of Aqueous Alteration on the Distribution of Oxygen Isotopes in Carbonaceous Chondrites A. A. Morris, L. Baker, I. A. Franchi, and I. P. Wright
Space Weathering on Asteroids S. K. Noble
OH and H ₂ O on Asteroids: An Astronomical Perspective A. S. Rivkin
Relict Olivine, Chondrule Recycling, and Evolution of Oxygen Reservoirs A. Ruzicka, H. Hiyagon, and C. Floss
Eu Valence Oxybarameter in Pyroxenes. Effects of Pyroxene Composition– Crystallization Histories–Crystallization Kinetics and a Comparison Between Lunar Basalts and Eucrites <i>C. K. Shearer, J. J. Papike, and J. M. Karner</i>
A Chemical Model of Micrometeorite Impact into Olivine A. A. Sheffer and H. J. Melosh
Exploring the Origin of Planetary Water Using an Atomistic Approach M. Stimpfl, M. J. Drake, D. S. Lauretta, and P. Demyer
The Hayabusa Asteroid Sample Return Mission H. Yano
What is the Water (OH) Content of the E Asteroids? M. E. Zolensky
Competitive Oxidation and Hydration During Aqueous Alteration of Asteroids M. Yu. Zolotov, M. V. Mironenko, and E. L. Shock

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PROGRAM

THURSDAY, JUNE 2, 2005

OXYGEN ISOTOPES: DATA AND PROCESSES 8:30 a.m.

Chairs: I. A. Franchi D. W. Mittlefehldt

Clayton R. N. * [INVITED] Correlation Between Chemical and Oxygen Isotopic Compositions in Chondrites [#7022]

Franchi I. A. * Greenwood R. C. Baker L. Morris A. A. [INVITED] Oxygen Isotopic Variation of Asteroidal Materials [#7007]

Greenwood R. C. * Franchi I. A. [INVITED] High-Temperature Chemical Processing on Asteroids: An Oxygen Isotope Perspective [#7006]

Mittlefehldt D. W. * Correlations of $\Delta^{17}O$ with Chemical Characteristics Among Chondrite Groups [#7005]

Guan Y.* Hsu W. Hua X. Leshin L. A. Oxygen Isotopes and Origin of Opaque Assemblages from the Ningqiang Carbonaceous Chondrite [#7011]

Ruzicka A. * Hiyagon H. Floss C. Relict Olivine, Chondrule Recycling, and Evolution of Oxygen Reservoirs [#7009]

12:00 – 1:30 p.m.

LUNCH

Thursday, June 2, 2005, continued

WATER AND LOW-TEMPERATURE PROCESSING OF ASTEROIDS 1:30 p.m.

Chairs: A. S. Rivkin M. E. Zolensky

Bland P. A. * [INVITED] Low-Temperature Chemical Processing on Asteroids [#7015]

Rivkin A. S. * [INVITED] OH and H₂O on Asteroids: An Astronomical Perspective [#7018]

Stimpfl M. * Drake M. J. Lauretta D. S. Demyer P. Exploring the Origin of Planetary Water Using an Atomistic Approach [#7029]

Vilas F. * Jarvis K. S. Cochran A. L. Zolensky M. E. Differences in Oxidation Level in Low-Albedo Asteroids as Determined from Reflectance Spectroscopy [#7031]

Howell E. S. * Rivkin A. S. Vilas F. Water Distribution in the Asteroid Belt [#7024]

Zolensky M. E. * What is the Water (OH) Content of the E Asteroids? [#7013]

Cohen B. A. Coker R. F. Effect of In-Situ Aqueous Alteration on Thermal Model Heat Budgets [#7012]

Zolotov M. Yu. * Mironenko M. V. Shock E. L. Competitive Oxidation and Hydration During Aqueous Alteration of Asteroids [#7004]

Morris A. A. * Baker L. Franchi I. A. Wright I. P. Determining the Effects of Aqueous Alteration on the Distribution of Oxygen Isotopes in Carbonaceous Chondrites [#7008] **FRIDAY, JUNE 3, 2005**

OXYGEN FUGACITY AND HIGH-TEMPERATURE PROCESSING OF ASTEROIDS 8:30 a.m.

Chairs: J. S. Delaney D. W. Mittlefehldt

Lauretta D. S. * [INVITED] Oxygen Fugacity Variations Within and Among Meteorite Parent Bodies [#7028]

Delaney J. S. * [INVITED] High Temperature Effects Including Oxygen Fugacity, in Pre-Planetary and Planetary Meteorites and Asteroids [#7019]

Karner J. M. * Papike J. J. Shearer C. K. Comparative Planetary Mineralogy: V Systematics in Planetary Pyroxenes and fO₂ Estimates for Basalts from Vesta [#7010]

Shearer C. K. * Papike J. J. Karner J. M.

Eu Valence Oxybarameter in Pyroxenes. Effects of Pyroxene Composition–Crystallization Histories–Crystallization Kinetics and a Comparison Between Lunar Basalts and Eucrites [#7003]

Jones J. H. *

Effect of Oxygen Fugacity on the Production of Asteroidal Basalts [#7032]

Delaney J. S. *

Ureilite Atmospherics: Coming up for 'Air' on a Parent Body [#7014]

Benedix G. K. * McCoy T. J. Oxidation/Reduction Processes in Primitive Achondrites [#7026]

Corrigan C. M. * McCoy T. J. Oxidation-Reduction in Meteorites: The Case of High-Ni Irons [#7023]

Marsh C. A. * Lauretta D. S. Correlation of Oxidation State with Thermal Metamorphism in Ordinary Chondrites [#7027]

12:00 – 1:30 p.m. LUNCH

Friday, June 3, 2005, continued

LINKING ASTEROIDS AND METEORITES: REMOTE SENSING OF OXIDATION STATE 1:30 p.m.

Chairs: T. H. Burbine M. E. Zolensky

Noble S. K. * [INVITED] Space Weathering on Asteroids [#7002]

Burbine T. H. * Rivkin A. S. [INVITED] How Well Can You Determine Asteroid Mineralogies? [#7033]

Sheffer A. A. * Melosh H. J. A Chemical Model of Micrometeorite Impact into Olivine [#7021]

Bottke W. F. * Nesvorny D. [INVITED] On the Formation Location of Asteroids and Meteorites [#7025]

Burbine T. H. * McCoy T. J. The Spectral Properties of Angritic Basalts [#7016]

Abell P. A.* Gaffey M. J. Hardersen P. S. Constraints on the Detection of the Solar Nebula's Oxidation State Through Asteroid Observations [#7020]

McCoy T. J. * Burbine T. H. [INVITED] Meteorite-Asteroid Links: Can They be Forged? [#7017]

Yano H. * [INVITED] The Hayabusa Asteroid Sample Return Mission [#7030] **CONSTRAINTS ON THE DETECTION OF THE SOLAR NEBULA'S OXIDATION STATE THROUGH ASTEROID OBSERVATIONS.** P. A. Abell^{1, 3}, M. J. Gaffey^{2, 3}, and P. S. Hardersen^{2, 3}, ¹Planetary Astronomy Group, Astromaterials Research and Exploration Science, NASA Johnson Space Center, Mail Code KR, Houston, TX 77058, <u>paul.a.abell1@jsc.nasa.gov</u>. ²Department of Space Studies, Box 9008, University of North Dakota, Grand Forks, ND 58202, <u>gaffey@space.edu</u>; <u>hardersen@volcano.space.edu</u>. ³Visiting Astronomer at the Infrared Telescope Facility, which is operated by the University of Hawai'i under contract from the National Aeronautics and Space Administration, Mauna Kea, Hawai'i 96720.

Introduction: Asteroids represent the only in situ surviving population of planetesimals from the formation of the inner solar system and therefore include materials from the very earliest stages of solar system formation. Hence, these bodies can provide constraints on the processes and conditions that were present during this epoch and can be used to test current models and theories describing the late solar nebula, the early solar system and subsequent planetary accretion. From detailed knowledge of asteroid mineralogic compositions the probable starting materials, thermal histories, and oxidation states of asteroid parent bodies can be inferred [1, 2]. If such data can be obtained from specific mainbelt source regions, then this information can be used to map out the formation conditions of the late solar nebula within the inner solar system and possibly distinguish any trends in oxidation state that may be present.

Limitation of meteorite studies: Terrestrial meteorite collections provide evidence that a wide range of oxidation states existed within the late solar nebula. However, the terrestrial meteorite collections are a biased and incomplete sample of the material that exists in the main asteroid belt and the locations of very few of the specific meteorite parent bodies are actually known. Mean motion and secular resonances that preferentially deliver asteroidal material to Earthcrossing orbits, can also act as effective barriers to the delivery of material from certain locations within the mainbelt [3]. Hence, a number of objects in the outer mainbelt will not contribute significant amounts (or possibly any) material into Earth-crossing orbits. Similarly objects in the inner belt, but located relatively far from a resonance, will contribute only weakly to the Earth approaching meteoroid population, and even then will still exhibit strong strength-related biases. Therefore, in order to understand the various formation mechanisms, thermal histories, and oxidation states within the asteroid belt, it is necessary to rely on information obtained by remote observation of asteroids in addition to laboratory studies of meteorites.

Visible and Near-IR observations: This wavelength region (~ 0.3 to 2.5 microns) is where the most common solar system materials have diagnostic absorption features. Mineral species such as pyroxene, olivine, feldspar, phyllosilicates, and spinel all have been detected on the surface of mainbelt asteroids through reflectance spectroscopy [1]. High signal-tonoise visible and near-IR spectroscopic observations can be used to constrain the mineralogies of asteroids. Laboratory calibrations and previous spectral studies of meteorites have provided the means to determine the abundance and chemistries of the minerals detected on the surfaces of asteroids [4 - 9]. Therefore using these calibrations, detailed spectroscopic studies of mainbelt asteroids have been able to provide insights into the diverse assemblages and thermal histories that can exist even within one taxonomic group of objects [e.g., 10].

Constraints on the oxygen state: Recent spectroscopic studies have demonstrated that it is possible to determine mineral chemistries and assemblages that constrain the oxidation state of the original asteroid parent body [11]. Hardersen et al. (2005) have shown that several M-type asteroids have absorption features indicative of mafic silicates on their surfaces. These silicates have been identified by Hardersen et al. (2005) as iron-poor orthopyroxenes which suggests that the parent bodies of these objects formed in reducing conditions. This suggests that the regions where the asteroids formed either had low intrinsic oxygen fugacities or that their parent bodies contained sufficient amounts of reducing agents (e.g., carbon) to reduce iron-bearing silicates during igneous processing [11].

Conclusion: The study outlined here is just a brief illustration of how detailed asteroid spectroscopic investigations can help constrain the oxidation state of the solar nebula and supplement the laboratory investigation of meteorites.

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Oxidation/Reduction processes in Primitive Achondrites. G.K. Benedix¹ and T.J. McCoy², ¹Washington University, Dept. of Earth and Planet. Sci., Saint Louis, MO 63130 USA (gbenedix@levee.wustl.edu); ²Dept. of Min. Sci., National Museum of Natural History, Smithsonian Institution, Washington, DC 20560-0119 USA.

Introduction: Primitive achondrites are characterized by having a bulk chondritic composition and non-chondritic texture [1]. They fall between enstatite and ordinary chondrites in mafic silicate compositions (Fig. 1). They include the winonaites/IAB irons and acapulcoites/lodranites [2]. Because of their unique textural and chemical features, the underlying goal of most studies of these groups is to understand the processes that modified chondritic bodies into fully-differentiated planetesimals (core, mantle and crust). Their intermediate oxidation state suggests either a significant role for oxidation/reduction during metamorphism and partial melting or a range of precursor oxidation states not fully sampled by chondrites. Here we discuss the relative influence of these processes on reduction/oxidation and suggest mechanisms by which these studies can be extended to asteroid studies.

Processes: Textural evidence for metamorphism and partial melting abounds in the both the winonaite/IAB [3, 4] and acapulcoite/lodranite [5, 6] groups. We have examined the role of oxidation/reduction during parent body processes from both an experimental and thermodynamic viewpoint.

Recent experiments heated the H chondrite Kernouve to partial melting temperatures under reducing conditions [8]. While some of the features of primitive achondrites (e.g., magnesian olivine and chromite compositions) were produced, other features would have required either unrealistically high temperatures (e.g., pyroxene reduction) or occurred through reactions (e.g., chromite-sulfide) that have not been observed in primitive achondrites. These experiments suggest that simple reduction of an oxidized precursor chondrite likely did not produce primitive achondrite.

The conclusion is supported by closure temperatures and fO_2 calculated from orthopyroxene/clinopyroxene and olivine/chromite mineral pairs in the range of ~900 to 1100°C and ~590 to 700°C respectively [7]. Several winonaites/IABs record oxygen fugacities in the range from 2.5 to 3 log units below the Fe-FeO oxidation buffer at both temperatures. This strongly suggests that reduction did not occur during cooling and metamorphism after peak heating. Further, the opx/cpx closure temperature is close to the peak temperature, suggesting that the precursor material of these meteorites was reduced.

Reduced Precursor: While relict chondrules in primitive achondrites point to a chondritic precursor, the identity of that precursor remains elusive. We suggest that association with carbonaceous chondrites and, specifically, with metal-rich carbonaceous (e.g., CR-like) chondrites may be appropriate. The negative $\Delta^{17}O$ of primitive achondrites would – almost by definition – point to a carbonaceous chondrite precursor. Further, the CR chondrites share many of the properties (e.g., intermediate mafic silicate compositions, metal-rich) seen in primitive achondrites. While an exact link may not be possible, further study of this postulated link seems warranted.

