Concluding Progress Report

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Title: Correlated petrographic, electron microprobe, and ion microprobe studies of selected primitive and processed phase assemblages in meteorites.

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Concluding Progress Statement

During the past three years we have received support to continue our research in elucidating the formation and alteration histories of selected meteoritic materials by a combination of petrographic, trace element and isotopic analyses employing optical and scanning electron microscopes and electron and ion microprobes. The awarded research funds enabled the P.I. to attend the annual LPSC, the co-I (Armstrong) to devote approximately 15% of his time to the research proposed in the grant, and partial support for a visiting summer post-doctoral fellow (Stephan Weinbruch, a former student of Herbert Palme) to conduct electron microprobe analyses of meteoritic samples in our laboratory. The research funds (along with support from the NASA Education Initiative awarded to P.I. G. Wasserburg) enabled co-I Armstrong to continue a mentoring program with inner-city minority youth.

The support enabled us to achieve significant results in the five projects that we proposed (in addition to the Education Initiative), namely: (1) studies of the accretional and post-accretional alteration and thermal histories in CV meteorites, (2) characterization of periclase-bearing Fremdlinge in CV meteorites, (3) characterization of Ni-Pt-Ge-Te-rich Fremdlinge in CV meteorites in an attempt to determine the constraints they place on the petrogenetic and thermal histories of their host CAI's, (4) correlated electron and ion microprobe studies of silicate and phosphate inclusions in the Colomera meteorite in an attempt to determine the petrogenesis of the IIE iron meteorites, and (5) development of improved instrumental and correction procedures for improved accuracy of analysis of meteoritic materials with the electron microprobe. This grant supported, in part or whole, 18 publications so far by our research team, with at least three more papers anticipated. The list of these publications follows this report. The details of the research results are briefly summarized below.

Specific Results

1. Post-accretional alteration and thermal histories in CV meteorites.

Although carbonaceous chondrites are generally considered to be among the most primitive materials surviving from the formation of the solar system, significant questions remain regarding the extent to which they suffered alteration during accretion and on their parent body. Determination of the degree of alteration occurring in parent bodies is critical for answering a number of important questions involving the early history of the solar nebula, e.g.: How early did accretion into parent bodies occur and how large did these bodies get? To what extent did "regolith farming" in the surface of early parent planetesimals play a role in altering the primitive materials? How widespread was $^{26}$Al in the early solar nebula; was it an important heat source for the parent planetesimals? Were the parent bodies of CV meteorites originally depleted in volatiles or were these driven off during parent body metamorphism?

A. Vigarano. To search for evidence of post-accretional alteration of CAI's in CV meteorites, we studied the Vigarano meteorite. CAI's in Vigarano are distinctive in typically not exhibiting the Na-Fe-alteration, found in meteorites like Allende, that is
thought to be pre-accretional in origin but that could mask matrix-CAI interaction. Vigaranore does not suffer from any terrestrial alteration affecting CV3's like Leoville. Our examination of Vigaranore (Armstrong, 1989) showed extensive signs of brecciation of CAI's to an extent not reported for other CV3 meteorites.

We performed extensive analyses of contacts between brecciated fragments of CAI minerals with matrix and chondrule phases that showed significant evidence of diffusion from post-accretional metamorphic events. Petrographically, little evidence of interaction is found between fragmented CAI's and their surrounding phases. Grain contacts are sharp and there is no evidence of resorption or presence of phases at the contacts not found elsewhere in the meteorite. X-ray analysis, however, showed definite evidence of exchange of Fe, Mn and Cr from the matrix phases with Ca, Mg and Al in CAI phases. For example, melilitie in the interior of CAI's contains less than 0.15% FeO, but in contact with the matrix it contains between 0.25 and 1.5% FeO appearing to substitute for Ca. The manner of zonation appears to be dominated by vein and grain boundary diffusion; FeO drops to background levels within 10 to 20 μm from areas of maximum concentration. Similarly, anorthite and fassaite in the interior of CAI's typically contain <0.1% FeO; within 20 μm of contact with the matrix, their FeO increases to 0.3 to 0.8% apparently substituting for Ca. Spinel in the interior of CAI's typically contains between 0.2 to 0.3% FeO; spinels in contact with the matrix contain 0.6 to 2.5% FeO. The Fe-content of individual spinels is homogeneous; the Fe-content increases with decreasing distance of the spinel from the CAI/matrix contact except in rare cases where veins or cracks are found directly leading from the matrix to the spinel grain. This suggests that bulk diffusion may be the dominant exchange mechanism for the spinels. The regular and widespread nature of element exchange between matrix and CAI fragments in Vigaranore suggests that appropriate diffusion experiments could be used to constrain the time-temperature history of the post-accretional phase of the meteorite parent body. Original results of our study were reported in Armstrong (1989); a final manuscript is in preparation.

