

Two situations were considered: (1) Water was formed in the protosolar nebula by oxidation of H₂ and (2) interstellar water was injected as grains (ice or clays) that subsequently evaporated in the protosolar H₂. In situation (1), water reached isotopic equilibrium with H₂ in the inner solar system (i.e., $f \sim 1$). During the cooling of the nebula, it is shown that f cannot exceed 1.5 (i.e., -750% in δ units). Since most objects (including Earth) in the solar system exhibit much higher δ D values, a solar origin for water must be rejected.

On the contrary, if the initial solar system water was enriched in D (situation 2) with a minimum D/H ratio similar to that measured in some smectites found in the matrix of Semarkona (3600‰; [3]), typical δ D values measured in carbonaceous chondrites are reached within $<10^6$ yr between 3 and 5 AU. Examples of the evolution of f with time and heliocentric distance are shown in Fig. 1. In Fig. 1, it can be noted that the minimum f value ($f = 3$) observed in LL3 chondrites as well as $f = 10$ in comets are accounted for by this model.

Therefore, water in the solar system would be mainly of interstellar origin and not synthesized by the thermal oxidation of the protosolar H. Such deuterated water was subsequently reprocessed in the turbulent nebula. All the possible nebula calculated in the framework of this theory yield this conclusion.

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EXPERIMENTAL AQUEOUS ALTERATION OF ALLENDE (CV3). C. L. Duke and A. J. Brearley, Institute of Meteoritics, Department of Earth and Planetary Sciences, University of New Mexico, Albuquerque NM 87131-1126, USA.

Introduction: A greater understanding of the reactions involved in the aqueous alteration of many carbonaceous chondrites can provide insight into the role of volatiles both in the solar nebula and on the asteroidal parent bodies. Several aspects of the fundamental characteristics of alteration reactions such as rates, mechanisms, and the role of fluid composition and the water to rock ratio are poorly constrained. In order to investigate the mechanisms and rates of the reactions involved in the aqueous alteration of carbonaceous chondrites, we have commenced a series of low-temperature hydrothermal experiments. The preliminary results of these experiments are presented below.

Methods: Small (~3 mm) cubes of the CV3 chondrite Allende were heated with deionized water in Teflon-lined Parr bombs. Experimental variables included temperature (100°–200°C), duration of heating (7–60 days), and the initial water to rock (W:R) ratio (1:1–6:1). After the experimental heating any residual water was analyzed using inductively coupled plasma-mass spectrometry (ICP-MS). Examination of the altered samples was carried out using a JEOL 5800LV SEM operated in low vacuum mode. Later the samples were carbon coated to analyze quantitatively the composition of the crystalline phases using EDS on the same scanning electron microscope.

Results: In all cases, the samples developed a reddish-brown discoloration after the experiment. Several new phases had crystallized on the surface of the cubes, the composition and morphology of which seem to be quite dependent on the experimental conditions. These new phases include Ca, Mg, and Na sulfates, Ca carbonates, and Fe-(hydro)oxides with a variety of different morphologies. The dominant sulfate crystals are hexagonal prisms of CaSO₄ that are perfectly formed in the lower W:R experiments and display considerable twinning and parallel growth as the W:R ratio is increased. Calcium carbonates also appear in a range of complexly twinned morphologies. Only in the highest W:R ratio experiment (6:1) did sulfate and carbonate phases coexist. Two morphologically distinct Fe-(hydro)oxide phases are present on some samples. One is very finely crystalline and the other occurs as submicrometer spherules both in clusters and as individual grains. Preliminary SEM analysis of sample thin sections indicates that there has been some dissolution of the matrix olivine as well as oxidation of sulfide grains.

Discussion: Our preliminary results demonstrate that even at low temperatures and after short reaction times quite extensive alteration of Allende occurs. Oxidation of sulfides may provide S for the growth of

sulfate phases and also the Fe seen in the secondary Fe-(hydro)oxide phases. Matrix olivine may be the source of the Mg and some of the Fe in the experimental system. The source of Ca is not clear, although in one sample evidence of melilite breakdown was observed. Other possible sources include high-Ca pyroxenes in the matrix as well as the little remaining chondrule glass.

