

Calcium-Aluminum-rich Inclusions: Major Unanswered Questions

G. J. MacPherson

Smithsonian Institution, Department of Mineral Sciences, National Museum of Natural History, Washington DC 20560, USA

S. B. Simon

Department of the Geophysical Sciences, and Chicago Center for Cosmochemistry, The University of Chicago, 5734 S. Ellis Ave., Chicago, IL 60637, USA

A. M. Davis and L. Grossman

Enrico Fermi Institute, Department of the Geophysical Sciences, and Chicago Center for Cosmochemistry, The University of Chicago, 5640 S. Ellis Ave., Chicago, IL 60637, USA

A. N. Krot

Hawai'i Institute of Geophysics and Planetology, School of Ocean and Earth Science and Technology, University of Hawai'i at Manoa, 2525 Correa Rd., Honolulu, HI 96822, USA

Abstract. Calcium-aluminum-rich inclusions (CAIs) preserve a record of events in the earliest solar system, the timing of these events and the conditions under which they occurred. Recent technical (analytical instrumentation) and theoretical advances have enabled researchers to extract an astonishing wealth of new information from CAIs, such as: (1) all CAIs may have formed in a restricted region or regions near the protosun and then were transported radially outward to the various chondrite-accretion regions; (2) the CAI formation “event” may have been very short in duration, possibly less than 10^5 years; and (3) within the region(s) where CAIs formed, there were multiple isotopic reservoirs that experienced little intermixing. However, major questions remain unanswered, and this review highlights those issues.

1. Introduction

Chondrite meteorites are aggregates of preplanetary grains and dust, accreted and compacted into rocks at the beginning of the solar system but still preserving their aggregate character as well as the distinctive individual characteristics of all the diverse particles composing them. Among their constituents are calcium-aluminum-rich inclusions (CAIs), which are minor in mass fraction (< 5%) but major in significance: CAIs preserve direct clues to the processes and environments that existed during the nebula phase of our solar system, during its first few million years, prior to the formation of planets. Intensive research over more than 30 years has demonstrated that CAIs are the oldest-known objects that formed in the infant solar nebula, that they formed in an environment that was hot and extremely reducing (consistent with hot hydrogen gas), that their elemental compositions are the result of volatility-controlled processes (evaporation-condensation), that their isotopic compositions retain a component of presolar nucleosynthetic origin, and that they record >1–2 million years of complex post-formation history that included repeated melting and secondary alteration both in the nebula and on asteroidal parent bodies.

Modern advances in analytical technology, especially the maturation of secondary ionization mass spectrometry (SIMS, a.k.a. the ion microprobe), permit more information to be extracted from these small pieces of ceramic rock than could ever have been imagined at the time these objects were first recognized in the late 1960s (e.g., Christophe Michel-Lévy 1968). Yet, important questions remain that, in their answering, will have a huge impact on our understanding of major processes that accompanied the formation of our star and its surrounding disk of gas and dust. By extension, these questions are important to the understanding of star formation in general and, thus, have astronomical significance.

This is not a comprehensive review of the properties or petrogenesis of CAIs, except briefly as background; for such reviews the reader is referred to e.g. Grossman (1980), MacPherson, Wark, & Armstrong (1988), Jones et al. (2000), Ireland & Fegley (2000), and MacPherson (2003). Rather, this paper highlights some of the major unresolved problems in our understanding of CAIs and their relationship to other early solar system objects such as chondrules. These problems will not be easy to solve, and will require a great deal of collaboration between scientists of diverse expertise working on limited amounts of precious sample. Fortunately, such a collaborative climate already exists in our science. It is our hope that this paper will help to focus consortium studies in such a way that major progress is made in the field.

2. A Brief Summary of What We Know About CAIs

2.1. Chemistry, Mineralogy, Shape, and Structure

The very largest CAIs are up to 2–3 cm in size, but these occur in only one chondrite type (CV3); most CAIs are < 1 mm in maximum size. Where large enough to see with an unaided eye or simple magnifier, they are easily distinguished from other chondrite components by their white, pink, or in some cases even blue colors. CAIs are composed mainly of oxides and silicates of calcium, aluminum, magnesium, and

titanium. Their primary minerals are notably deficient in volatile components such as iron, alkalis, and water. These minerals include many of the same phases encountered in synthetic high temperature ceramic materials and phase equilibrium diagrams pertinent to ceramic systems. CAIs invariably are enriched in certain lithophile trace elements such as scandium, yttrium, zirconium, hafnium, the rare earth elements, and certain siderophile trace elements such as those in the platinum group; enrichment factors typically are 10× to even 100× relative to average solar system abundances (CI chondrites) (e.g., Grossman 1980; Ireland et al. 1988). These diverse elements, together with the major components noted above, share the property of being refractory: they and their compounds have very high vaporization temperatures. Hence, a common synonym for CAIs is “refractory inclusions” (although not all refractory objects are Ca-Al-rich; see below). The primary mineralogy of CAIs is remarkably similar to the phases predicted to condense out of a hot solar vapor during cooling (e.g. Yoneda & Grossman 1995).

A wide diversity of CAI types exists (e.g., Fig. 1), differing in composition, mineralogy, structure, and size. Many phases have been identified in CAIs over the years, but most are either rare accessories or secondary minerals that clearly replace primary ones. The number of major primary phases that characterizes the span of CAIs is small: spinel *sensu stricto* (MgAl_2O_4), melilite solid solution ($\text{Ca}_2\text{Al}_2\text{SiO}_7$ - $\text{Ca}_2\text{MgSi}_2\text{O}_7$), hibonite ($\text{CaMg}_x\text{Ti}_x\text{Al}_{12-2x}\text{O}_{19}$, where $x < 1$), anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$), pyroxene solid solution (mainly $\text{CaMgSi}_2\text{O}_6$ - $\text{CaAl}_2\text{SiO}_6$ - $\text{CaTi}^{4+}\text{Al}_2\text{O}_6$ - $\text{CaTi}^{3+}\text{AlSiO}_6$), perovskite (CaTiO_3), and less commonly grossite (CaAl_4O_7) and corundum (Al_2O_3). The observed natural compositions of these phases show remarkably little deviation (generally $< \sim 0.5$ wt.% each of minor oxide component) from the ideal chemical formulae given above. An exhaustive review of the mineralogy and mineral chemistry of CAIs is given in Brearley & Jones (1998), to which the reader is also referred for structural formulae of other minerals named herein.