B. Allende. In order to further study the thermal history and post-accretional alteration of CV parent bodies, we undertook (with H. Palme and visiting post-doc S. Weinbruch) an electron microprobe investigation of the chemical composition of olivine and coexisting spinel in type-II chondrules as well as isolated Fe-rich olivine grains from the Allende meteorite. The Fe/Mg exchange reaction between olivine and spinel yields upper limits for peak metamorphic temperatures on the Allende parent body of approximately 800° K. This represents the closure temperature for Fe/Mg interdiffusion in olivine and spinel. Steep Fe/Mg concentration gradients in isolated olivine crystals in various textural settings in Allende provide an independent method for estimating peak metamorphic temperatures. Modelling of Fe/Mg interdiffusion in olivine leads to an upper limit of peak metamorphic temperatures between 600° and 750° K (the former more likely, based on our analysis of the available diffusion data), assuming a duration of the thermal event of 10^6 years. In some cases, forsterite grains with intense Fe/Mg interdiffusion at the core/rim boundary in Allende exceeds the 12 μm maximum interdiffusion length calculated from the crystallographic anisotropy. In these cases, the Fe/Mg interdiffusion must have occurred prior to accretion. The original findings of this study were published in (Weinbruch et al., 1992). A final paper on this research is currently in press (Weinbruch et al., 1993).
2. Studies of periclase-bearing Fremdlinge.

Among the most enigmatic components of CAI's are the complex opaque assemblages known as Fremdlinge. These objects have been studied in detail by a number of investigators, but to date there is relatively little general agreement about their origin and history. One hypothesis (El Goresy/Armstrong, e.g., Armstrong et al., 1985, 1986, 1987) is that, despite considerable post-accretional alteration, they contain some of the earliest phases condensed from the solar nebula and provide information regarding the variability of T and fO₂ in the early solar nebula. Another hypothesis (Wark/Blum/Wasserburg) is that these objects formed as late alteration products inside the CAI's and provide constraints about the low temperature thermal history of the parent body. Zinner et al. (1989) presented isotopic results which may support the El Goresy-Armstrong hypothesis that oxidation of some of the precursor alloys of Fremdlinge occurred in the solar nebula before aggregation of the precursor phases of CAI's. They reported identifying periclase in a Fremdling from a Vigarano CAI, a phase that is not predicted to condense from a solar nebula gas at nebular fO₂. Mg and O isotopic analyses of this periclase crystal showed different isotopic compositions than found in coexisting CAI phases. Zinner et al. interpreted this as suggesting the Fremdling was formed from a separate isotopic reservoir than the other phases in the inclusion. The Mg isotopic results of this experiment, however, were of relatively low precision due to the small grain size and the amount of material required for the oxygen analyses.

We proposed to search Vigarano CAI's to try to find other periclase crystals in order to confirm the isotopic analyses, hopefully with more precision. Our search was only partially successful. Rather than being a unique occurrence, periclase in Vigarano CAI’s appears to be relatively common-place. We identified several hundred periclase grains in dozens of Vigarano CAI’s. The periclase appears to always contain significant (greater than 5 to 10% FeO, as reported in the single crystal of Zinner et al.) and appears to be most concentrated in Fremdlinge rich in Ni-sulfides and Ni-rich (>65%) metal. Periclase commonly appears to be in intimate contact with the metal and sulfide grains. Unfortunately, the size of the individual periclase crystals is very small (typically 0.1 to 0.5 μm) and never larger than 1 to 2 μm. We were unable to find a periclase crystal thick enough and of sufficient cross-sectional area to perform in-situ Mg-isotopic analysis with the ion microprobe without serious interference by neighboring phases. This will require developing a technique to extract or otherwise isolate the individual submicron crystals to be embedded in a non-contaminating substrate for ion microprobe characterization. If and when such extraction techniques can be developed, abundant material exists to perform these important experiments. In any event, periclase must be considered a relatively common, not a rare phase in Vigarano Fremdlinge and serious attention need to be paid towards understanding where and how it was formed. The preliminary results of this work were published in Armstrong (1989, 1992).