The secondary mineral assemblages found in our experiments bear a close resemblance to those found in CI chondrites, but differ from CM chondrites. Although calcite is abundant in CM chondrites [1], sulfates are rare, whereas in CI chondrites sulfate phases such as those that occur in our experiments are common [2]. We have not yet fully characterized the red-brown Fe-(hydro)oxide in our samples, but it may well be ferrihydrite, a phase that is also common in CI chondrites [3]. In addition, the spherular Fe-(hydro)oxide phase found in our experiments closely resembles the magnetite crystals within the framboids in CI chondrites [4].

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CONDENSATION FROM COSMIC GAS MADE OF FREE ATOMS. D. S. Ebel¹ and L. Grossman^{1,2}, ¹Department of the Geophysical Sciences, 5734 South Ellis Avenue, University of Chicago, Chicago IL 60637, USA (debel@midway.uchicago.edu), ²Enrico Fermi Institute, University of Chicago, Chicago IL 60637, USA.

Introduction: It has long been known that the mineralogy of condensates from cosmic gases is strongly dependent on the atomic C/O ratio because of the great stability of the CO molecule [1]. If $C/O > 1$ as in C-rich stars, all O is combined as CO and the excess C is available to form graphite and carbides as high-temperature condensates. If $C/O < 1$ as in O-rich stars, all C is combined as CO and the excess O is available to form oxides and silicates as high-temperature condensates. In meteorites, a significant fraction of interstellar graphite and SiC grains of the X-type are thought to have condensed from type II supernova ejecta whose C/O ratio > 1 . In order to explain details of the isotopic compositions of these grains, matter from interior zones of the supernova must be mixed with matter from the exterior. Mixing calculations that quantitatively reproduce the isotope ratios, however, invariably give $C/O < 1$ for the ejecta, from which graphite and SiC cannot condense [2]. As a way out of this predicament, Clayton [3] has suggested that supernova ejecta are so intensely irradiated that CO and other gas-phase molecules are nearly completely dissociated, liberating C atoms from CO and making them available to form graphite and carbides, even in O-rich ejecta. While it is difficult to envision irradiation conditions that would prevent two atoms from bonding together to form a molecule while still allowing thousands of atoms to bond to one another to form a grain, we nevertheless performed condensation calculations from a gas of solar composition ($C/O = 0.42$) to see what condensate phases would form at equilibrium under two sets of conditions: (1) CO is prevented from forming, and (2) all polyatomic molecules are prevented from forming in the gas.

Technique: Calculations were done for a fixed total pressure of 10^{-6} bar using the method of [4]. Runs were performed without the silicate liquid models described in [4] and were terminated when refractory elements such as Ti became depleted in the gas phase to a mole fraction of $<10^{-20}$.

Results and Discussion: When the CO molecule is prevented from forming, most of the O forms CO₂ instead, reducing the partial pressure of O by slightly more than one log unit at 1570 K. Consequently, the phases corundum, hibonite, perovskite, melilite, spinel, pyroxene, and olivine all appear at temperatures 40°–60° lower than in a solar gas with CO present. Simple removal of CO does not cause graphite or carbides to become stable in a gas of solar composition.

When all molecular species are prevented from forming, strange things happen. As predicted by Clayton [3], the C liberated from CO does condense as graphite at 2110 K. The O liberated from CO, however, is avail-