The morphologies and internal structure of CAIs are almost as varied as their compositions and mineralogy. CAIs range in shape from irregular, highly porous aggregates of tiny crystals, to strings of crystals that stretch out across several mm of meteorite matrix with expanses of matrix intervening, to nearly spherical, densely crystalline objects. These diverse morphologies reflect diverse and complex histories, including deformation due to impact processes. Although some CAIs are obviously fragments of once-larger objects, it is very clear that most are whole objects that were always very small, and even the fragments were never part of objects much larger than the whole ones we now observe.

Amoeboid olivine aggregates (AOAs; e.g., Grossman & Steele 1976; Krot et al. 2004a) are commonly grouped together with CAIs but, although they can reasonably be described as refractory, they are not particularly calcium- or aluminum-rich. AOAs are irregularly shaped aggregates of mostly very fine-grained forsteritic olivine, but they enclose small CAI nodules that usually consist mostly of spinel and pyroxene, with lesser amounts of other phases.

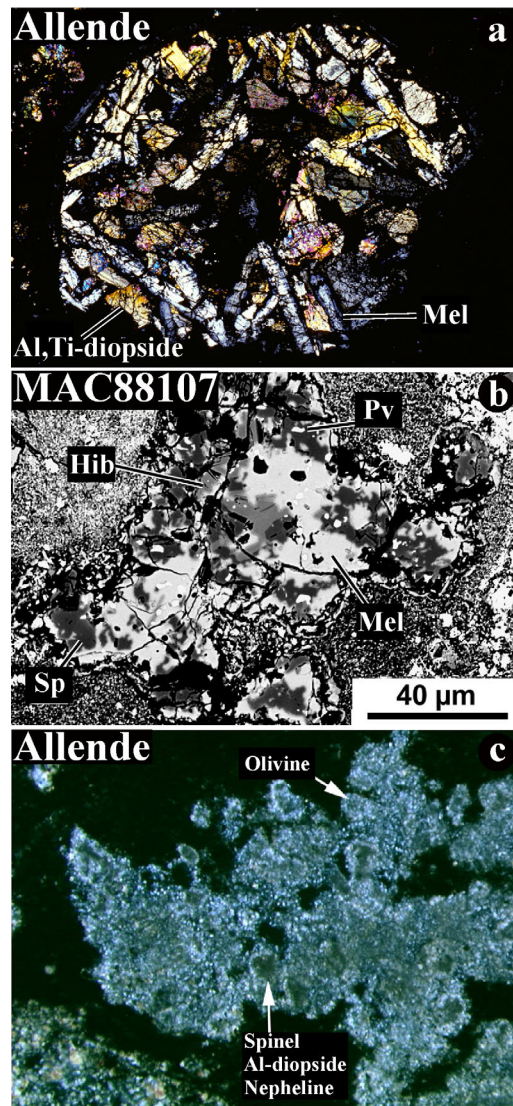


Figure 1. Photomicrographs of CAIs. (a) A Type B CAI from the Allende CV3 chondrite, photographed in transmitted light with crossed polarizers. The object was originally a sphere, approximately 1 cm in diameter, but is broken at the bottom and right edges. The minerals are melilite (blue-white and yellow-white laths), pyroxene (bright colors), and spinel and anorthite (not visible in this photo). The colors are interference colors caused by the polarized light. (b) Back-scattered electron photomicrograph of a small CAI from the CO3-like chondrite MAC 88107, consisting of melilite (Mel), hibonite (Hib), perovskite (Pv), and spinel (Sp). (c) An amoeboid olivine aggregate from Allende, photographed as in (a). The inclusion consists mainly of olivine (bright) and small CAI nodules (dark). The width of field is several mm.

2.2. Ages

CAIs are uniformly very old (see review by McKeegan & Davis 2003). The most precise ages are Pb-Pb measurements of two CAIs from the Efremovka CV3 chondrite, at 4.5672 ± 0.0006 Ga (Amelin et al. 2002). CAIs also possess the lowest initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of any known solar system material (Gray, Papanastassiou, & Wasserburg 1973; Podosek et al. 1991). Finally, CAIs alone preserve a record of the short-lived radionuclides ^{41}Ca and ^{10}Be and have the highest inferred initial $^{26}\text{Al}/^{27}\text{Al}$ ratio of any material formed in the solar system (MacPherson et al. 1995). For these reasons, the ages of CAIs are usually taken to define the age of the solar system.

2.3. Distribution

CAIs have been found in every known chondrite type except CI (although CAI mineral grains have been found in CI; Huss et al. 1995); however, their distribution by size and type is extremely varied. CAIs were first described in 1968 from the Vigarano meteorite (Christophe Michel-Lévy 1968), but they achieved prominence after the fall of the Allende CV3 chondrite in 1969. That meteorite provided, for the first time, a huge amount of carbonaceous chondrite material to the science community. Large pieces of Allende (and of its kindred CVs) exhibit prominent cm-sized white objects displayed starkly against the dark meteorite matrix and chondrules. Because of the large sizes and relative ease of study, these became the prototypical CAIs in most workers' minds. In fact, the opposite is true: only the CVs have such large and abundant CAIs. In all other chondrites, only rarely are CAIs even as large as 1 mm (200-700 μm is common). CAIs are significantly more abundant in most carbonaceous chondrites than in ordinary or enstatite chondrites. Finally, within the population of objects found in CVs, one variety of CAI achieved more prominence than others: these are the pyroxene-melilite-spinel-anorthite-rich spherules known as Type Bs (see Grossman 1975) that not only are large but also likely originated as molten droplets. Being igneous, they can be treated as once-homogeneous isotopic systems, which is a critical factor for the interpretation of short- and long-lived radioisotope systems (Kita et al. this volume). Type B CAIs became an important cornerstone of cosmochemical ideas about the earliest history of the solar system, and yet true Type B CAIs are found only in the CV3 chondrites.

The CAI populations in some of the other chondrite types are also distinctive. For example, although melilite is common in the CAIs of most chondrite types (including ordinary and enstatite chondrites), CAIs in CM chondrites only rarely contain melilite. Equally, the CAIs in CH and CR chondrites are notable for the common occurrence of the phase grossite, which is very rare in CAIs from virtually all other chondrite types. In the CH chondrite ALH85085, CAIs are exceptionally small: none has ever been found that exceeds ~ 110 μm in diameter.