Implications for Asteroid Spectroscopy: Asteroid spectroscopy may provide a tool for understanding the full range of oxidation states in the solar nebula. The olivine:pyroxene ratio and mafic silicate compositions change systematically with oxidation state and their simultaneous solution, particularly for pyroxene composition which is resistant to parent body reduction, might provide a measure of the range of oxidation states.

References: [1] Prinz M. et al. (1983) *LPS XIV*, 6 616-618. [2] Mittlefehldt D. W. (2004) *Treatise on Geochemistry, Vol I*, Chap. 11. [3] Benedix G. K. et al. (1998) *GCA*, 62, 2535-2553. [4] Benedix G. K. et al. (2000) *Meteoritics & Planet. Sci.*, 35, 1127-1141. [5] McCoy T. J. et al. (1996) *GCA*, 60, 2681-2708. [6] McCoy T. J. et al. (1997) *GCA*, 61, 623-638. [7] Benedix G. K. et al. (2005) *GCA*, in press. [8] Ford R. et al. (2005) *MAPS*, submitted.



Figure 1. Fs (mol%) of low-Ca pyroxene plotted vs. Fa (mol%) of olivine for the primitive achondrite groups Acapulcoites/Lodranites (blue diamonds) and Winonaites/IAB Irons (yellow triangles). These groups have Fs and Fa that fall between enstatite (square) and ordinary (circles) chondrites in composition.

LOW-TEMPERATURE CHEMICAL PROCESSING ON ASTEROIDS. P. A. Bland¹, ¹Dept. Earth Sci. & Eng., Imperial College London, South Kensington Campus, London SW7 2AZ, UK; <u>p.a.bland@imperial.ac.uk</u>.

Background: In terms of their chemistry, carbonaceous chondrites (CCs) are amongst the most primitive materials available to us. But it has become clear that their mineralogy is highly altered. Initially, the abundant magnetite found in some CCs was thought to be a nebula condensate [1], or, together with clay minerals, the product of aqueous alteration that occurred in the solar nebula by the reaction of water vapour and anhydrous minerals [2]. Evidence now suggests that aqueous alteration occurred in the meteorite parent body [3-8]. Theoretical work [9] showed that hydration reactions in the nebula would have been kinetically inhibited (although recent studies argue against this [10,11]). Compelling evidence for aqueous processing on asteroids includes alteration products that bridge matrix components, magnetite morphology consistent with precipitation from a liquid phase, altered zones around chondrules, and the presence of carbonates [12]. Modelling [9] suggests that CC parent bodies accreted water in the form of ice. Transformation of ice into liquid water could have taken several possible routes, either hydrocryogenic alteration, or melting due to external or internal heat sources (plausibly, the decay of short lived radionuclides).

Chemistry: CI chondrites have compositions that are within 10% of the solar photosphere for most elements [13]. Early analyses of gram-samples of meteorite from other CC groups showed uniform volatilitycontrolled depletions compared to CI in elements with condensation T <1350K [14]. All these rocks experienced varying degrees of aqueous alteration. To preserve solar abundances in elements which are easily mobilised in fluids it was postulated that aqueous processing in asteroids was isochemical [3,4,15]. More recent data indicates isochemical alteration on very short length scales. INAA analyses of 10-100mg aliquots [16] shows remarkable reproducibility between samples, and no evidence for element mobility. LA-ICP-MS analyses [17] of 80µm areas of matrix in C3 chondrites indicates minimal exchange between chondrules and matrix on this scale (although some aqueous mobility is apparent in C2s). These geochemical studies are apparently at odds with studies of chondrite petrography which find evidence for metasomatism around chondrules and CAIs in ordinary chondrites [18], CVs [19] and CRs [20].

Oxygen isotopes: Popular models invoke an initial phase of nebula interaction between solid and gaseous reservoirs, followed by parent body aqueous alteration involving simple exchange between a static fluid and anhydrous phases in a closed system [21]. More recently, continuum modelling has shown that the oxygen isotope diversity amongst the CC groups may be explained by as asteroidal process: down-temperature fluid flow and attendant aqueous alteration on a canonical CC parent asteroid [22].

Summary: A means of reconciling geochemical and petrographic studies in CCs involves considering the length-scale over which aqueous metasomatism took place: element mobility occurred, but in C3s it was restricted to zones within ~100-200µm of anhydrous chondrules. In C2s and C1s fluid transport did not occur over distances >>100µm. Oxygen isotope data can also be interpreted as consistent with closed system, isochemical alteration [21]. Numerical modelling of asteroidal alteration suggests flow of pore water may have been limited in parent bodies <80km diameter [23]. The available data therefore appear to be consistent with an environment where fluid flow was minimal, alteration was isochemical, and CC parent bodies were not more than a few 10's km in diameter.

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ON THE FORMATION LOCATION OF ASTEROIDS AND METEORITES. W. F. Bottke and D. Nesvorny. Southwest Research Institute, 1050 Walnut St, Suite 400, Boulder, CO 80302, USA (<u>bottke@boulder.swri.edu</u>).

Despite the advances made by the planetary science community over the last several decades, there are still fundamental questions about the origin and evolution of asteroids and meteorites. Here we concentrate on the iron meteorites, which currently dominate the fraction of distinct parent bodies represented in our meteorite collection (i.e., 27 chondritic, 2 primitive achondritic, 6 differentiated achondritic, 4 stony-iron, 10 iron groups, and 50 ungrouped irons; Meibom and Clark 1999; Burbine et al. 2002). Chemical and petrographic evidence indicates nearly all iron meteorites came from the cores of distinct differentiated asteroids; they cannot be explained away as impact melts or as fragments produced by the disruption of a few large differentiated bodies like D=530 km asteroid (4) Vesta (Scott 2002). Moreover, cooling rate and textural data suggests that many iron meteorites came from small parent bodies (e.g., 20 < D< 400 km; Mittlefehldt et al. 1998). Collectively, we infer from these constraints that differentiated asteroids and the geologic processes that formed them were once common in the solar system.

These data, however, stand in stark contrast to what observations of main belt asteroids tell us about planetesimal evolution. Despite intense searches (e.g., Burbine and Binzel 2002; Bus and Binzel 2002a,b), the only intact differentiated asteroid found to date is (4) Vesta. Fragments of differentiated bodies, however, have been identified. Observations suggest 22 A-type asteroids (out of a sample of 950) may represent mantle fragments (Burbine et al. 2002). (1459) Magnya, a D=30 km V-type asteroid located in the outer main belt, may sample the crust of a non-Vesta differentiated asteroid (Lazzaro et al. 2000: Michtchenko et al. 2002), but the number of these objects (1 known so far) is far lower than our expectations based on the iron meteorite record. Observations of asteroid families, which are the remnants of disrupted asteroids, indicate none have spectral signatures consistent with the expected coremantle-crust of differentiated asteroids (e.g., Cellino et al. 2002). Disrupted differentiated asteroids should produce large quantities of olivine-rich metal-free silicate meteoroids, yet none have been found in our meteorite collections (Burbine et al. 1996). We could easily go on, but the point is clear: our meteorite and asteroid collections appear to be telling us two very different stories about the nature and evolution of planetesimals coalescing out of the solar nebula.

Given these differences, we believe it is useful to reexamine the origin of differentiated asteroids. Current models suggest planetesimals (and planets) formed throughout the solar nebula. The fractionation

observed between different groups of chondrites appears to have resulted from differences in nebular conditions as a function of distance from the sun and, in some cases, differences resulting from sequential formation of planetesimals as a function of time (e.g., McSween et al. 2002). For the latter, consider that radionuclide heating sources with fast decay rates (e.g., ²⁶Al) should have the biggest effect on planetesimals that grow quickly, while accretion models indicate that planetesimal growth rates are highest for objects close to the sun. This information, when coupled to thermal models, predicts that small asteroids are more likely to melt and differentiate if they reside close to the Sun; far from the Sun, only the largest bodies with the right mix of volatiles accrete fast enough to differentiate (e.g., Vesta) (Grimm and McSween 1993; McSween et al. 2002). This scenario, if true, implies that many metamorphized and differentiated planetesimals (and putative meteorite parent bodies) formed < 2 AU (see Wasson and Wetherill 1979 and Wasson 1988).

According to existing planet formation models, the inner solar system planetesimals not accreted by planetary embryos were subjected to both collisional evolution and dynamical scattering events. Preliminary results from our numerical modeling work indicate that throughout the inner solar system, planetary embryos dynamically excite and scatter these planetesimals (and their fragments) away from their feeding zones. We believe this explains the observed spread of S-, C-, and P-type asteroids (D > 50 km) in the main belt (Gradie and Tedesco 1982). In certain cases, intact bodies or, more likely, fragments produced among a < 2 AU planetesimals, become trapped in stable regions like the main belt or Hungaria asteroid populations.

Although these main belt "interlopers" would be subject to Gy of collisional and dynamical evolution, some small fraction would have most likely survived to the present day. Our results indicate the majority of this material would reside in the innermost part of the main belt, making it relatively easy for meteoroids to later escape and reach Earth.

Note that iron meteorite precursors are not only are resistant to disruption events but they also have long dynamical lifetimes against Yarkovsky thermal drag forces (Bottke et al. 2002b). The same cannot be said for basaltic meteorite precursors; few embedded in the main belt 4.5 Ga are likely to be here today. We believe this scenario may explain the so-called meteorite "dunite shortage" without resorting to unphysical collisional models. Finally, our results imply that some meteorites (e.g., winonaites) may sample the long lost planetesimals that formed in the terrestrial planet zone (Wasson and Wetherill 1979). **THE SPECTRAL PROPERTIES OF ANGRITIC BASALTS.** T. H. Burbine¹ and T. J. McCoy², ¹Astronomy Department, Mount Holyoke College, South Hadley, MA 01075, USA (tburbine@mtholyoke.edu), ²Department of Mineral Sciences, National Museum of Natural History, Smithsonian Institution, Washington, DC 20560, USA.

Introduction: One type of material that tends to be relatively rare in our meteorite collections is basalt. Basalts are rocks rich in calcium-rich plagioclase feld-spar and augitic pyroxene that form as solidified lava. One meteorite group, the angrites, is primarily basaltic in origin and make up 0.1% of all meteorite falls. These meteorites are composed predominately of anor-thite, Al-Ti diopside-hedenbergite, and Ca-rich olivine. The type specimen, Angra dos Reis, is compositionally anomalous compared to other angrites since it is composed almost entirely of Al-Ti diopside-hedenbergite with only rare plagioclase.

The eucrites are the most common type of meteoritic basalt and appear genetically related to the howardites and diogenites (HEDs). HEDs show continuous variations in mineralogy and chemistry and almost all are believed to have formed on the same parent body. Eucrites contain primarily anorthitic plagioclase and low-Ca pyroxene with augite exsolution lamellae.

Jurewicz et al. [1] found that partial melts of carbonaceous chondritic material resembled either angrites or eucrites, depending on the oxygen fugacity during melting. Relatively oxidizing conditions produced partial melts similar to angrites while relatively reducing conditions produced partial melts similar to eucrites. Iron meteorites are generally believed to represent ~50-70 differentiated parent bodies; however, it is unclear if angritic- or HED-like surfaces were more common. The ~500-km diameter 4 Vesta and a number of much-smaller asteroids (called Vestoids) have reflectance spectra similar to the HEDs. Almost all Vestoids are thought to be fragments of Vesta.

The identification of possible angritic parent bodies was hampered by the fact that the only previously measured angrite, Angra dos Reis [2], has a spectrum unlike any known asteroid. The spectrum of Angra dos Reis is much redder (reflectance increasing with increasing wavelength) than almost all measured asteroids. Recently, the discoveries of two relatively large angrites (D'Orbigny and Sahara 99555) plus previously discovered Antarctic angrites (LEW 86010 and LEW 87051) have allowed for the measurement of the spectral properties of meteorites that may be more typical of the surface compositions of the angritic parent bodies.

Samples: Room temperature reflectance spectra for Angra dos Reis, D'Orbigny, LEW 86010, and Sahara 99555 were obtained using the bi-directional spectrometer at the Keck/NASA reflectance experiment laboratory (RELAB) facility located at Brown University. These samples were ground with a mortar and pestle and sieved to particle sizes less than 125 μ m for the Angra dos Reis, D'Orbigny, and Sahara 99555 samples and less than 74 μ m for the LEW 86010 sample.

D'Orbigny [3] and Sahara 99555 [4] both contain approximately one-third anorthite, one-third Ca-rich olivine, and 20-25% Al-Ti diopside-hedenbergite. LEW 86010 [5] is approximately 20% anorthite, 20% Ca-rich olivine, and 60% Al-Ti diopside-hedenbergite. Angra dos Reis [6] is ~90% Al-Ti diopsidehedenbergite.

Reflectance Spectroscopy: The roomtemperature reflectance spectra of D'Orbigny, LEW 86010, and Sahara 99555 have similar spectral characteristics. Both have broad features centered near 1 μ m and very weak absorption bands centered at ~2 μ m. This is in contrast to the strong 2 μ m band present in the Angra dos Reis spectrum. The spectra of D'Orbigny, LEW 86010, and Sahara 99555 are relatively red, but not as red as the Angra dos Reis spectrum.