able to form oxide and silicate condensates at higher temperatures than in a fully speciated solar gas, in which the SiO molecule stabilizes Si in the vapor phase. In the present case, the free Si combines with the free O to condense cristobalite (SiO₂) at 1860 K, a higher temperature than that for any other refractory oxide, and after 99.6% of the C has already condensed as graphite. At 1820, Ti₄O₇ condenses and is replaced by TiO₂ at 1790 K, where mullite (Al₆Si₂O₁₃) also appears. Anorthite (CaAl₂Si₂O₈) appears at 1770 K, and mullite disappears at 1750 K. Sphene (CaTiSiO₅) replaces TiO₂ at 1700 K, wollastonite (CaSiO₃) appears at 1680 K, and whitlockite (Ca₃(PO₄)₂) appears at 1610 K. Wollastonite is replaced by diopside pyroxene (CaMgSi₂O₆) at 1590 K. Cristobalite disappears at 1530 K, just before forsteritic olivine (Mg₂SiO₄) finally appears at 1520 K. In a solar gas composed entirely of monatomic species, at 10⁻⁶ bar total pressure, graphite and cristobalite are the most abundant condensates between 2100 K and 1600 K.

Suppression of the polyatomic molecular species in a solar gas at 10⁻⁶ bar total pressure changes the order of major-element condensation from Al-Ca-Ti-Si-Mg to C-Si-Ti-Al-Ca-Mg. The mechanism called upon by Clayton [3] is unlikely to yield SiC or TiC grains, even if grains could nucleate in an environment that destroys gaseous molecules. Our calculations suggest that, instead of SiC and TiC, SiO₂ would co-condense with graphite. One might expect extrasolar graphite to be accompanied by extrasolar SiO₂, if graphite did indeed form in the manner Clayton [3] suggests. Inclusions of SiO₂ have not been discovered in searches of extrasolar graphite.

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CHEMICAL COMPOSITION OF MARTIAN METEORITES. M. Ebihara¹, K. Shinotsuka², and P. Kong³, ¹Department of Chemistry, Graduate School of Science, Tokyo Metropolitan University, Hachioji, Tokyo 192-0397, Japan (ebihara-mitsuru@c.metro-u.ac.jp), ²National Institute for Fusion Science, Gifu 509-5292, Japan, ³Mineralogical Institute, Universität zu Köln, 50674 Köln, Germany.

We have analyzed three shergottites (ALH 77005, EET 79001, and Zagami), one orthopyroxenite (ALH 84001) and one nakhalite (Nakhla) by instrumental neutron activation analysis (INAA) for major, minor, and trace elements, radiochemical neutron activation analysis (RNAA) for siderophiles, and inductively coupled plasma mass spectrometry (ICP-MS) for REE, Th, and U. Our INAA data generally agree with the literature values for individual meteorites [1–3]. In spite of a large variety of petrological types, the constancy in Fe and especially Mn is remarkable. Very close coherence of Mn with Fe due to the similarity in ionic radius of Fe²⁺ and Mn²⁺ is obvious for martian materials, as was observed for the terrestrial and lunar rocks.

In contrast to Co, which is another element not variable among the six martian meteorites analyzed, Ni is highly depleted in ALH 84001. In fact, ALH 84001 is notably depleted in refractory siderophile elements such as Ir and Os compared to other martian meteorites. Lherzolitic shergottites have a Ir/Os ratio very close to the CI chondrite ratio [4]. This is also true for EET 79001, but Zagami has 2× CI ratio of Ir/Os. Nakhla has an even higher Ir/Os ratio (relative CI ratio) than four shergottites, while ALH 84001 has a much lower Ir/Os ratio than CI ratio. A large depletion of siderophile elements in ALH 84001 coupled with its very old formation age (4.5 Ga) suggest that the core formation took place at an early stage of martian history.

The chondrite-normalized REE abundance pattern of lherzolitic martian meteorites is characterized by the presence of a hump in the middle to heavy REE span. Whereas the abundance increases in the light REE span, the abundance decreases in the heavy REE span. Similar patterns are observed for EET 79001 and Zagami in this study. In addition to the hump in the middle REE region, a slight increase from Ce to La is commonly observed for shergottites including lherzolitic shergottites. This upward curvature at the lightest REE may require the third component of REE carrier in shergottites. The REE abundance pattern for ALH 84001

is completely different from those for shergottites; REE pattern is flat in light REE and is gradually and monotonously increased toward heavy REE. This pattern suggests that at 4.5 Ga, the partial or extensive melting occurred on Mars, with the melt being segregated from the mantle or cumulates, from which ALH 84001 was formed.