2.4. Isotopic Properties: Oxygen, Extinct Radionuclides, and Nuclear Anomalies

Shortly after the fall of Allende, two remarkable discoveries were made: (1) CAIs are enriched by several percent in the most abundant isotope of oxygen (^{16}O) relative to the Earth and all other solar system materials measured so far, in a manner that

cannot be due to physicochemical process such as evaporation or condensation (Clayton, Grossman, & Mayeda 1973); and (2) minerals within individual CAIs show enrichments in ^{26}Mg that correlate positively with the Al/Mg ratio of the host phase (anorthite having much higher Al/Mg than spinel, for example); such correlations were and are interpreted as fossil isochrons signifying the *in situ* decay of the short-lived ($t_{1/2} \sim 0.72$ My) radionuclide ^{26}Al (the parent for the excess ^{26}Mg) in the CAI (s) at the time of their formation (Lee et al. 1976). These two discoveries were very important because both the ^{16}O excess and the ^{26}Al were believed to be of presolar origin, carried into the infant solar system within presolar grains. Because of its short half-life, we know that the ^{26}Al must have been made shortly prior to its incorporation into the CAIs; this led to the concept of a nearby supernova trigger for the collapse of the protosolar nebula (Cameron & Truran 1977), with the supernova providing freshly made ^{26}Al . Subsequently, evidence has been found in CAIs and other meteoritic material for the former existence of a number of other short-lived radionuclides in the earliest solar system. Notable among these (relevant to CAIs) are ^{41}Ca (Srinivasan et al. 1994), ^{10}Be (McKeegan et al. 2000), and ^{53}Mn (Birck & Allègre 1985); see review by McKeegan & Davis (2003). A major debate is currently raging over whether all, some, or none of these extinct nuclides are presolar in origin or, instead, were formed by local irradiation processes near the infant sun. This debate is not new: Lee (1978) proposed such an origin for ^{26}Al . Without exception, however, all competing models have major implications for how our solar system formed and evolved.

Short-lived radionuclides can potentially be used as high-precision relative chronometers of early solar system events (assuming nebular isotopic homogeneity; see Section 4.2 below), and ^{26}Al is particularly attractive in this regard because aluminum is highly refractory and therefore enters the earliest phases and records the earliest, very high-temperature events. Moreover, aluminum is a major element and a stoichiometric component of many phases in CAIs and some chondrules. A wealth of data, largely from ion microprobe studies, is compiled in Figure 2 into a histogram of inferred initial $^{26}\text{Al}/^{27}\text{Al}$ ratios showing that: (a) most CAIs and chondrules differ systematically in their initial $^{26}\text{Al}/^{27}\text{Al}$ ratios, at 4.5×10^{-5} and $\sim 1 \times 10^{-5}$ respectively; (b) “normal” CAIs (as a population, and data within individual CAIs) have a bimodal histogram, with the peak at ~ 0 being due to secondary minerals and partial recrystallization or remelting of primary phases; and (c) one special category of CAIs, called FUN inclusions (see below), had little or no ^{26}Al at the time of their formation (Fig. 2). As discussed in Section 4.2, these differences in inferred initial $^{26}\text{Al}/^{27}\text{Al}$ ratios have been used to argue that chondrules began forming at least 1–2 My after CAIs, and that individual CAIs preserve isotopic records of 1–2 My-long nebular histories including remelting and secondary alteration (see reviews by MacPherson, Davis, & Zinner 1995; McKeegan & Davis 2003). The interpretation of the FUN CAI data is debated (below).

The nucleosynthetic model for the origin of the ^{16}O enrichment in CAIs has now been largely supplanted by local (solar nebula) or protosolar molecular cloud chemical models (Clayton 2002; Yurimoto & Kuramoto 2004; Lyons & Young 2005). There are competing models for the exact mechanism and each has

implications for the solar nebula itself but, independent of such models, CAIs have not lost their potential astrophysical significance.

In their paper proving the former existence of ^{26}Al in an Allende CAI, Lee et al. (1976) also reported data for another CAI in which there was no evidence for extinct ^{26}Al . This object, given the proper name C1 (not to be confused with CI chondrites), proved to be unusual in other respects. It and its isotopic twin, Vigarano 1623-5, have nonradiogenic isotope abundance anomalies in all elements analyzed (e.g., calcium, barium, titanium), and light elements such as magnesium, oxygen, and silicon show mass-dependent isotopic fractionation (Clayton & Mayeda 1977; Davis et al. 1991; Loss et al. 1994). C1 is the prototype for a small subset of CAIs that show such Fractionation and Unidentified Nuclear isotope properties (Wasserburg, Lee, & Papanastassiou 1977), and hence are known by the acronym FUN CAIs. In all other respects, FUN CAIs are identical to other CAIs and, in fact, can only be identified by isotopic analyses. Objects with large nuclear isotope anomalies are not confined to CV chondrites, where they are rare; in fact, rather numerous examples (some with and some without – so-called “UN CAIs” – large fractionation effects) have been found in e.g., CM chondrites as well (see review in Clayton, Hinton, & Davis 1988).

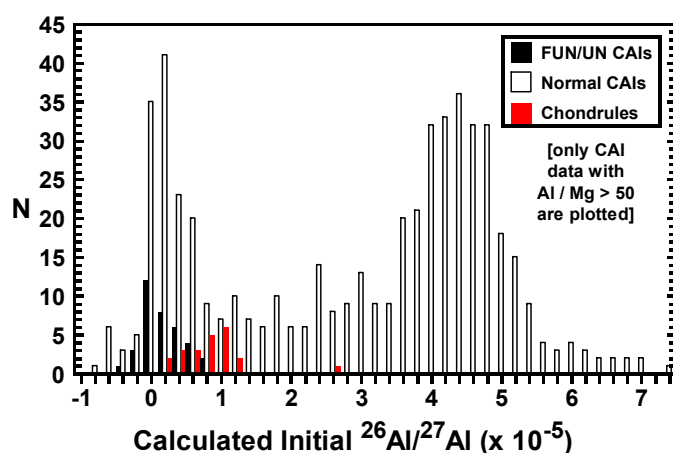


Figure 2. Histogram of calculated initial $^{26}\text{Al}/^{27}\text{Al}$ ratios in normal CAIs, FUN/UN CAIs, and chondrules.