3. Studies of Ni-Pt-Ge-Te-rich Fremdlinge.

As noted in section 2, there is considerable disagreement regarding the origin of Fremdlinge in CAI's. According to the Wark/Blum/Wasserburg hypothesis (henceforth,
WBW), these objects evolved as immiscible liquid metal droplets in the CAI that were altered after the CAI solidified by low temperature oxidation and sulfidization. According to the El Goresy/Armstrong hypothesis (henceforth, EGA), at least some Fremdlinge were originally composed of metal, oxide (and perhaps in rare cases sulfides) and then were incorporated into the CAI’s followed by partial or total melting and varying degrees of alteration with neighboring phases (including, in some instances, oxidation and sulfidization). EGA argue that some Fremdlinge show signs of considerable reequilibration, suggesting considerable alteration in the CAI, while other Fremdlinge show much less equilibration. There is a significant difference in interpretation between these two models regarding veins and patches of altered opaque phases in the vicinity of Fremdlinge. WBW argue that all opaque assemblages were formed by in-situ oxidation and sulfidization of pre-existing metal after the CAI solidified, and thus that vein transport of O, S and other volatiles into the assemblages had to occur. EGA argue that, while in certain instances this is true, in many cases veins and patches result from the melting and alteration of pre-existing oxide-phase-containing Fremdlinge. They note that numerous "well-preserved" Fremdlinge have no evidence of veins or other conduits for volatile transport in their vicinity. They also argue that, in many cases, Fremdlinge occur embedded in spinel crystals (an early crystallizing phase in CAI’s) that conform perfectly to the Fremdling boundaries, suggesting (2) that the Fremdling (or precursor) preexisted the spinel, and (b) that there was no significant volume expansion of the Fremdling after spinel crystallization. Unfortunately, the compositions of the veins and alteration patches around typical-oxide-sulfide-containing Fremdlinge provide ambiguous mineralogical evidence for use in evaluating the WBW and EGA hypotheses. The veins contain NiFe metal, oxides and sulfides that would be consistent with both transport in or melting and alteration out of the Fremdling precursor. In fact, the phases found in the veins typically do not contain refractory siderophile elements and are also consistent with low temperature alteration on the meteorite parent body totally unassociated with original CAI or Fremdlinge.

In order to provide a test for the WBW and EGA hypotheses, we undertook a detailed petrographic and chemical study on CAI that contain a relatively rare type of Fremdlinge, those rich in Ni, Pt, Ge, Sn, and Te, originally reported by Armstrong et al. (1985). We found that these Fremdlinge are considerably more abundant than earlier thought and occur in a number of CAI from the Allende and Bali meteorites. They are unique in containing, in high concentration, several volatile elements (Ge, Sn and Te) not found in low temperature opaque alteration (either in CAI’s or elsewhere in the meteorites). According to the WBW hypothesis, these elements should have been introduced after the CAI’s solidified by low temperature vapor or fluid phase alteration, and some evidence of concentration of these elements should be found in the veins or other alteration areas of the CAI’s. According to the EGA hypothesis, these elements could have been introduced into the Fremdlinge or their precursors before incorporation into the CAI’s, and thus there would not necessarily be any evidence of these elements in opaque alteration in the CAI’s except where produced by melting or digestion of the preexisting Fremdlinge. We thus conducted a detailed study of the chemical composition of all of the Ni-Pt-Ge--Te rich Fremdlinge in our collection along with veins and alteration patches in the neighboring CAI phases.
We concentrated our efforts on the Allende inclusion Egg3 since we have abundant areas of this CAI in thin section containing numerous Ni-Pt-Ge-Te-rich Fremdlinge and significant numbers of veins and alteration areas (Armstrong et al., 1985). Three petrographic types of alteration were studied: (1) veins in the CAI unassociated with Fremdlinge (as determined with backscattered electron SEM imaging and transmitted-light optical microscopy), (2) veins adjacent to Fremdlinge, and (3) patches of opaque alteration found in the vicinity of Fremdlinge that give the appearance of being altered, broken-up pieces of the original Fremdlinge (Armstrong et al., 1984, 1987). No evidence of Pt, Ge, Sn or Te was found in any vein unassociated with Fremdlinge (type 1). The mineralogy and chemical composition of phases found in these veins were identical to those found in veins of CAI that do not contain Ni-Pt-Ge-Te-rich Fremdlinge. The phases found in these veins include Pt-Ge-absent NiFe metal (of typical 60:40 composition found in Allende CAI's, not the Fe-poor, Ni-rich [>70%] composition found in these particular Fremdlinge), troilite, pentlandite, and Fe-oxide. No heazlewoodite (Ni sulfide) or tellurides were found, phases that are common in these Fremdlinge.