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GEOCHEMISTRY OF CARBONATES AND GLASS IN ALLAN HILLS 84001. J. M. Eiler¹, J. W. Valley², C. M. Graham³, and J. Fournelle², ¹Geological and Planetary Sciences, California Institute of Technology, Pasadena CA 91125, USA (eiler@gps.caltech.edu), ²Geology and Geophysics, University of Wisconsin, Madison WI 53706, USA, ³Geology and Geophysics, University of Edinburgh, Edinburgh Scotland, UK.

The stable isotopic geochemistry of carbonates in SNC meteorites constrains both the characteristics of martian volatile reservoirs and the origin of secondary mineralization in these samples. We here report new ion microprobe measurements of ¹⁸O/¹⁶O in carbonates and related phases in ALH 84001, supported with major-, minor-, and trace-element data on the same materials.

The background for these measurements is that carbonates in ALH 84001 display a large range in O-isotopic composition (~25‰: [1–4]), which has been ascribed either to variations in temperature [1,3,5] or Rayleigh distillation [4]. When examined in detail, variations in the O-isotopic ratio in carbonates have been shown to be correlated systematically with variations in their major-element composition [1,3,4]. Although the data from several different groups are generally consistent, one difference is that ankeritic carbonates (~50% CaCO₃) were reported by [3] to have δ¹⁸O_{SMOW} Å 0‰, but [4] found values of ~7‰ for carbonates in this compositional range.

We made 82 measurements of δ¹⁸O in carbonates from ALH 84001, including a range of ankeritic compositions not encountered in previous studies and ~20 measurements each of all of the major populations/textural types of carbonate known in this sample. Our results confirm the overall trend of δ¹⁸O with chemical composition seen in previous studies [1–4]: i.e., δ¹⁸O varies by ~25‰ and tends to decrease with increasing Ca content. However, our data reveal details in the correlations between δ¹⁸O and chemistry not observed in previous, smaller data sets. In particular, two distinct, offset trends occur in plots of δ¹⁸O vs. major elements: (1) decreasing δ¹⁸O (26 → 0‰) with decreasing Mg and increasing Ca and Mn in white magnesites and orange magnesio-siderites, and (2) ankerites having a large range in chemical composition (0.45 ≤ X_{Ca} ≤ 0.71) with essentially indistinguishable δ¹⁸O values (5.8 ± 1.9‰). There may be a subtle discontinuity in δ¹⁸O and chemical composition on the first trend, between magnesites (0.70 ≤ X_{Mg} ≤ 0.90; X_{Ca} ≤ 0.05) and magnesio-siderites (X_{Mg} < 0.70; 0.08 ≤ X_{Ca} ≤ 0.44). Our results for ankeritic carbonates are within analytical uncertainty of [4] and in disagreement with [3]. These two trends are associated with distinct carbonate textures: magnesites and magnesio-siderites are found principally in concentrically zoned “disks” [6] and ankerites are found exclusively in irregularly shaped patches.

Manganese concentration is strongly correlated with Ca in ALH 84001 carbonates. There are again two distinct trends, one for magnesites and magnesio-siderites and one for ankeritic carbonates, offset from each other in Ca/Mn ratio. On average, the ankerites also have higher La/Nd and Sr/Ba ratios, higher Sr and Y concentrations, and lower Ba concentrations than magnesites and magnesio-siderites. δ¹⁸O is negatively correlated with La/Nd and Sr/Ba among all analyses. On average, magnesites have higher La/Y ratios and Th concentrations than other carbonate populations. All populations of carbonate have LREE-depleted REE patterns relative to coexisting feldspathic glass [see also 7].

Differences in REE abundances between carbonates and feldspathic glasses are not those predicted by carbonate/silicate-melt distribution