FUN CAIs and their kin have achieved an aura and fame that are far out of proportion to their rarity. Their nonradiogenic nuclear anomalies are of unquestioned nucleosynthetic origin, and these objects allowed the first actual laboratory study of the products of different types of stellar nucleosynthesis. Their distinct isotopic properties relative to “normal” CAIs testify to the fact that the solar nebula was isotopically heterogeneous at some level, which adds a degree of complexity to (for example) interpreting differences in extinct radionuclides as being due to chronology. But one of the most significant features of the FUN/UN CAIs is that, without exception, they contained little or no ^{26}Al at the time of their formation: the highest initial $^{26}\text{Al}/^{27}\text{Al}$ ratios measured in FUN CAIs are $\sim 1 \times 10^{-5}$ (e.g., McKeegan et al. 2005), and in another inclusion, “HAL”, the value is 5×10^{-8} (see review by

MacPherson *et al.* 1995). Thus large nonradiogenic nuclear anomalies and abundant extinct ^{26}Al are mutually exclusive in CAIs (see Fig. 7 of Clayton *et al.* 1988 and an updated version, Fig. 16 of MacPherson 2003). Other CAIs have been found that also formed with a near absence of ^{26}Al , such as some hibonite grains in CM chondrites (Ireland 1988) and many grossite-bearing CAIs from the CH group of carbonaceous chondrites (Weber *et al.* 1995). Every comprehensive model for the origin of CAIs sooner or later stumbles over this conundrum: if the FUN CAIs preserve nonradiogenic nuclear anomalies better than their non-FUN counterparts, then presumably they must be less reprocessed, and likely are older; where then is the ^{26}Al ? Proposed solutions include late injection of ^{26}Al after the FUN CAIs formed (what happened to the nonradiogenic nuclear signatures when the non-FUN CAIs formed?), or simultaneous formation of differing CAI populations from isotopically distinct and separate reservoirs in the nebula (how did they stay so perfectly separate?), or even that the FUN CAIs are presolar in their entirety (why are they otherwise identical to non-FUN CAIs?; why are they not more isotopically anomalous?). None of these is entirely satisfying, and the entire argument could be largely laid to rest by making one measurement that has never been made: a high-precision absolute age date of a FUN CAI. We will return to this later.

3. A Brief Summary of What We Can Reasonably Infer about CAIs

3.1. Formation in the Innermost Solar System

In most workers' opinions, the beryllium isotopic systematics of CAIs point to most CAIs having formed very near the protosun. An efficient mechanism for producing ^{10}Be is energetic particle bombardment from the early sun; ^{10}Be cannot, however, be produced by stellar nucleosynthesis (interestingly, a lack of correlation between ^{10}Be and ^{26}Al in CAIs supports the idea that the ^{26}Al is of nucleosynthetic origin; see review by McKeegan & Davis 2003). The beryllium evidence also potentially sheds light on the origin of the oxygen isotopic signatures of CAIs. Most CAIs from all chondrite varieties had (before any secondary processing) almost the same oxygen isotopic composition, despite the fact that their host chondrites do not. This suggests that all CAIs formed in a relatively restricted region of the solar nebula and were subsequently dispersed to their chondrite-accretion sites. The beryllium evidence suggests that this restricted site was near the protosun (see Section 4.8 below).

3.2. Melted and Not Melted

Chondrules by definition are once-molten droplets; CAIs are not defined that way, and both melted and unmelted types are common (see MacPherson *et al.* 1988, for a review). CAIs were originally interpreted as preserved samples of solar nebula condensates, because their mineralogy so closely approaches that predicted by equilibrium calculations for the highest-temperature phases to condense from a hot solar gas upon cooling (e.g., Grossman 1972). We now know that many CAIs have experienced such severe reprocessing (including melting) that all morphological or textural evidence of condensation has been obliterated.

CAIs that to some degree appear to preserve their condensate origins include irregularly-shaped aggregates spanning a wide range of bulk composition and mineralogy, such as many melilite-rich (“Fluffy” Type A) inclusions (MacPherson & Grossman 1984), fine-grained spinel-rich aggregates that have condensation trace element fractionation patterns (Group II; see below), hibonite aggregates that occur in CM chondrites (e.g., MacPherson et al. 1984), and amoeboid olivine aggregates (Grossman & Steele 1976; Krot et al. 2004a).

Other CAIs clearly were melted. This conclusion is based partly on textural and mineral-chemical grounds and also on experimental synthesis studies that effectively reproduce the properties of some natural CAIs (see Stolper 1982). The melted objects span much of the same wide range of composition-mineralogy space as do the unmelted ones, and there is reasonable likelihood that the latter represent precursors to the former.

3.3. Nebular Formation by Volatility-Controlled Processes

Several lines of evidence lead to the robust conclusion that the bulk chemistry of CAIs originated through volatility-controlled processes, including both gas condensation and melt volatilization. The most direct clue is of course the bulk major element chemistry of CAIs, which closely resembles that of the first solids predicted by equilibrium calculations to condense out of a cooling high-temperature gas of solar composition (e.g., Yoneda & Grossman 1995). Similar compositions have been produced experimentally by evaporation of a melt of chondrite composition (e.g., Notsu et al. 1978). Important constraints also come from refractory trace element abundances in CAIs, including both lithophiles (silicate-preferring) such as the rare earth elements (REE) and scandium, and siderophiles (metal-preferring) such as the platinum group metals. Like calcium and aluminum, these refractory trace elements will be enriched in either the first (highest temperature) condensates or the last vestiges of residual melt during high temperature melt evaporation. Particularly important is how related elements are fractionated with respect to each other. The REE are particularly instructive in this regard; they are very geochemically coherent as a group, and they fractionate with respect to each other very differently during condensation or evaporation than they do during igneous crystallization. Some examples of REE abundance patterns in CAIs are plotted on Figure 3; the data are normalized to CI chondrite (solar) composition. Many CAIs exhibit patterns that are flat on such chondrite-normalized line diagram, like the one labeled “unfractionated” on Figure 3. In other words, the REE in these CAIs have the same relative abundances as they do in the sun; this rules out large-scale planetary processes such as igneous differentiation or core formation. Other CAIs do have fractionated trace element patterns, but these are totally unlike the kind of patterns that would result from any igneous fractionation processes. The pattern labeled in Figure 3 as “Group II” is important because such patterns can only be explained by fractional condensation (Boynton 1975; Davis & Grossman 1979). Yet another variety of fractionated pattern, labeled in Figure 3 as “HAL-Type” (named after the Allende FUN CAI, “HAL”), is believed to be the result of melt distillation (Davis et al. 1982; Ireland et al. 1992; Floss et al. 1996; Wang et al. 2001).

Two points should be made regarding condensation. First, during perfect equilibrium condensation, condensed solids continually equilibrate with the cooling gas and in many cases react with it to form new solid species. If such a process went to completion, CAIs would no longer exist. The fact that they do means that any condensation was fractional (e.g., Petaev & Wood 1998b), in the sense that some solids became isolated from contact with the gas and thus were prevented from reacting with it. The second point is that few if any CAIs are actual preserved condensate grains; invoking condensation as a process by which they originated implicitly refers to their precursors, because most if not all CAIs have been extensively reprocessed (including melting).