Veins touching or immediately adjacent to the Fremdlinge (type 2) have a similar mineralogy and chemistry to the isolated veins with one exception; small concentrations of Ge (typically <0.5%) were detected in the NiFe metal. No Sn, Te or Pt was detected in any phase; no heazlewoodite was observed; and, interestingly, the Ni-Fe composition of the metal was the same as that found in typical matrix or unassociated veins, ~60:40, not Fe-poor as in the adjacent Fremdlinge. It should be noted that the Ge/Ni abundance in these associated veins is less than one-tenth of that found in the Fremdling metal. As is seen with other types of Fremdlinge, the patches of opaque phases leading away from these Fremdlinge in Egg 3 and similar CAI, that appear to have been partially melted (type 3), contain the same phases as found in the adjacent Fremdling. In these cases, the neighboring Fremdling is typically irregularly shaped and appears to be missing some of its original material.

The results of this study provide no supporting evidence that the volatile elements Ge, Sn and Te, found in high concentrations in all Fremdlinge in these CAI's, were introduced by vapor or liquid transport at low temperatures after the CAI solidified, as proposed for other types of Fremdlinge by the WBW model. In order for the data to be consistent with the WBW model, another alteration event, after original opaque assemblage alteration, would had to have taken place, erasing all evidence of the transport of Ge, Sn and Te. Alternatively, a scenario could be proposed that Ge, Sn and Te were preferentially leached out of the transport veins into the surrounding CAI silicates or oxides (unlikely at the low temperature predicted by the WBW model and inconsistent considering relative metal/silicate distribution coefficients for Ni, Co and Ge. Even ignoring the improbability of the above alternatives, in order to be consistent with the WBW model, a means of concentrating Ge, Sn and Te with respect to other elements at low T would have to be discovered. However, the evidence is consistent with the EGA hypothesis that these elements were incorporated into the Fremdling precursors before they were emplaced into the CAI's. The only distribution of these elements in the rest of their host inclusions is seen in what appear to be broken-up fragments of the original Fremdlinge. The results of this study underscore the principal conclusion reached by EGA in the study of other types of Fremdlinge, namely that these objects demonstrate that the early solar nebula had to be
quite variable in its temperature, $f_{O_2}$, $f_{S_2}$, and chemical composition in the region of formation of CAI precursors. An initial report of this study was published by Armstrong (1992). A final manuscript is in preparation.

4. Petrogenesis of the Colomera meteorite.

The IIIE iron meteorites are exceptional in being one of two groups to contain cm-sized multicrystal silicate inclusions. These inclusions have been extensively studied, both isotopically to provide radiometric ages and petrographically to provide hints regarding the genetic relationships between iron and stony meteorites (e.g., Bunch et al., 1970; Sanz et al., 1970; Scott and Wasson, 1976). Despite these investigations, the petrogenetic history of the II E's remains complicated and poorly understood.