The presence of a 1 μ m band but a very weak 2 μ m feature is characteristic of some high-Ca pyroxenes where iron is located almost entirely in the M1 site. Calcium is found in the slightly larger M2 site. These pyroxenes have two absorption bands centered at ~0.90 and ~1.15 μ m that partially overlap; however, the presence of olivine in these angrites wipes out this structure in the angrite spectra.

Asteroid Spectra: Currently, no asteroid has been found to be a suitable spectral match to the angrites. Asteroids classified as Sr in the Bus and Binzel [7] taxonomy have visible spectra that match angrites, but do not spectrally match angrites in the near-infrared. Many asteroids with distinctive olivine absorption bands (such as A types) have similar spectral slopes to the newly measured angrites; however, angrites do not have these distinctive olivine bands.

Conclusions: The parent body or bodies of the angrites had to have existed in the asteroid belt, but presently no spectral analogs to the angrites have been identified.

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Although there is growing support for the role of isotopic self-shielding in the photolysis of gaseous carbon monoxide as the main process leading to the "anomalous" isotopic fractionation of oxygen in the early solar system, there is no consensus concerning the physical site of this process [1, 2, 3]. Many recent SIMS studies of refractory inclusions (CAIs) and chondrules have elucidated the mineralogical, chemical, and spatial systematics, which may provide constraints on P,T conditions and timescales for condensation, melting, evaporation, and alteration processes. It is well-established that the primary formation of CAIs involved condensation from a gas of solar chemical and oxygen isotopic composition. An ¹⁶O-rich solar isotopic composition, with δ^{18} O and δ^{17} O both near -50% relative to SMOW, is implied from the meteorite data [1], and from solar atoms implanted in lunar soil grains [4]. Primary condensates were subsequently altered isotopically by exchange with a gas, probably H₂O [2, 3] or atomic O [5], which had been enriched in ¹⁷O and ¹⁸O by the photochemical process. A clue to the conditions of this secondary process may come from correlations of oxygen isotope abundances with chemical properties related to oxidation reactions, such as the ferrous iron content of chondritic silicates. Such correlations have been seen in chondrules, rims, and crystals in several contexts: in chondrules and their rims in Allende [6], in whole chondrules in Allende [7], in isolated olivine grains in Allende [8], in chondrules in ALH 77307 [9], in relict and host olivine in porphyritic chondrules in Y 81020 [10]. These correlations all show enrichments in ¹⁷O and ¹⁸O associated with increases in oxidized (ferrous) iron. The examples cited all occur in carbonaceous chondrites, in which the oxygen isotope data fall on or near a slope-1 line in the three-isotope diagram, implying incomplete (non-equilibrium) exchange between a ¹⁶O-rich condensed object and a ¹⁶O-poor gas species. A similar oxygen-iron correlation is observed in whole-rock analyses of ureilites, which are thought to have carbonaceous-chondrite-like precursors [11].

The correlation between oxygen isotopic composition and the oxidation state of iron is less clear for unequilibrated ordinary chondrites. There is still an isotopic distinction between refractory forsterite cores and FeO-rich rims [12], but an early study of whole chondrules [13] showed no correlation between $\Delta^{17}O$ and Fa in six chondrules from Hallingeberg and Semarkona. Furthermore, the range in isotopic compositions for these L3 chondrites is much smaller than that in carbonaceous chondrites, and the data define a shallower slope, near 0.7. These features suggest a more complete approach to isotopic equilibrium for ordinary chondrite chondrules that for carbonaceous chondrite chondrules that for parent-body effect.

The observed correlations between oxygen isotopic compositions and ferrous iron content (both non-equilibrium properties) in chondrules in carbonaceous chondrites argue in favor of the acquisition of both properties in the same event: chondrule formation. In the photochemical scenarios of [2, 3], the ¹⁶O-poor reservoir is segregated from the nebular gas as water ice, and its formation is decoupled from the chondrule-forming process. In the X-wind scenario [1, 4], the photochemical formation of atomic ¹⁷O and ¹⁸O is directly responsible for the chondrule chemical and isotopic compositions.

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Introduction: CM chondrites experienced relatively low-temperature aqueous alteration, at least some of which happened on their parent body. The conditions under which aqueous alteration occurred are: fluid temperatures of $0-25^{\circ}$ C [1], from the time of asteroid formation up to 15 Myr [2-4] and mobility over scales of only tens of μ m [5, 6].

Asteroid thermal models [7] have been successful in describing high-temperature parent-body processing, but no models yet completely characterize CMtype parent bodies. We continue to use our thermal model [8], which addresses the characteristics and physics of the liquid water phase, to develop scenarios that produce liquid water consistent with observed thermal and spatial constraints in CM meteorites.

In-situ alteration budgets: Exothermic alteration reactions (represented by a simple serpentinization reaction) are the chief cause of thermal runaway in our previous work. To further explore the effect of this heat source, we created scenarios that begin with serpentine in the parent body, which might be from aqueous activity in the nebula [9] or in previous parent bodies. We began these runs with 25%, 35%, and 45% initial serpentine by volume and included only enough initial reactants (forsterite and enstatite) to create ~50% total serpentine (the difference in initial serpentine among runs is made up in inert rock).

As expected, in all three cases, the peak temperature at the center of a 20-km parent body is lower than achieved previously (<330K). The peak temperature as a function of radius is shown in Fig. 1 for the 25% initial serpentine run. Since this run undergoes more reactions, it has the largest heat budget. However, even in this case, only the central 5 km reaches the melting temperature of ice so that the volume of the body further altered to ~50% serpentine is only approximately the central 1/6 of the asteroid volume. This total volume doesn't change significantly between these three scenarios. In addition, in all three cases, radial transport of water occurs over scales of kms rather than µms. This is due to the hydration reactions, which start in the center of the parent body, generating a strong enough temperature gradient to push both liquid and vapor upwards for kms through the rock pore space. The final serpentine and ice composition of the 25% initial serpentine case is shown in Fig. 2. Excess liquid water is pushed up to the outer radius of reactions where it meets the inward moving cooling wave and freezes, nearly filling up the pore space.

Conclusions: Hydration prior to final parent body formation and evolution is insufficient, in itself, to resolve the mismatch between thermal models and CM meteorite observations. Ongoing simulations are exploring parameters such as macroporosity and kinetics of heat release.

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Fig. 1. Maximum temperature in the central region of a 100-km parent body starting 25% initial serpentine.



Fig. 2. Final volume fractions of serpentine and ice in the central region of the parent body.

OXIDATION-REDUCTION IN METEORITES: THE CASE OF HIGH-NI IRONS. C. M. Corrigan¹ and T. J. McCoy², ¹Johns Hopkins University Applied Physics Laboratory, 11100 Johns Hopkins Road, Laurel MD 20723, <u>cari.corrigan@jhuapl.edu</u>; ²National Museum of Natural History, Smithsonian Institution, 10th St. and Constitution Ave. NW, Washington DC, 20560-0119.

Introduction: In recent years, our research group has studied a range of asteroidal processes intimately linked to oxidation-reduction on meteorite parent bodies. These include the formation of oxidebearing clasts on the aubrite parent body [1], melting of ordinary chondrites in the presence of graphite to understand the formation of primitive achondrites [2] and the formation of vesicular basalts from the eucrite and angrite parent bodies by oxidation to form Our most recent foray into oxidation-CO [3]. reduction and its influence on the formation of meteorites has been the study of high-Ni irons. specifically the Ni-rich ungrouped iron Tishomingo [4]. While we have previously explored the role of fractional crystallization in the formation of high-Ni irons, this work specifically examines the role of oxidation.

Our Previous Work on **Tishomingo:** Tishomingo is an ungrouped iron meteorite that is both rich in Ni (32.5 wt.%) and poor in phosphorus (<0.01 wt%). The martensitic structure of Tishomingo is consistent with cooling of a high-Ni, low-P taenite and diffusionless transformation to martensite during cooling to ~80K. Oxygen isotopes in a single SiO₂ grain are similar to angrites in Δ^{17} O and similar in δ^{18} O and bracketed in δ^{17} O by the CR chondrite Renazzo and the metal-rich chondrite GRO 95551. Chemically, Tishomingo is broadly similar to IVB irons for many siderophile elements. IVB irons are the most Ni-rich of the main groups (15.6-18 wt.% Ni) and share the volatile siderophile element depletion of Tishomingo (Fig. 1). Both crystallization and high-temperature fractional condensation have difficulties explaining the composition of Tishomingo [4].



Fig. 1: CI normalized siderophile element concentrations for Tishomingo and the IVB iron Hoba [4].

Oxidation. Oxidation might explain the origin of several features in Tishomingo, including the high-Ni and low-P composition, the presence of SiO₂, and the fractionated (Fe/Pd)_{CI} and (W/Ir)_{CI} ratios. A recent study of IVB irons [5] advocated a role for oxidation and further argued that the silicate complement to the oxidized IVB irons might be the oxidized angrites. This is an intriguing suggestion in light of the similarity in Δ^{17} O between these groups. This oxidation might occur in either the solar nebula or, as suggested by [5], on the parent body.

In their pioneering work, [6] suggested mechanisms for nebular oxidation at a range of temperatures, including reaction of Fe⁰ with H₂S, O₂ and H₂O. Mechanisms for oxidizing the core on the parent body have not, to our knowledge, been The fundamental problem is how to proposed. deliver a large quantity of oxygen to the core of a body during or after differentiation. Foreign sources (e.g., comets) would have to penetrate (and likely disrupt) the mantle. The most likely scenario would seem to be reaction of metal with water during differentiation. In this vein, the CR chondrites are particularly interesting. With a Ni concentration in metal on the order of 10 wt.% [7], ~70% of the Fe in the metal would need to be oxidized to produce a core with ~32.5 wt.% Ni. The metal in CR chondrites (~15 wt.%) would require ~3 wt.% H₂O, assuming a simple stoichiometric reaction of $Fe^{0}+H_{2}O=FeO+H_{2}$. This may be realistic, given the hydrated nature of CR chondrite matrix and the high ratio of matrix to metal (~44:7, in vol.%) [7].

We suggest that the most likely precursor for Tishomingo and IVB irons was a volatile-depleted chondrite which contained both metal with moderate Ni concentrations and hydrated matrix. Oxidation by reaction of metal with water occurred during melting, producing one or more parent bodies with small, Nirich cores that underwent fractional crystallization. The complex interplay of condensation, oxidation and fractional crystallization produced the Ni-rich irons in our collections.

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UREILITE ATMOSPHERICS: COMING UP FOR 'AIR' ON A PARENT BODY.

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Introduction: The ureilite group is unusual. Petrographically, ureilites appear to be samples of a coherent suite that differentiated on a single parent body. The oxygen isotope ratios of the ureilites vary along a massindependent fractionation (MIF) trend rather than the mass-dependent trend typical of most differentiated asteroids sample suites. The individual ureilites cannot be linked to one another by mass dependent fractionation of oxygen isotopes. Isolated lithic clasts in an individual polymict ureilite cannot be linked to a common process, by mass-dependent fractionation yet they are, by definition, samples of the same parent body. The MIF trend for oxygen is as fundamental property of ureilites, as the intense redox exchange products visible in all samples. While mixing of heterogeneous precursors might explain the variation of ureilite oxygen isotope ratios, it is implausible that such variation would survive the very high temperature processes implicit in ureilite petrography.

The petrographic/experimental evidence suggests that a "smelting" process may be responsible forming ureilites (e.g. Walker and Grove, 1993; Singletary and Grove, 2003). The smelting reaction can be written as: $Fe_2SiO_4 + C \leftrightarrows FeSiO_3 + CO + Fe$. (A comparable reaction exists for CO_2). The reaction consumes graphite to reduce silicate FeO to Fe metal with CO/CO_2 as a byproduct. The assumption is made that graphite is the reactant and CO gas, the product, even though both graphite/diamond and metal are present in most ureilites. The reaction, as stated, implies that the only mechanism, affecting the oxygen isotope ratios, is mass dependent fractionation. It provides no explicit explanation for the mass independent effects that are so characteristic of ureilites. However, if the CO acts as an oxidizing agent, in reaction with metal, and is reduced back to graphite, then the gas phase reactions can be exploited.

CO or CO_2 may provide oxygen in a form that enables symmetry dependent gas phase reactions to produce mass-independent enrichment of ¹⁶O relative to ¹⁷O and ¹⁸O (Theimens 1996). The reaction of such mass independent effects interacts with the solid fraction (ureilite matrix) to produce variable amounts of isotopically heavy olivine and pyroxene as well as a C-polymorph. Alternately if the process occurs in communication with the parent body surface, the presence of a transient CO atmosphere would permit photochemical disequilibrium in the form of self shielding reactions (Clayton, 2005). In this case, the heat source for ureilite melting and the cause of the CO-photolysis reactions is likely the same – intense solar radiation +/inductive coupling to magnetic fluctuations both associated with X-wind processing. Accretion and differentiation of a ureilite parent asteroid, should be intimately associated with at least partial mass-independent fractionation of oxygen in the parent body 'atmosphere'. Interaction of the oxygen fugacity buffering reactions and oxygen isotopic signatures of the final lithic fragments seen in the meteorites is an inevitable consequence. References:

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HIGH TEMPERATURE EFFECTS INCLUDING OXYGEN FUGACITY, IN PRE-PLANETARY AND PLANETARY METEORITES AND ASTEROIDS.