There is increasing consensus that many CAIs show the combined effects of both condensation and melt evaporation. However, agreement is lacking on the relative contribution and timing of each process. We will return to this issue below.

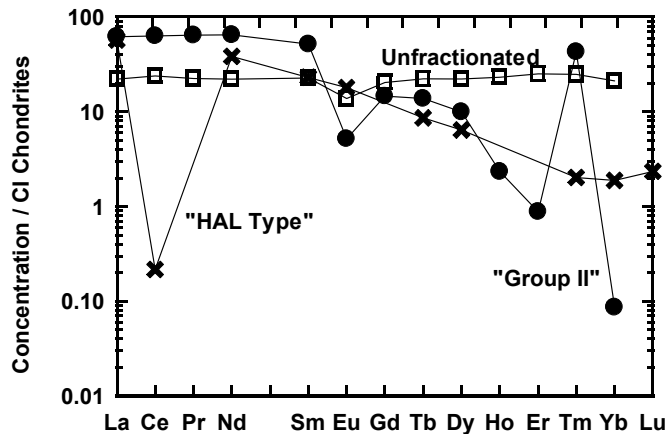


Figure 3. Examples of three different kinds of rare earth element fractionation patterns in CAIs

3.4. Formation Conditions

CAIs formed at very high temperatures, and in a very reducing environment. Many CAIs were melted, and at least some of those cooled too slowly to have done so by simple radiation of heat from a molten droplet into a vacuum.

During equilibrium condensation from a hot solar gas at a total nebular pressure of 10^{-3} atm, hibonite first condenses at $\sim 1470^{\circ}\text{C}$ and melilite first appears at $\sim 1355^{\circ}\text{C}$ (from the calculations of Yoneda & Grossman 1995). Even though few CAIs preserve direct evidence of their likely condensate heritage, their precursors probably began forming at such temperatures. For those CAIs that were melted, appropriate liquidus phase equilibria and CAI synthesis experiments in the laboratory yield directly applicable temperature constraints. For example, dynamic crystallization experiments on synthetic melts of Type B CAI composition by Stolper & Paque (1986) demonstrate that natural Type Bs experienced melting temperatures on the order of 1400°C . This temperature, which is well above the solidus ($\sim 1230^{\circ}\text{C}$;

Stolper 1982) but below the liquidus, was required to reproduce experimentally the textures and mineral chemistry of the natural CAIs. Other, more silica-deficient CAIs likely experienced far higher melting temperatures. For example, Simon et al. (1994) used existing phase equilibrium diagrams to argue that a grossite-bearing spherule from the Murchison meteorite began crystallizing at a temperature close to 2100°C.

MacPherson et al. (1984) and Stolper & Paque (1986) reported controlled cooling rate experiments on synthetic CAI melts. Such experiments attempt to reproduce as closely as possible the textures of natural objects. One of the conclusions of this work is that Type B CAIs (the only variety for which such experiments have been done) must have cooled at rates of a few to a few tens of degrees per hour. This is far slower (by orders of magnitude) than expected for a small (mm–cm) molten droplet cooling radiatively into vacuum. Grossman et al. (2000) introduced the further complication that Type B CAIs underwent fractional evaporation while molten. Follow-up studies by Mendybaev, Richter, & Davis (2003), Richter (2004), and Richter, Mendybaev, & Davis (2005) yielded experimental and numerical results that independently support the cooling rate estimates of Stolper & Paque (1986). Any successful models for CAI formation need to account for such externally constrained cooling rates.

Burns & Huggins (1973) and Dowty & Clarke (1973) showed that the pyroxene in Type B CAIs contains both trivalent and tetravalent titanium, in sub-equal abundance. Beckett (1986) showed experimentally that pyroxenes of such composition can only form in an extremely reducing environment ($\log f_{\text{O}_2} \sim -19$ at 1200°C), characteristic of a hot gas of solar composition.

4. Important Unresolved Problems in CAI Genesis and Evolution

4.1. What Were the Relative Roles of Solid Condensation and Melt Distillation in Determining CAI Bulk Compositions?

As noted above, it is generally accepted that CAIs owe their bulk compositions to volatility-controlled processes. Although most workers believe that condensation in some form was the original and dominant process, there is not universal agreement on that point. Even among those who favor condensation as the primary mechanism, there is no agreement about what the effects of melt distillation were. In some cases, especially some FUN inclusions and possibly even the Type B1 CAIs, late-stage melt distillation clearly modified the CAIs in ways that can be recognized petrologically. For example, in some extreme cases the mineralogy on the exterior of a CAI is chemically incompatible with that on the interior (see Davis et al. 1991). But these are second-order phenomena. The fundamentally important case concerns the overall bulk compositions of the entire span of earliest solar system objects, from CAIs through aluminum-rich chondrules through magnesium-rich (“normal”) chondrules.

The essential problem is illustrated in Figure 4, where the bulk compositions (silicate fractions) of a variety of CAIs and aluminum- as well as magnesium-rich chondrules are plotted on a diagram¹ suitable to display such a broad range of

¹ This diagram was originally constructed to show the crystallization behavior of spinel-saturated melts within the CaO-MgO-Al₂O₃-SiO₂ system, but is useful and completely valid

compositions (see MacPherson & Huss 2005). Shown for comparison is the predicted trend of the bulk composition (non-metallic fraction) of the total condensed solids during equilibrium condensation of a hot solar gas at 10^{-3} atm. The similarity of the two trends is remarkable, and yet there is a very clear and systematic deviation between the two. This deviation has been recognized for over 20 years (e.g., Stolper 1982), and continues to be the subject of much debate.