The II E meteorites show two distinctive ages (Niemeyer, 1980). Silicates from Colomera and Weekeroo Station date at 4.54 to 4.61 x $10^9$ years, while Kodaikanal and Netschaevö date at about 3.8 x $10^9$ years. Scott and Wasson (1976) proposed that Netschaevö represents the parent material of the II E silicates (Contradicted by its young age) and that II E’s were formed by mixing shock-liquified Fe metal with the low melting fraction of a parent silicate. Wasserburg et al. (1968) proposed that the silicates formed from strongly differentiated silicate melts trapped in the cooling metal. Olsen and Jarosevich (1970) suggested that the composition of the silicates was similar to that produced from removal of olivine from a chondritic melt. Niemeyer (1980) proposed that the II E silicates were formed on two different parent bodies and mixed with II E metal in a shock event.

What had been missing in the study of II E inclusions is the determination of trace element abundances, particularly REE, in the coexisting phases. We undertook such analyses on the silicates, silicate glasses, apatite and whitlockite in Colomera using the ion microprobe. Techniques developed in our laboratory for REE analyses were employed (e.g., Kennedy et al., 1989). We combined these results with a detailed SEM and electron microprobe investigation of Colomera silicate inclusions in an attempt to better constrain its petrogenesis. The initial results of our Colomera studies were presented in Armstrong et al., 1990. With these results we are better able to limit the reasonable hypotheses for the petrogenesis of the II E’s.

We were able to perform higher precision and accuracy electron probe analyses of the phases (particularly the alkali-rich glass) in the Colomera silicate inclusions than had been previously reported. This was particularly important for characterization of the glass due to the very high degree of alkali mobility during electron bombardment--more severe than we have ever encountered. By using special techniques, we were able to obtain sufficient precision and accuracy to determine that, in all inclusions examined, the sum of Na + K + (2 x Ca) matched within 1 to 2% relative of the amount of Al present. This suggests that the glass was not formed by volatile loss of Na and K in the shock melting of a feldspar precursor, but rather formed from a precursor dominantly composed of feldspar and quartz (a rhyolite-type melt). The composition of the glass varies from inclusion to inclusion, but each case matches a precursor rich in feldspar and quartz, with the main variation being in the amount of quartz required (usually 20 to 30%).
The results of the ion probe determinations of the REE and other trace element content of the various phases in the Colomera inclusions are described in detail in Armstrong et al., 1990. The results for the glass showed that it (1) was depleted in REE relative to chondritic values with respect to other incompatible elements such as K, Ba and Ti; (2) was greatly depleted in LREE; (3) contained a large positive Eu anomaly, consistent with having a feldspar precursor; (4) was increasingly enriched in HREE; and (5) contained a large negative Yb anomaly, consistent with a source that underwent an evaporation/condensation event. The apatite (1) has a similar REE pattern to the glass, except for Eu, and (2) is enriched in REE relative to the glass (~150x for LREE, ~30x for HREE). Pyroxene in these inclusions (1) is depleted in LREE relative to the glass; (2) has a negative Eu anomaly; and (3) has a similar HREE distribution and Yb anomaly as the glass.

The REE abundances found in Colomera inclusions show that (1) these inclusions are depleted in REE relative to other incompatible elements suggesting a more complicated origin than simple differentiation; (2) the glass REE pattern is similar to silicate inclusions in I-AB irons; and (3) pyroxene/glass REE partition coefficients are typical of literature values, suggesting pyroxene crystallized from the melt. Apatite does not appear to be in equilibrium with the glass (LREE K_D's are 2 to 7 times larger than the glass for similar HREE distributions); and the Yb anomaly must result from a previous evaporation-condensation process.

The results of our investigations suggest, regarding Colomera petrogenesis, that (1) the silicate precursor contained a REE component formed by an evaporation-condensation process; (2) the silicate precursor lost a fraction of REE without affecting its group III-type REE pattern; (3) the early differentiation involved in forming the silicate precursor did not result in loss of other incompatible elements such as K, Ba, Ti or Pb; (4) the silicate precursor was composed of an alkali-feldspar, quartz and pyroxene (a rhyolite-type liquid or rock); (5) Colomera formed by shock melting and mixing of metal and a rhyolite-type component; (6) the silicate precursor is unlikely to have been an undifferentiated component (such as chondrules with silica-rich mesostasis) because the inclusions are alkali-rich and relatively poor in the mafic components found in chondrites, but rather must have been a late-stage differentiated liquid or early partial melt; (7) the heterogeneity of the silicate inclusions suggests that the precursor was a relatively fine-grained solid with each inclusion forming from different proportions of feldspar, silicate and quartz; (8) the texture and chemistry of the apatite and spinels in these inclusions suggest that they formed by reaction between the silicates and the metal during or after the shock mixing event; (9) the partial crystallization of molten silicates and subsequent metamorphic history was slow enough to enable normal partitioning of REE between glass and pyroxene, and partial reequilibration of the pyroxenes; and (10) the parent body was evolved enough and large enough to have a rhyolite-type component at the start of core formation 4.5 x 10^9 years ago. We anticipated publishing one more manuscript summarizing our total studies of this interesting meteorite.
5. Instrumentation and analytical procedure development.