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Introduction: The properties of asteroids are established by early solar system accretion processes. The elemental and isotopic compositions of a meteorite, and by extension its parent body, reflect the composition of the nonvolatile nebular components available at the time of assembly. The chemical state of the elements, in contrast, is a reflection of both these condensable components and, provides a proxy for volatile components such as H₂, H₂O, CO, CO₂, CH₄, SO₂, that are not usually present in the available samples. High temperature processes produce the gross properties of both pre-planetary and planetary asteroids.

Pre-planetary asteroids that have not experienced planetary differentiation are more abundant than the fully differentiated planetary asteroids. *Pre-planetary* asteroids are most closely associated with chondritic meteorites of various types. *Planetary* asteroids, or planetoids, are represented by achondrite groups. All stages from zero differentiation, through intermediate states, to complete differentiation, are represented by meteorites.

Processes: Accretionary processes are manifested as impact signatures in *all* meteorite types. Craters and, of necessity impact processes, are prominent features of most asteroids. While impact is one source of heating, internal processes of radioactive decay and gravitational overturn also produce heat. External heat sources associated with, for example, X-wind effects must also be considered. Thermal effects range from minimal to metamorphic overprints to wholesale melting. The softening effects of melting in the interior are probably essential for planet scale differentiation.

Although oxygen is volumetrically the most abundant element in most preplanetary and planetary samples, it is often assumed to provide a passive 'framework' in which cation exchange reactions occur. However, the importance of redox processes in determing the final outcome of both preplanetary and planetary reactions is paramount. Although oxygen is more abundant than most heavier elements the solar system, it is significantly depleted in most available samples relative to nebular abundance. As a result, there is often too little oxygen to balance the charge on most cation species, thus, most meteorite samples are reduced. Much of the original oxygen in the nebula has been incorporated into volatile species that precipitate in low temperature regimes that exist outside the solar system's frost line (in the outer asteroid belt). Only samples that originate outside the frost-line will have excess oxygen and may therefore be considered oxidized. This fundamental dichotomy will have very far reaching effects in our interpretation of both oxygen chemistry and its isotopic signatures.

Thermal regimes and oxygen fugacity: High temperatures are not exclusive to the inner solar system, but material that has obviously been processed at high temperatures (planets) is most easily observed there. It is tempting to suggest that the majority of differentiated planetoids formed in our inner solar system, but this is probably a gross oversimplification. Oxygen depletion is typically quantified in terms of oxygen fugacity(fO_2). In particular, the chemical state of iron, the most abundant of the multivalent transition elements, is used as a proxy for fo2. Unlike the water-rich surface of the earth, where Fe²⁺ and Fe³⁺ coexist, the reduced oxygen content of the inner solar system, has forced the coexistence of Fe⁰ and Fe^{2+} with Fe^{3+} much less common. The implied low oxygen fugacity of most meteorites also requires consideration of the oxidation states of other transition elements such as Cr, V and Ti as proxies.

Because iron is a major element in both preplanetary and planetary meteorites, it's oxidation state is important to all associated phase equilibria and hence the magmatic and metamorphic evolution of meteorites and their parent asteroids. The buffering effect of iron metal (Fe in excess of available O) constrains many systems but other oxygen buffering reactions are also important. In rare cases, relatively oxidizing reactions such as those buffered at quartz-fayalite-magnetite appear in meteorites where physical separation of Fe metal has occurred previously (e.g. core formation). More commonly, reduced buffers such as C-CO or CO-CO2 are recognized. Measurement of the products of these oxygen buffering reactions is increasingly important. The development of microanalytical techniques that determine the chemical state of meteoritic systems at the same spatial scale as elemental and isotopic abundance measurements is critical to progress.

Summary: The abundance of oxygen in both preplanetary and planetary meteorites and asteroids and its representation as oxygen fugacity is fundamental. The high temperature evolution of asteroids and planetoids, particularly when melting occurs, is critically dependent on the buffer assemblages originally present. Achondritic meteorites provide very clear examples of this influence but chondritic samples show more extreme variations. If differences between the volatile abundances of inner and outer asteroid belt are reflected in the oxygen fugacity of representative meteorites, a more complete understanding of the links between oxygen isotope signatures and fugacity will be a fundamental tool. **OXYGEN ISOTOPIC VARIATION OF ASTEROIDAL MATERIALS.** I. A. Franchi, R. C. Greenwood, L. Baker and A. A. Morris Planetary and Space Sciences Research Institute, Open University, Walton Hall, Milton Keynes, MK7 6AA, United Kingdom. (Email: i.a.franchi@open.ac.uk)

Introduction: The vast meteorite collections now available reveal a fantastically diverse range of different rock types and minerals that originate from asteroids. This suite contains minerals that have existed prior to the formation of the Solar System, grains which formed from the gas and dust of the solar nebula and minerals that are the result of secondary process once these early formed grains, together with ices, had accreted onto planetisimals. As such these rocks and minerals record a large range in oxygen isotopic compositions, reflecting the location, sources and conditions of their formation. This offers an important tool in tracking the origin and evolution of asteroidal and planetary material. Differential incorporation of these components into the planetisemals has led to oxygen isotopic variations persisting at all scales, even measurable isotopic variations between a large number of asteroids and planets. As such, oxygen isotopic measurements are a useful tool in the determining the relationships between randomly collected and diverse meteorites. However, this is only possible as we develop our understanding of the isotopic variation within individual asteroids and the internal processes which modify the oxygen isotopic signatures.

Interstellar Grains: Interstellar oxides grains isolated from acid residues of primitive meteorites have oxygen isotopic enrichments/depletions of up to two orders of magnitude in ¹⁸O and ¹⁷O [1]. However, with an abundance of ≈ 0.01 ppm [e.g. 1] these can have no measurable effect on the macro isotopic variation observed in meteorites. More recently, in situ studies of matrix material in primitive chondrites has revealed higher abundances of oxides (up to 50 ppm) and interstellar silicates up to 130 ppm [2]. These higher abundances raise the possibility that some measurable differences at the macro scale could be the result of differential accretion of such grains, particularly if the original abundance was even higher -e.g. interplanetary dust grains contain up to 400 ppm pre-solar silicates [3].

Nebula Components: Primitive meteorites contain high temperature condensates from the solar nebula – CAIs, chondrules and mineral fragments. The earliest formed are the CAIs – with oxygen isotopic signatures enriched in ¹⁶O by over 40‰ [4]. Chondrules, which formed slightly later than the CAIs, are the dominant component of many primitive chondritic meteorites. The oxygen isotopic signature

of chondrules from ordinary, enstatite and carbonaceous chondrites are all different [5] indicating distinct formation histories, spatially and/or temporally. It is clear that the oxygen isotopic signature of both CAIs and chondrules has been affected by secondary processes [e.g. 6,7]. Resolving the primary and secondary signatures is needed to understand the origin of these primitive components, particularly for chondrules where there is less consensus about the nature of their formation.

Asteroidal Processing: There is clear evidence of asteroidal processes affecting the primitive materials mentioned above. CM, CI and CR chondrites now contain large amounts of phyllosilicates, carbonates, salts, etc which have been produced by water-rock interaction. Such reactions re-distribute oxygen isotopic signatures and generate large isotopic fractionations, which can be used to determine the conditions at which these secondary minerals formed – providing key information about early asteroidal processes. Such work has led to the development of a number of models describing the oxygen isotopic systematics observed [e.g. 8,9] – but uncertainty persists about the fluid conditions during this process.

At higher temperatures, thermal metamorphism and melting lead to homogenization of oxygen isotopic heterogeneity – eventually generating well defined mass fractionation lines – such as those defined by the HED (possibly from Vesta) and angrite meteorites [10], martian, lunar and terrestrial samples. Where such processes are not sufficiently advanced (primitive achondrites) isotopic heterogeneity persists [*e.g.* 11,12] which can be used to define local areas of homogeneisation (*i.e.* local reservoirs) and to track the onset of melting.

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Introduction: Small planetary bodies accreted within 2.4 Myr of solar system formation [1]. The primitive materials (CAIs, chondrules, matrix) incorporated into these asteroids were altered by a variety of secondary processes, including aqueous alteration, shock metamorphism, thermal metamorphism and melting. Here we look primarily at the role played by thermal metamorphism and melting in altering the oxygen isotope systematics of asteroidal materials.

Metamorphism and melting: Peak temperatures recorded by meteorites range from 400°C in the least altered type 3 chondrites [2], to over 1500°C for achondrites formed during large scale planetary melting [3]. This range can be subdivided as follows: i) thermal metamorphism (400°C to 950°C), ii) limited partial melting (950°C to 1250°C), and iii) extensive partial melting (1250°C to >1500°C). These divisions loosely correspond to the thermal regimes experienced by i) chondrites, ii) primitive achondrites, and iii) differentiated achondrites.

Chondrites (400°C to 950°C): Slow rates of oxygen diffusion in the solid state mean that, where thermal metamorphism was essentially dry, only limited disturbance of primary oxygen isotope signatures took place. Consequently, chondrites preserve important information about nebular processes [4]. However, chondrites are not pristine materials. Recent studies of the ordinary chondrites demonstrate that they have complex histories with low-temperature hydrothermal assemblages being progressively obliterated by later thermal metamorphism [5]. Systematic shifts in oxygen isotopes have been recognized in the CO3 chondrites, with a subtle increase in Δ^{17} O values from grades 3.1 to 3.4 indicating that an aqueous fluid phase was present during metamorphism [6]. In contrast, a systematic increase in δ^{18} O values in the enstatite chondrites from type 3 to type 6 is not the result of any simple parent body process [7]. In the carbonaceous chondrites significant difficulties exist in establishing genetic links between unequilibrated (type 3) and equilibrated (type 4 to 6) groups. A genetic relationship has been proposed for the CV3 and CK groups [8], which display a trend of decreasing oxygen isotope variation with increasing grade.

Primitive achondrites (950°C to 1250°C): Eutectic melting occurs at about 950°C in the Fe-FeS system, with silicate partial melting commencing at ~1170°C. Asteroidal materials that experienced these conditions show complete recrystallisation followed by progressive loss of Fe-Ni-S and silicate partial melts [9]. Termed primitive achondrites, these meteorites include the ureilites, acapulcoites and lodranites, aubrites, brachintes, winonaites and associated IAB and IIICD irons. In terms of oxygen isotope systematics they show less heterogeneity than chondrites, but still retain significant levels of variability [10]. Thus, acapulcoites and lodranites display textures indicative of about 1% to 20% partial melting of a single parent body [11]. Their Δ^{17} O values (-0.99‰ to -1.49‰) display a significantly greater range than seen in the differentiated achondrites [10]. Likewise, ureilites display major oxygen isotope variation and scatter about the slope 1 line defined by primitive chondrites [10].

Differentiated achondrites (1250 to >1500°C) At relatively high degrees of partial melting complete isotopic homogenisation takes place, with subsequent mass-dependent fractionation resulting in variation along lines with slope 0.52 on δ^{17} O v. δ^{18} O diagrams [10]. Examples of differentiated achondrites include the HEDs and angrites. Pallasites, mesosideites and IIIAB irons show similar oxygen isotope variation to the HEDs and may be fragments from the same parent body [9].

Conclusions: Meteorites provide clear evidence of widely varying thermal conditions within asteroids in the early solar system. With increasing temperature there is a progressive loss of primary oxygen isotope variation, complete homogenization occurring at high degrees of partial melting.

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OXYGEN ISOTOPES AND ORIGIN OF OPAQUE ASSEMBLAGES FROM THE NINGQIANG CARBONACEOUS CHONDRITE. Yunbin Guan¹, Weibiao Hsu², Xin Hua^{2, 3}, Laurie A. Leshin^{1, 4}, ¹Dept. of Geological Sciences, Arizona State University, Tempe, AZ 85287, USA. ²Laboratory for Astrochemistry and Planetary Sciences, Purple Mountain Observatory, Nanjing, 210008, China. ³Dept. of Mechanical/Aerospace Engineering; ⁴Center for Meteorite Studies, Arizona State University, Tempe, AZ 85287, USA.

Opaque assemblages (OAs), also called Fremdlinges, are complex objects that normally contain Fe-Ni metals, magnetite, sulfides, phosphates, silicates, Pt-metal nuggets and their oxides. OAs occur in Ca-Al-rich inclusions (CAIs), chondrules, and matrix of carbonaceous chondrites [1-10]. The unique and complex mineral components of OAs indicate that they formed at a wide temperature range and under highly variable redox conditions [1]. Oxygen isotopes of OAs, unavailable until now, can help us understand the origin of these objects and provide us insights about the early processes in solar nebula or on asteroid bodies.

The OAs (~100 to ~350 μ m in sizes) from the Ningqiang carbonaceous chondrite were observed in its chondrules and matrix. The morphology, texture, and mineralogy of these OAs closely resemble those of CAI OAs [10]. Briefly, they appear as round to oblate spheroids. Major mineral phases are magnetite, Ni-rich metal, troilite/pentlandite, and whitlockite. Minor phases include silicates (olivine and pyroxene) and mesostasis (mixture of silicates and phosphates). Os-Pt-rich Fe-Ni grains (~150 nm in sizes) are rare and appear only in magnetite.