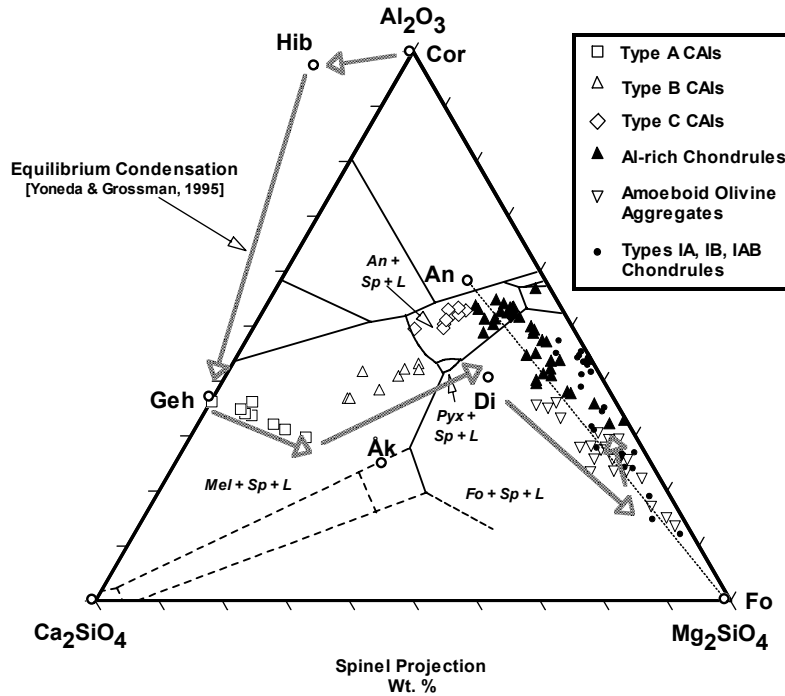


Figure 4. Compositions of three varieties of silica-rich CAIs (Types A, B, C), aluminum-rich chondrules, and ferromagnesian chondrules, plotted on the spinel-saturated ternary liquidus system Al_2O_3 - Ca_2SiO_4 - Mg_2SiO_4 (see MacPherson & Huss 2005). Also shown is the calculated trend for total condensed solids arising from equilibrium condensation of a hot solar gas (Yoneda & Grossman 1995). The field boundaries are applicable to spinel-saturated melts, which includes most of the objects plotted herein except the magnesium-rich (Type I) chondrules. Abbreviations: An—anorthite; Cor—corundum; Gro—grossite, CaAl_4O_7 ; Geh—gehlenite; Hib—hibonite; Mo—monticellite; Fo—forsterite; Pyx—calcium-rich pyroxene; Mel—melilite solid solution; Di—diopside; L—liquid; Sp—spinel.

here for showing bulk compositions of objects. It also gives a mineralogical frame of reference for the objects and theoretical trends that are plotted. Only objects with <3 wt% each of Na_2O and FeO are plotted, in part because the diagram is only valid for such compositions, but also because this reveals the primary bulk composition trends free from the later effects of secondary processes such as chondrule melting under variably oxidizing conditions after low-temperature condensation of alkalis.

Figure 5 shows a different aspect of the problem, in a plot of bulk CAI and chondrule CaO vs. Al_2O_3 contents. During perfect equilibrium condensation of a hot solar gas at 10^{-3} atm, the composition of the bulk condensed solid converges on the bulk chondritic (solar) Ca/Al ratio after melilite begins to condense, and maintains that ratio thereafter. As expected, the most refractory CAIs (e.g., hibonite-rich varieties) have distinctly subchondritic Ca/Al whereas less refractory materials (Al-rich and ferromagnesian chondrules) do have close to solar ratios. If CAI precursors formed by condensation, all CAIs should have subchondritic to chondritic ratios. Yet most Types A and B CAIs have superchondritic ratios. This has led to speculation (Grossman et al. 2000) that the methods used to calculate CAI bulk compositions systematically under-represent spinel in the As and Bs, producing superchondritic Ca/Al as an artifact.

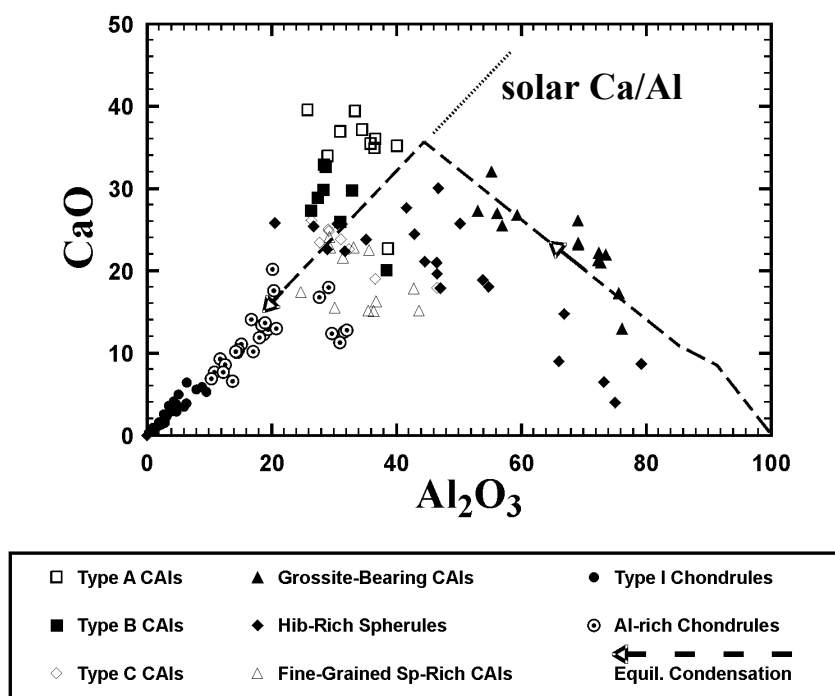


Figure 5. Bulk CaO vs. Al_2O_3 of diverse CAIs, aluminum-rich chondrules, and ferromagnesian chondrules. Also shown is the calculated trend for total condensed solids arising from equilibrium condensation of a hot solar gas (Yoneda & Grossman 1995).

The problem illustrated in Figure 4 is more difficult and complex. Indeed, the projection in Figure 4 does not reveal the full extent of the discrepancy between observed vs. calculated trends, particularly in magnesium and silicon. Two very different models currently exist to explain the discrepancies. In the first model,

original equilibrium condensates (i.e. plotting on the calculated trend on Fig. 4) were later melted and the melts underwent fractional distillation (Grossman *et al.* 2000, 2002; Richter *et al.* 2002; Davis & Richter 2004). Fractional distillation of a CMAS (CaO-MgO-Al₂O₃-SiO₂) melt will result in preferential loss of magnesium and silicon relative to calcium and aluminum. This model was proposed specifically to explain the Types A and B CAIs. The model addresses the observation that many Type A and B CAIs show small degrees of isotopic mass-dependent fractionation in favor of the heavy isotopes, which is consistent with melt distillation. The model is shown schematically on Figure 6a, where it can be seen that the effect of fractional distillation of melts derived from equilibrium condensates is to drive them toward the observed Type B trend. What this model does not explain are either the Type C (anorthite-rich) CAIs or aluminum-rich chondrules, which fall off the condensation trajectory in a direction that cannot be explained by distillation.