As an adjunct to the meteoritic research we have performed under support of this grant, we have made major instrumental, analytical procedure, and correction procedure developments to enable ever-more accurate quantitative analyses with the electron microprobe. These developments have been summarized in detail in our previous proposals and progress reports. All developments and software produced through this research have been made readily available to the NASA-research community. A list of instrumentation and analytical development papers supported in part or in whole by this grant is included in the attached publication list.


An educational program with inner city junior and senior high school youth has been initiated under the direction of co-investigator John Armstrong. A group of twenty-four male and female students from Thomas Starr King Junior High School and John Marshall Senior High School have been selected for initial evaluation. Dr. Armstrong has been meeting with these students in a mentoring (and youth group leader) capacity on a weekly basis for over the past three years. Students who have expressed an interest in participating in a science program at Caltech have been brought to our laboratories (in groups of 3 to 6 at a time) to spend a Saturday or Sunday afternoon working with members of our laboratories. These half-day sessions occur regularly on a bimonthly basis. Dr. Armstrong has given them a series of short lectures introducing them to principles on which the scientific instruments in our laboratory work, as well as giving them a series of example problems of how algebra and geometry (the math courses they are taking) are applied to real scientific problems. Dr. Armstrong has also been involved in individually counselling the students regarding educational problems; working with them, their parents, and their school counsellors on developing a good academic schedule and study habits; and has participated with them in college and career planning days.

The students have performed a series of chemical, mineralogical and computer experiments under Dr. Armstrong’s supervision. They have operated optical microscopes, a scanning electron microscope, an electron microprobe, an x-ray fluorescence spectrometer and a x-ray diffractometer in these experiments. (SEM images taken by these students of phases from refractory inclusions in the Allende meteorite were used in the presentation by Dr. Armstrong at a recent LPSC.) In a typical experiment the students make a SrCO₃ precipitate by mixing Na₂CO₃ and SrCl₂, test the precipitate and supernatant using flame tests, examine the precipitate crystals formed under the optical and electron microscopes, analyze them with x-ray fluorescence and EDS/SEM analysis, determine a powder diffraction pattern and then compare the results with similar experiments that they perform on natural samples of halite and strontianite. In other typical experiments, the students have (1) studied reactions occurring on the surfaces of natural and man-made materials--comparing desert varnish and clay formation with corrosion of metals; (2) have taken air pollution samples and examined and analyzed the individual particles with the optical microscope and SEM/EDS; and (3) have compared textures of rocks and meteorites using the optical microscope and SEM and worked with Dr. Armstrong in speculating how the textures may indicate the formation and alteration history.
The students keep a notebook of their results and go over the experiments both at the time and a few weeks later in mentoring sessions. This summer Dr. Armstrong will choose three of the most promising of the students to work on special projects involving use of the SEM and electron microprobe. A strong majority of the students involved so far have responded enthusiastically, have show excellent comprehension for their age, and want to continue the program.

This program is being done in cooperation with the principals and science faculty of both school involved. We have the enthusiastic support of the principals of both schools. We have made plans to initiate a series of regular meetings with science teachers from both schools with the participation of Dr. Wasserburg. We have agreed to assist Marshall High School in their plans to initiate an astronomy/space science course. We plan to set up a committee with teachers from the two schools to help decide which students will participate as regular members of this program (if we are able to get the necessary funds to continue it) and to evaluate their progress. Thomas Starr King is one of two 'feeder' Junior High School for Marshall Senior High School, enabling us to be able to work with the students involved throughout their junior and senior high school years.

Selected Publications supported in part or whole by this Grant