In situ oxygen isotopic compositions were obtained for 12 magnetite and 1 whitlockite grains from 5 Ningqiang OAs. Eight olivine grains adjacent to the OAs were also analyzed. The results are plotted in Fig. 1. Oxygen isotopic compositions of magnetite show variations both among OAs (~16‰ in δ^{18} O) and within one OA (~9‰ in δ^{18} O) of a compound olivine chondrule. All the magnetite data fall along a regression line with a slope of 0.51, which is parallel to the terrestrial fractionation (TF) line with an offset of -2.9‰ in Δ^{17} O. Oxygen isotopic composition of the whitlockite grain falls close to the magnetite regression line (Fig. 1). Oxygen isotopic heterogeneity exists in olivine grains within and among chondrules. The olivine data points plot below the magnetite regression line but above the carbonaceous chondrite anhydrous mineral (CCAM) line. A regression line through olivine data has a slope of ~0.7. Magnetite has higher Δ^{17} O values than its adjacent olivine. In the OA of a compound olivine chondrule, the average Δ^{17} O of magnetite is (- 2.7 ± 0.5)‰, much higher than that of adjacent olivine (-6.1±0.5‰).

It has been proposed that OAs could have formed by: 1) direct nebular condensation [2, 3, 6], 2) crystallization from immiscible metallic-sulfide-oxide liquids during CAI and chondrule formation [7, 8], and 3) low temperature oxidation of preexisting metal alloys [4, 8, 9]. The oxygen isotopic compositions of OAs in chondrules and matrix from Ningqiang present conclusive evidence that OAs formed by aqueous alteration of metal alloy precursors on parent bodies. Therefore, OAs do not represent the oldest solids in the solar nebula, instead, they provide constraints on secondary processes on asteroidal bodies.

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Fig. 1 Oxygen isotopes of Ningqiang OAs and adjacent olivine. Previous bulk data of are from [11, 12].

WATER DISTRIBUTION IN THE ASTEROID BELT. E. S. Howell, Arecibo Observatory, Arecibo PR 00612, USA, (ehowell@naic.edu), A. S. Rivkin, Dept. Earth, Atm. and Planetary Sciences, MIT, Cambridge, MA 02139, USA, F. Vilas, NASA JSC, Houston, TX 77058, USA.

Water is abundant in the solar system, reactive, and a sensitive thermal tracer in asteroids. We learn a great deal about the formation conditions and thermal history of asteroids by measuring where the water is and is not. Water ice was presumably incorporated into at least the middle and outer belt asteroids. If these objects were heated, melting the ice, the water would quickly react with any silicate minerals forming phyllosilicates, containing structural hydroxyl groups and possibly also interlayer water molecules. We see the spectral signatures of these hydrated minerals in the reflectance spectrum of asteroids at 3 microns. The 3-micron absorption feature is a very useful diagnostic spectral feature on asteroids (Lebofsky et al., 1981; Jones et al., 1990). It has been suggested that the 3-micron band could be produced by effects unrelated to water/OH, but all of the alternative interpretations proposed make predictions that are not supported by the observations (Rivkin et al., 2003). In spite of improved infrared instrumentation, it remains difficult to observe the 3-micron band from the ground because of strong atmospheric absorption. Another spectral feature that is easier to observe, and can be detected by smaller telescopes on fainter objects, is the 0.7-micron phyllosilicate feature (Vilas and Gaffey, 1989; Howell et al., 2002). This absorption band is a Fe²⁺-Fe³⁺ charge transfer band in iron-bearing phyllosilicates. Although there is clearly a correlation between the 0.7 and 3-micron features, there are inconsistencies as well. Hiroi et al. (1996) showed that mild heating subsequent to aqueous alteration can explain objects that have the 3-micron feature but not the 0.7 feature. However, the 0.7-micron feature should never be present without the 3-micron feature, at the same rotation phase. Our observations bear this out: In all cases we have found the 3-micron band present on objects with a 0.7-micron band at the same rotation phase.

If the 0.7-micron band is seen, Fe-bearing hydrated minerals are present. However, if it is not seen, no conclusion can be drawn about the hydration state. In a fairly small sample (though not unbiased) about half of the objects without the 0.7-micron band did have the 3-micron band, the other half did not. Our observations of the 0.7-micron absorption band at different rotation phases reveals that a large fraction of hydrated asteroids do show variations in the spectral band occurrence and depth on different faces. On a compositionally heterogeneous asteroid, we might expect to see hydrated spots exposed on the surface at some places and not others. However, thermal models suggest that, since aqueous alteration is exothermic, once it starts, the entire body becomes hydrated: Hydration is expected to be homogeneous. Our observations clearly show variability in hydration. This conflict could be resolved if the hydration reaction is limited by the amount of water available. These observations are primarily of larger asteroids (D> 100km). We do not (yet) know the spatial scale of the hydrated areas, or whether the patchy exterior necessarily implies a heterogeneous interior. We are pursuing observations of smaller asteroids that will answer these questions and help constrain aqueous alteration models.

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Comparative planetary mineralogy: V systematics in planetary pyroxenes and fO_2 estimates for basalts from Vesta. J.M. Karner¹, J.J. Papike¹, and C.K. Shearer¹. ¹Institute of Meteoritics, Department of Earth and Planetary Sciences, University of New Mexico, Albuquerque, NM 87112.

Introduction: As part of the Lunar and Planetary Institute's "Oxygen in the Solar System" initiative, we have been developing V valence oxybarometers (VVOs), as measured in basaltic phases. Vanadium can exist as V^{2+} , V^{3+} , V^{4+} , and V^{5+} , and thus VVOs record at least 8 orders of magnitude of fO_2 , and are especially applicable to reduced planetary materials. Our first V work concentrated on basaltic glasses [1, 2], but now we are developing VVOs for chromite [3, 4], olivine [5] and pyroxene [6]. A VVO for pyroxene will be particulary useful for the study of basalts from asteroids (i.e. eucrites), and from Mars, in which pyroxene is an early crystallizing phase. This study explores the behavior of V in pyroxenes from planetary basalts and estimates the fO_2 of basalts from 4 Vesta.

Comparative planetary mineralogy-pyroxene: The samples we studied are basalts containing pyroxene from the Earth, Moon, Mars and Vesta. The terrestrial sample is a Hawaiian basalt, while the lunar sample, 12075, is an Olivine basalt from the Apollo collections. The martian samples are DaG 476 and Shergotty, both basaltic shergottites. Pasamonte is an unequilibrated eucrite basalt presumed to be from Vesta. Pyroxene grains from each sample were analyzed by EMP to determine their major element compositions and then by SIMS to determine V concentrations.

V systematics in pyroxene: Figure 1a, b plots Ca and Fe# content in pyroxene grains versus V pyroxene / V rock. Here we use the measured V in pyroxene and normalize to literature values of V in the rock, and call this value V*. V* is not a true D-value because some of these basalts are not melts but cumulates, and thus V* does not represent the equilibrium distribution of V between pyroxene and the coexisting melt. The plots show that V* values are lowest in terrestrial pyroxene, slightly higher in martian pyroxene, and much higher and comparably equal in pyroxene grains from the Moon and Vesta. The figure also shows that V partitioning appears to be little affected by either Ca content or Fe# of the pyroxene, except perhaps slightly in the lunar and Vesta case. We believe the most controlling factor on V partitioning in pyroxene is the variable fO_2 conditions of the planets. At relatively high fO2 conditions, such as on Earth and Mars (~ IW+1 to IW+4), low V^{3+}/V^{4+} in basaltic melts results in low V* values because V⁴⁺ is slightly incompatible in pyroxene from Earth and more compatible for Mars. Conversely, low fO2 conditions on the Moon and Vesta lead to high V^{3+}/V^{4+} in melts, and subsequently high V* values because V^{3+} is quite compatible in pyroxene. Furthermore, the slight decrease in V* with crystallization in both lunar and Vesta pyroxenes is the behavior one would expect for a highly compatible element. Lastly, these systematics demonstrate that the charge-balance couple ${}^{M1}V^{3+}$ - ${}^{IV}AI$ is much more compatible in the pyroxene crystal structure than ${}^{M1}V^{4+}$ - $2{}^{IV}AI$ [6].

 fO_2 estimates for basalts from Vesta: V systematics show that eucrite pyroxene grains crystallized from melts with high V³⁺/V⁴⁺, and thus low fO_2 conditions, and that lunar pyroxenes experienced similar histories. Our VVO for glass [1, 2] shows that basaltic melts are dominated by V³⁺ at fO_2 conditions below IW+1, and that lunar basalts crystallized at IW-1 to IW-1.7. Based on these arguments we believe eucrites crystallized at similar fO_2 conditions. Our results are in agreement with recent estimates [7] of IW-1 for basalts from both the Moon and Vesta.

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OXYGEN FUGACITY VARIATIONS WITHIN AND AMONG METEORITE PARENT BODIES. Dante S. Lauretta, Lunar and Planetary Laboratory, University of Arizona, Tucson, AZ 85745. lauretta@lpl.arizona.edu

Introduction: Meteorites consist essentially of the silicate minerals olivine and pyroxene, iron-nickel alloys, sulfide minerals, and an enormous variety of accessory minerals. Most meteorites originate from the asteroid belt. The geologic diversity of asteroids and other rocky bodies of the solar system are displayed in the enormous variety of textures and mineralogies observed in meteorites.

Different classes of chondritic meteorites are discernable by their bulk chemistry, mainly the oxidation state and distribution of iron. Chondritic meteorite classes are subdivided by petrologic type. These designations reflect the extent to which these materials were altered by parent-body processes. Type-3 chondrites are the most primitive and have experienced minimal alteration. Silicate compositions in type-3 chondrites span a wide range of Fe-contents, reflecting a wide range of oxidation states for the formation of their varied components.

Type-1 and type-2 chondrites have experienced aqueous alteration while types 4-6 have experienced varying degrees of thermal metamorphism. Thermal metamorphism results in significant changes to meteorite textures and mineralogy. In particular, the compositions of silicate minerals become increasingly homogenous throughout the sample. Because of their varied oxidation states, silicate compositions in equilibrated chondrites vary among the different classes.

Oxygen Fugacity – An Introduction:

In many gaseous systems it is appropriate to assume that gases follow an ideal equation of state, known as the ideal gas law:

$$P \cdot V = n \cdot R \cdot T$$

P = pressure, V = volume, n = the number of moles, R is the gas constant, 82.06 cm³ atm mol⁻¹ K⁻¹, and T = temperature. However, in many systems, interactions among gas molecules result in deviations from ideality. Thus, it is often necessary to apply a correction to adjust for non-ideal behavior. A common way to correct for the effects of non-ideality is replace the pressure (P) with fugacity (f). The fugacity of a gas is related to the pressure through:

$$f_i = \gamma_i \cdot P_i$$

 γ_i is the fugacity coefficient and P_i is the partial pressure of component i in the gas. For an ideal gas, $\gamma_i = 1$.

Whenever dealing with the chemical potential of a component in a gas phase, or a component that may be in a gas phase, fugacity can be used to account for the variation in the chemical potential of interest. More precisely, since chemical potential is a quantitative measure of the reactivity of a component in a phase, fugacity is a measure of how much the chemical potential of the component in the gas deviates from the chemical potential of the pure substance in its standard state, due to changes in P and the mole fraction of the component. Therefore, f_{O2} is a function of the mole fraction of the component in the gas phase and of the total pressure of the gas phase. A high f_{O2} means a high chemical potential of oxygen, which indicates an "oxidized" system.

Oxygen Fugacity – Buffers:

Oxygen fugacity is a master variable used to describe geologic environments. Reducing conditions are "low f_{02} ", and oxidizing conditions are "high f_{02} ". However, thermodynamics is quantitative and, therefore, f_{02} must be well defined. In practice this is done by reference to well-known f_{02} buffers.

In the solar nebula, the most abundant O-bearing gaseous molecules were $H_2O(g)$, CO(g), and $CO_2(g)$, assuming that chemical equilibrium was achieved. The f_{O2} in such a system is controlled by the relative abundances of these molecules. For example, the f_{O2} in a nebular system can be calculated using the ratio of $CO_2(g)$ to CO(g) via:

 $2 CO(g) + O_2(g) = 2 CO_2(g)$

Using the equilibrium constant for this reaction (K_1) , the f_{O2} is expressed:

$$\mathbf{f}_{O_2} = \left(\frac{\mathbf{f}_{CO_2}}{\mathbf{f}_{CO}}\right)^2 \cdot \frac{1}{\mathbf{K}_1}$$

Since gaseous molecules dominated the inner region of the solar system during the formation of meteoritic components, the variation in oxidation states observed in unequilibrated chondrites suggests that either: 1) these components formed in separate regions of the solar nebula or 2) these components did not equilibrate with the nebular gases.

On asteroids, f_{O2} may have been controlled by solid mineral buffers. For example, when both iron metal and the iron oxide wustite (Fe_{0.947}O) are present as pure homogenous compounds, f_{O2} is buffered by:

 $1.894 \text{ Fe} + O_2(g) = 2 \text{ Fe}_{0.947}O$

In this case, f_{O2} is expressed:

$$f_{O_2} = \frac{1}{K_2}$$

Thus, the oxidation states of equilibrated chondrites are a reflection of the oxygen fugacity established on the parent asteroid. **Correlation of Oxidation State with Thermal Metamorphism in Ordinary Chondrites.** C. A. Marsh¹ and D. S. Lauretta¹, ¹University of Arizona, Lunar and Planetary Laboratory, Tucson, AZ 85721, USA (celinda@lpl.arizona.edu)

Introduction: All meteorites retain evidence of a heating event or events that occurred within the first few Ma of the appearance of the first solids in our solar system [1]. In chondrites the degree of thermal alteration or metamorphism experienced is measured through a classification system called petrologic type [2]. Heating of asteroids through the decay of ²⁶Al has been robustly studied and is generally favored as the heating mechanism for chondrite parent bodies [3]. Induction heating has been proposed as an alternate heating source [4]. While it has come under sharp criticism for requiring parameters that did not fit observations of T-Tuari winds [5], the induction heating mechanism has never been disproved [3].