The second model involves only condensation, and focuses on the fact that the relative condensation sequence of the minerals anorthite and forsterite is pressure dependent (Krot *et al.* 2004b). This matters because the evolving bulk composition of the total condensed solids depends greatly on the sequence of condensing minerals. Most standard condensation models are calculated at 10⁻³ atm total nebular pressure, and under this condition forsterite condenses at a higher temperature than anorthite. Petaev and Wood (1998a) showed, however, that at lower pressure (the critical value of which is debated; see below) anorthite precedes forsterite and condenses immediately following diopside. MacPherson, Petaev, & Krot (2004) and Krot *et al.* (2004b) argued that the textures, mineralogy, and bulk compositions of many CAIs are most consistent with a low-pressure condensation sequence in which anorthite preceded forsterite, and that this is at the heart of the discrepancy shown in Figure 4.

The condensation paths shown in Figure 4 track the progressive sequence of condensing phases: at 10⁻³ atm, forsterite begins condensing immediately following calcic pyroxene, and the bulk composition trend evolves down to the lower right away from diopside and misses the region of the diagram occupied by Type C CAIs and aluminum-rich chondrules. However, at 10⁻⁵ atm (from the calculations of MacPherson *et al.* 2004), the calculated trend (Fig. 6b) evolves from diopside toward anorthite and projects much closer to the Type Cs and aluminum-rich chondrules. It should be emphasized, however, that the diagrams in Figures 4 and 6 do not reveal a major problem all condensation models have in explaining very SiO₂-rich compositions of some Al-rich and ferromagnesian chondrules.

Both models have advantages, and both may have played a role in CAI evolution. It is important to test and evaluate both models. For the condensation-evaporation model, what are needed (e.g., Davis & Richter 2004) are detailed high-precision measurements with high spatial resolution, of isotopic mass-dependent fractionation within a variety of CAIs, particularly focusing on core-to-rim variations, with the goal of establishing chemical *vs.* isotopic correlations.

On the condensation side, different sets of calculations by different workers give different results; although there is agreement that the anorthite - forsterite condensation order is pressure-sensitive, there is disagreement over what the critical pressure is. MacPherson *et al.* (2004) found the forsterite-anorthite condensation

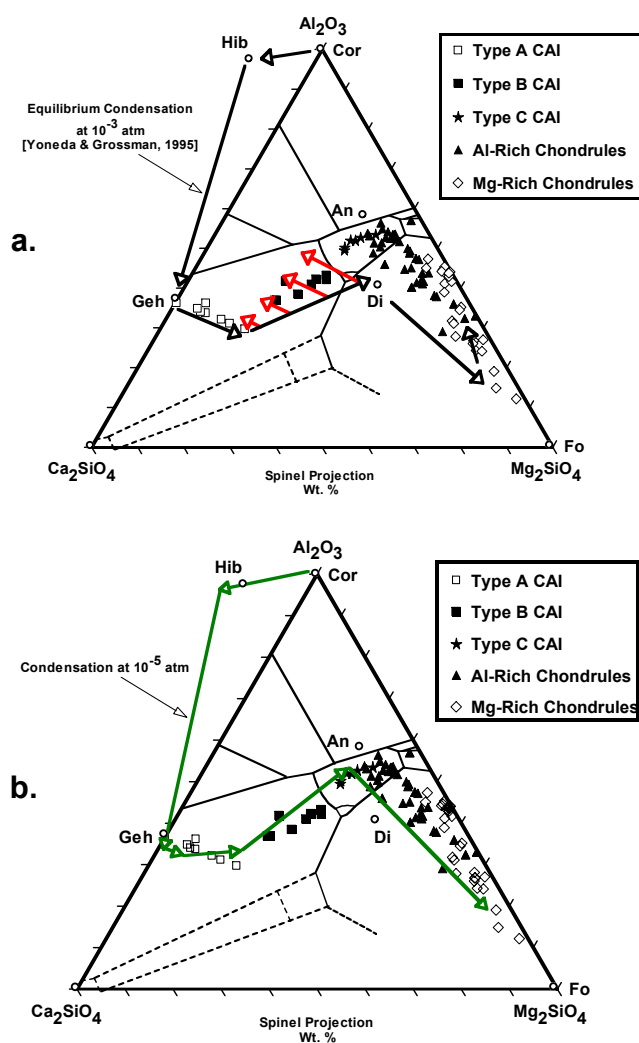


Figure 6. Two models (see text and references therein) for explaining the discrepancy between observed CAI bulk compositions and the predictions of equilibrium condensation. In both cases, the compositions of silica-rich CAIs and aluminum-rich chondrules are plotted as in Figure 3. (a) Fractional distillation of melts derived from equilibrium condensates (Yoneda & Grossman 1995) drives the melt compositions toward the observed Type B CAI trend. However, the Type C CAI and aluminum-rich chondrule trends are missed. The distillation arrows as shown are highly schematic, but give the sense of the effects of volatilization as outlined by, e.g., Grossman et al. (2000). (b) Equilibrium condensation at very low nebular pressures causes anorthite condensation to precede that of forsterite, with the result that the predicted trend passes through Types B and C CAIs and comes much closer to the field of the aluminum-rich chondrules. The condensation trend shown is taken from MacPherson et al. (2004).

crossover pressure to be $\sim 10^{-5}$ atm, whereas the calculations of Ebel and Grossman (2000) indicate the crossover pressure to be more like 10^{-7} atm. This disagreement arises from the different thermodynamic data used to make the calculations. Assessment of the internal consistency of the different sets of thermodynamic data and independent estimates of nebular pressures are important to help resolve this issue.

4.2. What (If Any) Are the Age Differences between CAIs and Chondrules Within Each Chondrite Type, and between Different Kinds of CAIs?