Observations of Oxidation State: Conflicting reports on changes of oxidation state with thermal metamorphism have been made over the years e.g.[6, 7]. While direct measurements of oxygen fugacity with petrologic type have been made, those authors only inferred a reduction trend with metamorphic grade based on bulk abundances of Fe metal and Ni compositions in metal measured by others [6]. The ratio of Olivine (Ol) to low-Ca pyroxene (Opx), bulk Fe-rich metal abundances and Ni and Co abundances in metal were used to infer increasing oxidation with petrologic type [7, 8]. The presence of varying amounts of oxidizing vapor derived from accreted ices has been proposed to explain this trend [7]. However, this hypothesis has been criticized because of the lack of oxygen isotope variation between metamorphic grades, which would be expected if varying amount of ice were present [9].

New Measurements: We have developed a rapid calibrated mapping technique to make measurements of major element compositions in olivine and pyroxene. Maps covering a 1.28 by 1.28 mm region with 10 μ m diameter pixels have been collected using a Cameca SX50 electron microprobe. The map regions are selected such that they are not dominated by a single large chondrule, but rather contain a number of chondrules as well as matrix material. The pixels are sorted using Si wt% and then filtered for appropriate total wt%. The ratio of olivine to low-Ca pyroxene pixels from a suite of L chondrites is reported in Table 1.

Table 1:		
Meteorite	Class	Ol/Opx ratio
LEW 87284	L3.6	0.59
ALH 77197	L3.7	6.16
ALH 85045	L3.8	1.74
ALH 85033	L4	1.75
Saratov DL	L4	0.77
Saratov LL	L4	1.16

Our results cover a different range of petrologic type than has been previously been reported. We found one L3, ALH77197 to be strangely low in pyroxene abundance. Saratov DL and LL refer to a dark and light lithology visually observed on the same sample of Saratov. The percent mean deviation and mean composition of both olivine (PMD = 4%), mean Fe wt % = 16) and low-Ca pyroxene (PMD = 8%, mean Fe wt% = 11) in these two regions was within error. However, we found that the olivine to orthopyroxene ratio from these two regions, varies by more than 0.3. The total change in olivine to orthopyroxene ratio between L4s and L6s is less than 0.3 [7,8]. While our results are preliminary, they do not support a correlation between metamorphic grade and oxidation state.

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Building the Chain: Born as scientific disciplines within six years of each other at the end of the 18th century, meteoritics and asteroid astronomy are intimately linked. Links between asteroids and meteorites satisfy both our basic curiosity as to the origin of these rocks and allow both communities to address the range of materials and processes operating during Solar System formation. In particular, identifying the parent asteroids for meteorites would elucidate compositional or thermal gradients present in the solar nebula. An excellent recent overview of meteorite-asteroid links is provided by [1] and is heavily referenced here. I review the disparate datasets used by asteroid astronomers and meteoriticists, discuss the merits of several such links, and point to directions for future research.

The Tools of the Blacksmiths: The key obstacle to asteroid-meteorite links is the nature and precision of data used by meteorite and asteroid scientists. Meteoriticists group objects from a common parent body primarily on the basis of extremely precise analyses of bulk chemistry, often for trace elements; mineral compositions, which mirror bulk chemistry; oxygen isotopes, which fingerprint unique nebular reservoirs; and cosmic-ray exposure ages, which point to liberation during a common impact event. In contrast, asteroids astronomers primarily use reflectance spectra to infer, through laboratory analysis of samples, approximate mineral abundances and, in some cases, mineral compositions. Knowledge of meteorite delivery mechanisms can point to the most promising main belt asteroids and complementary data (e.g., radar, spacecraft data) exist for small numbers of asteroids. Meteorite and asteroid datasets rarely overlap and uncertainties often prevent confident matches.

The Weakest Link?: Four asteroid-meteorite links are examined in order of increasing degree of confidence.

M asteroids/Irons/E chondrites The relatively featureless, red-sloped M asteroids are similar to spectra for both irons and E chondrites and have lower albedo and lack the ~0.5 μ m feature observed in E asteroids [2]. High radar returns are consistent with highly-porous irons or non-porous E chondrites, although low densities may preclude an iron analog. This case illustrates the difficulty of establishing asteroid-meteorite links without spectral absorptions.

C asteroids/CM chondrites The link between C asteroids (e.g., 19 Fortuna) and CM chondrites is supported by the presence of a 0.7 μ m spectral feature, the presence of C asteroids near the 3:1 resonance, and relatively low CRE ages. In this case, limited data provides a compelling link.

Vesta/HED's The link between 4 Vesta and HED's is the only one between a specific asteroid and meteorite group to be widely accepted, largely on the basis of spectral similarity; existence of a large, intact asteroid; and linkage of

Vesta to meteorite-delivery resonances through small Vestoids likely derived from a polar impact basin on Vesta. The Vesta-HED link may not be solid. Ibitira [3] appears to and NWA 011 does differ from other eucrites and may sample different parent bodies. Additional space-weathered basaltic asteroids have been identified among the S-class [4], including 17 Thetis with an average semi-major axis close to the 3:1 resonance that delivers meteorites to Earth.

S(IV) asteroids/Ordinary Chondrites The long-debated link between S asteroids and ordinary chondrites came to the forefront with the NEAR mission to 433 Eros. Despite exhaustive analyses, uncertainties in calibration and inadequate knowledge of regolith formation made it impossible to confidently distinguish whether Eros was composed of a partially-melted primitive achondrite or a space-weathered ordinary chondrite. This debate continues [5,6], although a space-weathered ordinary chondrite seems favored, with no consensus as to chemical group (H, L, LL).

The desire to match specific asteroids to meteorites may be futile, particularly as the number of meteorite groups (with concomitant decrease in the differences between them) and characterized asteroids increase. Our best option remains links between types of meteorites and classes of asteroids, with the best matches for those meteorites and/or asteroids that are compositionally anomalous (e.g., angrites).

Stoking the Fire: Pointing to sample return missions as the ultimate solution would be misguided. Missions will never visit even a fraction of asteroid types and resolve questions about stratification in the asteroid belt. A unique contribution that missions can accomplish is the return of regolith, particularly a core sample including the optical regolith, to understand its unique formation and properties.

Ultimately, meteoriticists and asteroid scientists need to better focus on complementary data. Asteroid spectroscopists need better calibration curves for mineral compositions and proportions in multi-mineral mixtures, better characterization of samples used for spectral analyses, and additional data sets (e.g., radar). Meteoriticists need accurate silicate modes and bulk major element compositions in all meteorite types. Finally, both communities should form and foster active collaborations, funded by NASA in recognition of the importance of cross-disciplinary research, to address question of Solar System evolution.

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Introduction: Demonstration of massindependent O isotopic variations in solar system materials was a seminal discovery of meteoritics. These variations were thought to reflect incomplete mixing of O from different nucleosynthesis sources [1]. Since then, two non-nucleosynthetic causes have been suggested: (i) differential photodissociation of distinct isotopomers of CO, enriching nebular gas in chemically reactive heavy O [2], and (ii) gas-phase molecular reactions producing mass-independent O isotopic Nebular processes caused chemical exchange [3]. fractionations that are observed in chondrite bulk compositions [4]. If nebular processes also produced mass-independent O isotopic variations, then these may correlate with chondrite bulk chemistry.

Models: Three models invoked to explain O isotopic heterogeneity in solar system materials are summarized in the table. The photodissociation model has several variants with different locations where photodissociation occurs [2, 5]. The predictions given in the table are for the model favored by Clayton [2, 6], which assumes the Sun is enriched in ¹⁶O. This may [7], or may not [8], be the case. The molecular reactions model does not allow for clear predictions [3].

model	proponent	carrier	predictions
incomplete mixing	Clayton et al. [1]	high-T solids: ¹⁶ O-rich	no correlation with low T chemistry
photo- dissociation	Clayton [2, 6]	H ₂ O gas: ¹⁶ O-poor	possible correla- tion with high-T and low-T chemistry
molecular reactions	Thiemens [3]	several gas species	unclear

Chondrites: Negative correlations exist between CI-normalized refractory-lithophile-element/Si or Mg ratios and Δ^{17} O among chondrite groups (figure). Although correlation coefficients (R^2) are typically only $\sim 0.55-0.70$, the probabilities that the data could reflect an uncorrelated parent population are typically <0.5%. This is impressive considering averaged chondrite data were used, and that the bulk compositions and O isotopic data were not determined on identical suites of samples. These correlations are consistent with incomplete mixing and photodissociation models. Refractory-siderophile elements show a similar trend -Ir/Ni decreases with increasing Δ^{17} O. This could reflect mixing of differing amounts of ¹⁶O-enriched CAIlike components into bulk chondrites à la the incomplete mixing model or the photodissociation model.

There are also weak positive correlations of moderately-volatile-lithophile-element/Mg ratios. Mass balance shows this is not due to dilution by volatilepoor, ¹⁶O-enriched CAIs - i.e. simple mixing cannot explain the correlation. The trend could indicate evolution of reactive nebular gas to more ^{17,18}O-enriched compositions with falling temperature. The situation is complex for moderately-volatile-siderophile elements. For most chondrite groups, Ga/Ni increases with Δ^{17} O as is the case for Na/Mg. However, ordinary and R chondrites are distinctly depleted in Ga/Ni compared to that trend. Thus, nebular temperature and O isotopic composition are not linked in a simple way, and factors such as nebular location relative to sites of O isotopic fractionation may have been important.

The correlations include the highly reduced EH and EL chondrites, which are believed to have formed in a much more reduced nebular region of different composition [9]. EH and EL chondrites are devoid of FeO, eliminating simple oxidation of metal by heavy H_2O as the cause of their O isotopic composition. This may support the molecular reactions model, in which isotopic anomalies are transferred to gas species such as SiO [3] that are the building blocks of condensates.



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DETERMINING THE EFFECTS OF AQUEOUS ALTERATION ON THE DISTRIBUTION OF OXYGEN ISOTOPES IN CARBONACEOUS CHONDRITES. A. A. Morris, L. Baker, I.A. Franchi and I.P. Wright. Planetary and Space Science Research Institute, The Open University, Milton Keynes, MK7 6AA (a.a.morris@open.ac.uk)

Introduction: Carbonaceous chondrites play a key role in determining the history of the early Solar System; a knowledge of the oxygen isotope variation within these materials will not only help in our understanding of the origin and evolution of those meteorites, but also the early Solar System reservoirs from which they formed [1].

However, several problems present themselves when trying to interpret early Solar System history. One is identifying the isotopic signature of oxygen from specific component compounds in a complex mixture of materials that existed in the solar nebula, and deconvoluting this from signatures developed during parent body processing (e.g. aqueous alteration, thermal metamorphism). Only then is it possible to develop an understanding of the nature and conditions of these secondary processes.

Background: Of all the meteorite groups the carbonaceous chondrites (particularly the CI, CM and CR meteorites) have the most diverse range of high and low temperature mineral phases, and display the widest range of oxygen-isotopic compositions [1,2]. Volumetrically, much of these meteorites consists of a very fine grained matrix material composed largely of low temperature alteration minerals but intimately mixed with a fine grained fraction of the anhydrous, isotopically distinct phases [3]. A full understanding of the oxygen-isotopic systematics between these different phases is required in order to constrain the processes that led to their formation [3]. However most previous oxygen isotope studies have concentrated on the silicate portions which in the case of the matrix means studying complex mixtures [3,4]. Aqueous reactions can not only promote chemical redistribution and changes in petrological relationships but also generate large isotopic fractionation of oxygen isotopes [5].

Models to account for the variations in oxygenisotopic compositions in carbonaceous chondrites e.g. [6,7] generally involve mixing of a solid anhydrous silicate component, with an isotopic composition enriched in ¹⁶O, with liquid water depleted in ¹⁶O along with mass-dependent isotopic fraction between various phases at low temperature [3]. Isotopic evolution of the fluids involved in these reactions would be expected to lead to significant isotopic heterogeneity within the components e.g. [7]. Recent studies have shown that structural water (OH) can be extracted from phyllosilicate components in the CM meteorites by incremental heating, and used for oxygen isotope measurements. This also provides the ability to resolve oxygen from a number of different components within the complex mixture of minerals in the matrix of these meteorites[3,4]. The (OH) from the CM phyllosilicates is found to have a similar $\Delta^{17}O$ to co-existing carbonates, analysed by [8] indicating that they formed from the same fluid reservoir, and may infact have formed in isotopic equilibrium.

We are employing a number of approaches to better determine the distribution of oxygen isotopic components within these complex meteorites. Stepped heating extraction to liberate water and structural (OH)⁻ permits isotopic measurements of resolved components [4], the identification of which is being established by a detailed study of the thermal release temperature of water (OH)⁻ components from meteorites and a range of terrestrial analogues. Artifical weathering experiments using isotopically labeled water are being used to trace the location of different oxygen reservoirs as alteration proceeds.

Such data may then be used to constrain temperature of equilibrium between the phyllosilicates and carbonates minerals and water-rock ratios involved; important constraints for evolution models of carbonaceous chondrites [6,7].

Summary: The initial stepped heating experiments for carbonaceous chondrites revealed considerable variation in δ^{18} O [3]. Much of our new work is aimed at determining the extent of isotopic fractionation associated with the formation of the common phyllosilicates found in meteorites, and identifying the specific minerals liberating (OH)⁻ at each temperature.

This will be used ultimately to better constrain the isotopic composition of the fluids involved in the alteration process.

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Young E. D. et al. (1999) Science, 286. 452-455.
Benedix. et al. (2000) LPSC XXXI Abs #1840 **SPACE WEATHERING ON ASTEROIDS** S. K. Noble¹, ¹U.S. House of Representatives, House Committee on Science, 394 Ford Building Washington D.C. noble@porter.geo.brown.edu.

Introduction: "Space weathering" is a blanket term that is used to describe the processes and products by which physical and optical changes are incurred by a surface exposed to the harsh environment of space. Our understanding of space weathering comes almost exclusively from studies of lunar soils. The array of space weathering processes in the lunar regolith are illustrated in Fig. 1 [1, as modified from 2].



Figure 1. The major processes and products associated with space weathering.

There are two main products produced by space weathering: rims and agglutinates. Detailed microanalyses [3, 4] have shown very thin (60-200 nm) patinas, or rims, developed on individual lunar soil grains from mature soils. These rims are created by both subtractive (radiation damage) and additive (vapor deposition and solar wind sputtering) processes. The rims often contain abundant single domain metallic iron particles, referred to as nanophase iron (npFe⁰) [3] or SMFe [5]. The other major product of space weathering is agglutinates. These glass-welded aggregates also contain npFe⁰.

The Importance of Space Weathering: Since remote sensing methods generally do not sample the pristine rocks of the body, but rather the exposed regolith, it is imperative to understand the processes by which rocks become soils, and specifically, the effects of soil formation processes on the properties of a soil in order to get accurate results from remote datasets. Understanding space weathering is important because the products produced by space weathering have distinct and predictable effects on the optical properties of soils [5,6]. The optical effects on lunar soils, the so-called "space weathering continuum", is largely the result of the accumulation of npFe⁰. These effects have traditionally been described as threefold: weathering causes the reflectance spectra in the vis-nearIR to be both darker and redder, and also results in an attenuation of the characteristic absorption bands. Recent work has shown that the process is more complex than simply "reddening" and "darkening", rather, as a soil acquires npFe⁰, its continuum changes in a regular and predictable way [7].

Space Weathering on Asteroids: In general, the spectra of asteroids do not match the spectra of our collection of meteorites. Particularly, the spectra of S-type asteroids, the most abundant type, do not correspond well to the spectra of the most abundant type of meteorites, ordinary chondrites (OCs). The asteroid spectra tend to be redder than the meteorites with a steep curvature in the visible wavelengths. It has been suggested by many [e.g. 6,8,9] that this spectral mismatch is the result of space weathering.

In the asteroid belt, the environment is significantly different than lunar conditions. Collisions are on average slower, so micrometeorite bombardment will cause less melting and considerably less vaporization than on the Moon. Also, as the distance from the sun increases, the solar wind particle flux decreases, thus less sputtering and implantation occurs. Finally, the impact rate is greater, comminuting fresh material at a faster rate and diluting any weathering products. These arguments suggest that soils on asteroids will accumulate npFe⁰ at a significantly lower rate than those on the Moon. Studies of regolith breccia meteorites support this conclusion: weathering products such as npFe⁰bearing rims [10] and agglutinates [11] are found to be extremely rare (but not absent) in these lithified asteroidal regoliths.

However, even very small degrees of space weathering can have quite dramatic consequences for the optical properties of soils [10]. The shape of the space weathering continuum is strongly dependent on the amount of npFe⁰ present. Very small amounts of npFe⁰ result in a strong curvature in the visible, while the near-IR remains nearly unaffected.

Conclusions: The optical effects of very small degrees of space weathering differ substantially from the more general reddening/darkening effects of larger amounts of weathering. These trends can account for most differences observed between ordinary chondrite and S-type asteroid spectra.

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OH AND H₂O ON ASTEROIDS: AN ASTRONOMICAL PERSPECTIVE

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The vast majority of meteorite parent bodies are thought to reside in the asteroid belt. In addition to the known samples in the collections, there is a large amount of unsampled material among the asteroids. Because of the current impractibility of sampling a large number of asteroids via space mission, remote sensing techniques have been developed to determine asteroidal compositions from ground-based (and occasionally space-based) observations.

In the 35 years since the first modern asteroid spectra were published, a large amount of data have been collected, which provide us with direct and/or indirect evidence of the presence of phyllosilicates, oxidized and reduced forms of iron, pyroxene and olivine, troilite, and other minerals on asteroidal surfaces.

I will address what these observations tell us about the oxygen distribution and low-temperature processes in the asteroid belt, focusing on what we've learned about hydroxyl/water-bearing minerals, but also touching on other relevant data as appropriate.

RELICT OLIVINE, CHONDRULE RECYCLING, AND EVOLUTION OF OXYGEN RESERVOIRS. A. Ruzicka¹, H. Hiyagon² and C. Floss³. ¹Portland State University, Dept. of Geology, Portland, OR 97207, USA., ²Dept. of Earth and Planetary Physics, Graduate School of Science, University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, ³Washington University, Laboratory for Space Science, Campus Box 1105, St. Louis MO 63130, USA.

Introduction: Using SIMS techniques we have analyzed oxygen isotopes and trace elements in relict olivine grains [1], together with co-existing overgrowths and normal olivine, within chondrules of the Chainpur (LL3.4) and Sahara 97210 ("Sahara", LL3.2) chondrites. As relict olivine grains predate the formation of host chondrules, they provide an opportunity to study how chondrule components evolved.

Results: Fig. (a-c) shows standard 3-isotope oxygen plots for selected data we have obtained. Typical ordinary chondrite materials (OCM) cluster around the average compositions of equilibrated H-, L- and LLchondrites and are distinct from the carbonaceous chondrite anhydrous materials (CCAM) line [2,3].

Magnesian olivine relicts enriched in ^{16}O . Fig. (a) shows that some magnesian relict olivine grains, including refractory forsterites (RFs) and other anomalous Mg-rich grains, are distinctly enriched in a ^{16}O component compared to more ferrous olivine in the chondrules. These data are consistent with the idea that nebular reservoirs evolved over time to heavier oxygen compositions [2-5].

Magnesian olivine relicts not enriched in ^{16}O . The O-isotopic compositions of some Mg-olivine grains are similar to co-existing ferrous grains and lie close to the terrestrial fractionation (TF) line (Fig. b). The relict RFs in Sah-9 and Ch-3 have similar major- and traceelement compositions, yet very different O-isotopic compositions (Fig. a, b). This suggests that chemical and isotopic compositions of chondritic olivine may be strongly decoupled, in contrast to the models of others [4,5].

Dusty olivine relict grains. Fig. (c) indicates that dusty and normal olivine grains have overlapping Oisotopic compositions with no evidence of a difference between them in Δ^{17} O. There is a hint of mass fractionation between dusty and normal olivine in Ch-7 but not in Ch-9. The similar Δ^{17} O values between dusty relicts and normal olivine are consistent with a reduction reaction to form dusty olivine from more ferrous olivine during chondrule recycling [6].

Chondrule recycling. Taken as whole, our data can be understood if chondrule precursors were recycled during chondrule formation under different conditions. Some Mg-olivine, dusty olivine, and Fe-olivine formed when oxygen reservoirs were isotopically heavy and approaching the composition in which OCM formed; other, possibly earlier, Mg-olivine formed when the reservoir composition was isotopically light and similar to that in which carbonaceous chondrites formed.

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Eu Valence Oxybarameter in Pyroxenes. Effects of Pyroxene Composition-Crystallization Histories-Crystallization Kinetics and a Comparison Between Lunar Basalts and Eucrites. Shearer, C. K., Papike, J. J., and Karner, J. M. Institute of Meteoritics, Department of Earth and Planetary Sciences, University of New Mexico, Albuquerque, New Mexico 87131-1126 cshearer@unm.edu.

Lunar basalts and eucrites are Introduction: thought to crystallize at fO_2 conditions below IW. The FeO contents of these basalts have been interpreted as indicating that both basalts crystallized at IW-1 [1]. To better understand potential subtle differences among lunar basalts and between lunar basalts and eucrites, we are investigating the behavior of multivalent cations (Eu, V) in pyroxenes. The behavior of Eu in martian basalts has been demonstrated to be an effective measure of f_{02} [2]. Here, we compare the Eu/Eu* in pyroxenes from the more reducing environments of the Moon and the HED parent body, evaluate the dependence of Eu/Eu* on pyroxene compositioncrystallization sequence-crystallization kinetics and contrast the relationship between Eu/Eu* and V.

Pyroxenes in Lunar Basalts and Eucrites: To compare Eu/Eu* in lunar basalts and eucrites and to better understand the variables that may affect this indicator of f_{02} in basalts, we selected four nearly isochemical lunar pigeonite basalts (15058,12021,12052,15499) and Pasamonte, an unequilibrated eucrite. The lunar basalts have experienced different cooling [3] and crystallization [4] histories. Basalt 15499 cooled at a rate of 5 to 20°C/hour, whereas 15058 cooled at a rate of $< 1^{\circ}C$ /hour [3]. The two other lunar basalts and Pasamonte have intermediate cooling rates. Variations in pyroxene chemistry are partially illustrated in Figure 1. The incoming of plagioclase is reflected in the pyroxene by Ca, Al, and Ti/Al. The Al and Ti/Al in the pyroxene in Pasamonte reflect co-crystallization of plagioclase, in 15499 they reflect near absence of plagioclase crystallization, and in the other lunar basalts plagioclase co-crystallization occurs after variable amounts of pyroxene crystallization.

 f_{02} and the Eu/Eu* in pyroxene: Of the lunar basalts analyzed, 15058 has the slowest cooling rate, exhibits the widest range of major element zoning, and has substantial co-crystallization of pyroxene and plagioclase (Figure 1). Although the lunar basaltic melts are enriched in Eu²⁺ relative to Eu³⁺, the earliest pigeonites have a calculated Eu²⁺/Eu³⁺ of approximately 0.03. These early pyroxenes have a Eu/Eu* of approximately 0.4 -0.5. This value decreases with increasing Ca and eventually reaches 0.2 -0.3 in high-Ca pyroxene which co-crystallizes with plagioclase. This value stays constant throughout plagioclase crystallization. It is unclear at this time whether the changing Eu/Eu* is a function of Ca in the M2 site or plagioclase reaching the liquidus. Early pigeonite in Pasamonte has a calculated Eu^{2+}/Eu^{3+} similar to that of the early pigeonite in 15058. The Eu/Eu* of the pigeonite overlaps with that of the early pigeonite in 15058 and does not radically change with increasing Fe and Ca. This overlap in Eu/Eu* appears unusual due to differences in the timing of plagioclase crystallization and suggests slight differences in f_{02} . This needs to be explored further. Plagioclase in lunar basalts and eucrites appear to have similar Eu/Eu* [5].

 f_{02} , V, and V/Sc in pyroxene: In addition to Eu, V valence changes over a range of f_{02} and affects V partitioning behavior[6]. A companion abstract illustrates the usefulness of V in pyroxenes as an indicator of fO₂ [7]. In the lunar pyroxenes, V increases with Ca and then substantially decreases with Fe. V partitions differently between growth surfaces normal to (110) and (010). V/Sc consistently decreases from early to late pyroxene. V and V/Sc in the early pigeonite from Pasamonte are lower than the early pyroxene from the Moon. In the pyroxenes from Pasamonte V and V/Sc decrease slightly with increasing Ca and Fe.





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A CHEMICAL MODEL OF MICROMETEORITE IMPACT INTO OLIVINE. A. A. Sheffer and H. J. Melosh, Lunar and Planetary Laboratory, University of Arizona, Tucson, AZ 85721, abigailw@lpl.arizona.edu, jmelosh@lpl.arizona.edu.

Introduction: Laboratory simulations of space weathering using laser irradiation have been successful in reproducing space weathering characteristics such as the reduction of olivine to form nanophase iron particles [1,2]. However, the chemistry of the reduction of Fe^{2+} in olivine to Fe metal has not been fully explored. We present a thermodynamic model of olivine undergoing post-impact cooling and decompression.

Shock Melting: The cooling path of rocks melted by hypervelocity impact is much different than for rocks melted at a constant pressure [3]. A strong shock causes both the pressure and temperature to jump to very high values. Since the shock compression is irreversible, the rock's entropy also jumps. Decompression is isentropic, thus cooling follows a specific P-T path.

Modeling: The equilibrium module in the HSC Chemistry package [4] was used to model the Gibbs energy minimization. Equilibrium compositions were computed for the pressures 0.001, 0.01, 0.1, 1, 10, 100, 1000, and 10000 bars over the temperature range 1500-6000 K. Entropy calculations were performed in Excel. We used the composition of Fa_{10} similar to the San Carlos olivine used in [1,2] as a starting composition. Only the elements Si, Mg, Fe, and O were included in the model.

Results: We modeled the isentropic cooling path for S= 5000 J/K-kg. This is an intermediate value in the range (S=3000 to 6000 J/Kg-K) required to vaporize forsterite but allow formation of a liquid upon decompression and cooling.

The ratio of moles of O to moles of Si, Mg, and Fe is an indicator of oxygen enrichment. The higher the number, the more oxygen is available for bonding with the other elements. The starting material value is 1.33.



Except for at the lowest temperature and pressure, the vapor phase at this entropy contains a higher ratio of oxygen to other elements than the liquid phase or the starting material. Therefore, any loss of vapor would leave the liquid reduced compared to the starting material.

The dominant equilibrium species along the correlated P-T path are MgO and MgSiO₃. At the lowest temperature and pressure, $Mg_{(g)}$, $O_{(g)}$, and $SiO_{(g)}$ become the most abundant species. The Fe-bearing species are plotted below. Fe metal is present in the liquid phase for the entire cooling path, but $Fe_{(g)}$ is also present for the majority of the cooling path.



Discussion: Since both Fe metal and $Fe_{(g)}$ are present along the cooling path, droplets could form both inside the quenched glass and as a product of vapor deposition. These results support previous work that reducing agents are not necessary [1,2,5], and that micrometeorite impact can produce iron metal.

Future work will include modeling the isentropic cooling path of a bulk chondritic composition.

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EXPLORING THE ORIGIN OF PLANETARY WATER USING AN ATOMISTIC APPROACH. M. Stimpfl¹, M. J. Drake¹, D. S. Lauretta¹, P. Demyer². ¹Lunar and Planetary Laboratory, ²Material Science and Engeneering; University of Arizona, Tucson, Arizona 85721-0092, U.S.A stimpfl@lpl.arizona.edu

The origin of Earth's water and, by extension, water in other inner solar system bodies has been long debated. Two main scenarios have been proposed to account for the delivery of water to the inner planets: either the water originated outside of the inner solar system and was later delivered to the terrestrial planets or the source of water was local and was concomitantly accreted to the accreting bodies. Isotopical and geochemical fingerprints seem to indicate that comets and asteroids alone could not have been the principal source of water for the Earth. Furthermore, these exogenous sources of water would have delivered the water, after the planet had reached more than 85% of its size, after core formation [1, 2]. However, such late delivery of water seems to be in contrast with geochemical requirements [3]. If the Earth acquired its water locally, this source of water could be represented by hydrous material that formed at 1 AU. Under this scenario, hydrous material was incorporated directly into the accreting Earth early on, thus influencing the geochemical behavior of elements partitioning between the mantle and the core, the oxidation state of the mantle, and also keeping the surface of the planet at a T high enough to sustain a magma ocean. However, most models of the solar nebula do not allow stable hydrous minerals at 1 AU [4].

We explore the role of adsorption onto grains prior to planetary accretion as a possible new mechanism that could bring water to the Earth. Monte Carlo simulation of adsorption at nebular T, P and $f_{\rm H2O}$ onto a flat surface showed that this mechanism can store on dust grains in the pre-accretion disk up to 3 times the Earth's oceans [5]. This model, however, did not take into account the specific surface interactions between water gas and the crystalline surface nor did it investigate rigorously the role of porosity. To fill this gap, we are performing molecular dynamics simulation of the system water and olivine using the code GULP [6]. The bulk olivine will be modelled using periodic boundary conditions (PBC) and Buckingham potentials for the short-range interactions with a cut off distance of 10 Angstroms for both short and long range interactions. The "virtual crystal" was then cleaved by removing the PBC in the positive z direction and thus creating a free surface. After the top layer relaxed we inserted water molecules and studied their trajectories. This simulation will allow construction of surface site adsorption probabilities and site energies at nebular T.

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Introduction: On 9th May 2003, the Japanese spacecraft MUSES-C was successfully launched from Uchinoura. The spacecraft was directly inserted into an interplanetary trajectory and renamed as "Hayabusa", or "Falcon", to be the first sample return spacecraft to visit a near-Earth asteroid (NEA) [1]. The target is NEA (25143)Itokawa (formerly known as 1998SF36). Its size is 490 (\pm 100) x 250 (\pm 55) x 180 (\pm 50) m with a ~12-hour rotation period [2]. It has a red-sloped S(IV)-type spectrum with strong 1- and 2-micron absorption bands, analogous to ordinary LL chondrites exhibiting possible space weathering effect [3]. The asteroid could be olivine rich compared to typical S asteroids. Assuming a bulk density of ordinary chondrites, the surface gravity of Itokawa is on the order of 10 micro-G, with an escape velocity = ~20 cm/s.

Mission Sequences: At present, the spacecraft operates with three ion propulsion engine systems. In June 2005, the spacecraft will be inserted into an orbit which is nearly identical to the orbit of the target asteroid itself. As it draws nearer the asteroid, the spacecraft will conduct global mapping with an multi-color optical camera, near-infrared spectrometer, X-ray fluorescence spectrometer, and LIDAR for up to three months

Sample Return Strategy: After completing global mapping, the first descent for touch-and-go sampling will be conducted. Before touching the surface, however, one of three target markers will be dropped to track its passage by autonomous navigation. Also a hopping rover called MINERVA will be deployed. Since the actual surface conditions of Itokawa are unknown, HAYABUSA employs a sampling mechanism that should work for a diverse heterogeneity of target surfaces, from hard metal-silicate surfaces to fluffy regoliths [4]. Within 0.3 seconds after the tip of the sampler horn touches on the asteroid surface, a Ta projectile of 5-g mass is shot at 300 m/sec by a small projector onto the asteroidal surface. Impact of the projectile produces surface ejecta, which is concentrated through a conical capture horn toward the sample catcher. The catcher is transferred into the reentry capsule, which is hermetically sealed. During testing, the mass of samples recovered ranged from several hundred mg to several g per shot. The majority of recovered samples were fine-grained (sub-mm size) particles, rather than large chips. The sampling will occur at as many as three locations in November 2005.

Preliminary Sample Analysis: In July of 2007 the samples will be returned to Earth within the hermetically-sealed capsule, and flown to a new dedicated curation/preliminary examination lab in Sagamihara for \sim 1 year of preliminary investigation in Japan. During this time investigations of the

vestigations of the samples will be made by largely Japanese teams, though with some foreign participation. These teams are being chosen through competitions. A maximum of 15 mass% could be consumed to characterize representative samples during this 1-year long preliminary examination phase. Following the initial analysis period an international announcement of opportunity for detailed analyses of another 15 mass% of the samples will be released. Another 10 mass% will be transferred to NASA's Johnson Space Center.

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Introduction: Attempts to match the E asteroids with enstatite-rich meteorites universally conclude that the aubrites or enstatite chondrites are natural candidates, and accordingly conclude that E asteroids as a class are very water-poor [1]. Accordingly, the highly reduced nature of typical enstatite-rich meteorites suggests that aqueous alteration was an improbable process on any E asteroid. However, there are spectroscopic observations of several E-class asteroids that suggest the presence there of hydrated phases [2]. Examination of the Kaidun meteorite reveals the true situation.

Kaidun: The unique Kaidun meteorite completely consists of a disparate assemblage of extraterrestrial materials, ranging from carbonaceous chondrites, to ordinary chondrites, to basaltic achondrites, to enstatite chondrites [3]. All of these materials exhibit the complete range of alteration state, from fully anhydrous lithologies through to completely altered on a very fine scale. There are even clasts which are frozen in a state of halfaltered and half-unaltered. This observation requires aqueous alteration to have occurred at a different location than the place of final assembly of Kaidun. Indeed, much if not most of the materials within Kaidun must have formed on many different asteroids, and possibly other bodies as well.

In most regards the EH lithologies in Kaidun are like the typical EH meteorites [1]: Enstatite, plagioclase, silica, Fe,Ni, schreibersite, troilite, niningerite and unusual Fe,Crsulfides are present, carbon and perryite are present but less abundant, oldhamite. sphalerite, djerfisherite, schöllhornite, daubreelite, roedderite and Ca,Fe-phosphate are The critical feature is that hydrated rare. phases are abundant in practically all EH lithologies in Kaidun, in contrast to all other examples of EH chondrites which are entirely anhydrous.

There is evidence that E, C, and D asteroids, at the very least, provided the various materials now in Kaidun [3]. The mechanism for transport of these diverse materials to a single site on one parent asteroid must have involved numerous impacts. A record of some of these impact events remains in Kaidun in the form of melt clasts and shock melt veins, some even in carbonaceous chondrite lithologies. The Kaidun lithology clasts are micrometeorite-sized, and dynamical studies reveal that sampling of the solar system is much more representative for such small objects than for much larger meteorites [4]. Some EH chondrite lithologies in Kaidun show evidence of incomplete, late-stage aqueous alteration otherwise unknown from these classes of meteorites. This observation buttresses the spectroscopic data indicating the presence of water of hydration on some E-asteroids [1].

Water On the E Asteroids: Thus water was widespread throughout the early solar system, and not confined to regions beyond the putative snow line. Our perception that the Easteroids are completely reduced and anhydrous are driven by the biased sampling we have from meteorites. Even the most reduced objects in the solar system could not escape periods of aqueous alteration, due to influx of hydrated bodies from heliocentric distances beyond the point where ice was, technically, stable.

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COMPETITIVE OXIDATION AND HYDRATION DURING AQUEOUS ALTERATION OF ASTEROIDS. M. Yu. Zolotov¹, M. V. Mironenko³, and E. L. Shock^{1,2}, ¹Department of Geological Sciences, ²Department of Chemistry and Biochemistry, Arizona State University, Tempe, Arizona 85287, ³Vernadsky Institute of Geochemistry and Analytical Chemistry, Russian Academy of Sciences, Kosygin Str. 19, Moscow 119991, Russia. E-mail: zolotov@asu.edu.

Introduction: Studies of chondrites show that incorporation of H₂O ice during formation of asteroids followed by radioactive heating caused partial oxidation and hydration of primary reduced and anhydrous rocks [1-3]. Oxidation of kamacite, phosphides, troilite and organic polymers occurred through consumption of water's oxygen and release of H₂. Hydration caused formation of serpentine, saponite, chlorite, talc and hydrated salts. Since H₂O was the major reactant in oxidation and hydration, these processes could have been competitive. Redox reactions in asteroids should have been closely connected to hydration (dehydration) during aqueous alteration and thermal metamorphism. For example, dehydration and reduction release H₂O that can be consumed in oxidation and hydration, respectively. We model asteroidal processes in order to quantify the fate of H₂O and water's oxygen in major redox and hydration/dehydration reactions.

Model: Equilibrium compositions in the gas-solid-liquid type closed system O-H-Mg-Ca-Na-K-Fe-Ni-Co-Cr-Mn-Si-Al-C-Cl-S-P were calculated with our codes [4] in ranges of temperature (T, 0-350°C), pressure (P, 0.006-300 bar), water to rock mass ratio (WRR, 10⁻⁵-10³), porosity and alteration progress, which designates a fraction of rock reacted. Waterfree compositions of several H3, LL3, CV3, CM2 and CI chondrites were used to exemplify types of asteroidal rocks. A relative degree of oxidation vs. hydration was quantified as (2H)-(2OH)⁻¹, where 2H represents molar amounts of H in gas and solution and 2OH stands for the molar quantity of OH and H₂O in minerals.

Results: Water is consumed in different proportions in oxidation and hydration processes. Formation of magnetite usually marks a prevalence of oxidation, except extremely H₂O-deficient cases. Lower T (< ~50-130°C), which also correspond to lower stability of magnetite, favor hydration. At higher T, the degrees of oxidation and hydration do not change much and are often controlled by the magnetite-serpentine assemblage.

Water to rock ratio appears to be an influential parameter that affects degrees of oxidation and hydration. *WRR* may reflect bulk water content and/or represent a stage of alteration (metamorphism) of a partially reacted rock. In the presence of solution (*WRR* > 0.1-0.2), hydration usually dominates except low-*P* cases (< ~2-10 bar at 100°C). At very low *WRR* (< 10⁻²-10⁻³), that could be typical for parent bodies of ordinary chondrites, oxidation prevails. At intermediate *WRR* (10⁻²-0.2) without solution, predominant pathways of water consumption are sensitive to *WRR* and also depend on *P*. Formation of saponite and other hydrous silicates marks a hydration maximum at lower *WRR*, and formation of



Figure 1. Relative degree of oxidation vs. hydration as a function of alteration progress of the Semarkona LL3.0 ordinary chondrite at bulk WRR of 10^{-3} and original porosity of 0.3 at $100^{\circ}C$.

magnetite signifies an oxidation peak at slightly higher WRR. At $T < \sim 130^{\circ}$ C, higher P (> 2-10 bar) can suppress formation of magnetite, which favors hydration. At elevated P, degrees of oxidation and hydration do not change much.

As alteration progresses, three peaks of oxidation and two hydration maxima can be observed, especially in H₂Odeficient asteroids (Fig. 1). Early stages of aqueous alteration are characterized by interaction of solution with a very small fraction of rock and cause low-P oxidation of kamacite, phosphides and troilite. Formation of abundant OH-bearing silicates at later stages designates a hydration maximum. Then, formation of magnetite indicates a second oxidation peak. Shortly after consumption of aqueous solution, H2-rich conditions create potential for reduction of magnetite to ferrous silicates (olivine), while hydrous silicates (saponite) remain stable. At this stage, alteration can be inhibited. If T and/or time permit reactions at the metamorphic stage, both reduction and dehydration occur. Complete dehydration of silicates and preservation of some ferrous silicates designates net prevalence of oxidation at that stage. Note that in H₂Orich CM/CI type bodies, alteration did not reach an advanced metamorphic stage. Results also show that higher porosity favors oxidation due to lower P. In addition, H_2 escape in a porous medium must have driven further oxidation.

In summary, low P and high T favor oxidation, and high P and low T support hydration. As the alteration progresses, the fate of water's O in redox and hydration/dehydration reactions is unsteadily affected by changing temperature, pressure, porosity, and an amount of reacted rock.

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