Knowing the formation ages of different kinds of early solar system materials is critical to understanding the sequence of events in the solar nebula and the duration of the nebular phase itself. Until recently, the only tool for addressing this problem has been to measure inferred initial $^{26}\text{Al}/^{27}\text{Al}$ ratios because the precision of the best absolute radiometric chronometer (Pb-Pb) was ± 1 My, which is comparable to the inferred age differences between objects being compared (e.g. chondrules vs. CAIs). But there have been two problems with using ^{26}Al . First, in order for the data to have any chronologic significance, it must be established that the isotopic reservoir out of which different objects formed was the same; i.e. the nebula was homogeneous with respect to ^{26}Al . The difficulty here is that there are objects, such as FUN CAIs, that are presumably (because they preserve nuclear anomalies) the same age as or even older than non-FUN CAIs, yet they had little or no ^{26}Al at the time of their formation. Second, if the inferred (from ^{26}Al) 1–2 My age differences between CAIs and chondrules or between CAI primary minerals and the secondary minerals replacing them are taken at face value, that difference is significantly longer than the time scale required for CAIs to fall into the sun due to gas drag. For that reason, some workers were unwilling to attach any age significance to the ^{26}Al data. Amelin *et al.* (2002) made a major step forward by obtaining Pb-Pb ages of chondrules and CAIs with precisions significantly ≤ 1 My; their data showed, for the first time, unambiguous age differences between chondrules and CAIs of ~ 2.5 My. Note however, that the measured chondrules were from the CR chondrite Acfer 059 and the CAIs were from CV3 Efremovka. More recently, the waters have been muddied again by three developments: (a) Amelin *et al.* (2004) found ages for Allende (CV3) chondrules that are nearly indistinguishable from those of the Efremovka CAIs; (b) Galy, Hutcheon, & Grossman (2004) and Young *et al.* (2005) reported high-precision magnesium isotope analyses of CAIs, using multi-collector inductively coupled plasma mass spectrometry (MC ICP-MS), that imply initial $^{26}\text{Al}/^{27}\text{Al}$ ratios of $6\text{--}7 \times 10^{-5}$, significantly greater than the “canonical” value of 5×10^{-5} ; and (c) Bizzarro, Baker, & Haack (2004) reported high precision MC ICP-MS magnesium data suggesting that Allende chondrules span a range of ages from 1.4 My younger than CAIs to the same age as Allende CAIs. It is important to emphasize that the evidence for supercanonical $^{26}\text{Al}/^{27}\text{Al}$ comes entirely from analyses of low Al/Mg phases; no reliable data for high Al/Mg phases have ever been reported that are consistent with such high initial ratios. Therefore the significance of the new data is the subject of considerable debate. Much more work is needed to evaluate these results.

The trend of CAI bulk compositions shown on Figure 4, paralleling as it does the equilibrium condensation trend, naturally suggests an evolutionary trend for the CAIs, starting with hibonite-rich varieties and progressing through melilite-rich Type

As, the Type Bs, and finally the Type Cs. However, there are no systematic comparative absolute age data for different types of CAIs to show whether there are any temporal differences between them; Amelin et al. (2002) did analyze two very different CAIs (a Type A and a forsterite-bearing Type B) and found no resolvable age difference between them. The only potential evidence for a spread in CAI formation ages may come from the short-lived radionuclides such as ^{26}Al . On histograms such as that in Figure 2 for example, the width of the peak at the maximum inferred initial ratio (in this case, centered at initial $^{26}\text{Al}/^{27}\text{Al} \sim 4.5 \times 10^{-5}$) could be used to infer a spread in CAI ages if the data are sufficiently precise. Unfortunately, the peak width in Figure 2 is probably due to analytical uncertainty in the ion probe data (MacPherson et al. 1995). However, several recent studies have applied more precise analytical techniques to the problem of trying to resolve a real component to the peak width. The studies by Galy et al. (2004), Bizzarro et al. (2004), and Young et al. (2005) employed MC-ICPMS to obtain initial $^{26}\text{Al}/^{27}\text{Al}$ values on CAIs, ranging from $\sim 5 \times 10^{-5}$ (Bizzarro et al.) to $\sim 7 \times 10^{-5}$ (Galy et al.; Young et al.). Bizzarro et al. (2004) concluded from their very tight data set that the CAI formation interval might have been as short as 5×10^4 years; however, Young et al. (2005) concluded that CAIs evolved in the nebular disk for as long as 3×10^5 years before the apparent canonical initial $^{26}\text{Al}/^{27}\text{Al}$ value 5×10^{-5} was effectively locked into most CAIs.

Thus the development of high precision magnesium isotopic analysis techniques—MC-ICPMS and multicollector SIMS—is allowing new questions to be addressed about early solar system chronology: (1) are the differences between different kinds of CAIs, and between chondrules and CAIs, the result of temporal or spatial separation or both?; (2) is there an age sequence among the different (volatility-ordered) CAI varieties?; and (3) what is the real width of the ^{26}Al histogram?

The importance of knowing the relative ages of CAIs and chondrules, of the duration of CAI formation, and of CAI nebular evolution time scales, cannot be overstated. All physical models for the evolution of the earliest solar nebula will be severely constrained by the data. The following data are urgently required: (1) paired high-precision absolute ages for chondrules and CAIs from the same meteorites, for a variety of meteorite types; (2) high-precision absolute ages for a spectrum of CAI types, to see if there is an evolutionary sequence; (3) paired high-precision whole-CAI and whole-chondrule magnesium isotope data, together with internal mineral isochrons for the same objects; and (4) a high precision absolute age for at least one *bona fide* FUN CAI.

4.3. What is the CAI – Chondrule Connection?

CAIs and chondrules both formed by high temperature processes in the earliest stages of the solar nebula, and they both ended up being accreted into the same parent bodies. And, as noted in the previous section, there is a further suggestion from both short-lived radionuclides and absolute radiometric ages that the onset of CAI formation and the onset of chondrule formation may have been offset in time by as much as 2.5 My. Regardless of the time interval, however, the two groups of objects remained largely separate until their accretion into mutual parent bodies, and we do

not understand the mechanism of the separation. We do not know if chondrules and CAIs formed by the same process or whether two entirely different processes were involved. We do not know if they formed in different places, or simply at different times, or both.

From a chemical and petrologic point of view, aluminum-rich chondrules and compound CAI-chondrule objects link the ferromagnesian chondrules and CAIs. It is precisely the properties of these materials that document just how separated CAIs and chondrules were. The bulk composition data plotted on Figure 4 shows that the aluminum-rich chondrules disperse along a line that extends from the direction of the mineral forsterite towards the mineral anorthite and the compositions of Type C CAIs, which are anorthite and pyroxene-rich, melilite-poor CAIs. The critical point is that the trend does *not* extend at all in the direction of melilite or melilite-rich CAIs. Whether aluminum-rich chondrules formed by melting of relatively pristine condensates or by remelting of chondrule-CAI hybrids, melilite was missing from the precursors. Because melilite and melilite-rich CAIs presumably existed at the *time* that the aluminum-rich chondrules formed, they must have been missing from the *place* where the chondrules formed; only plagioclase-pyroxene-spinel-rich CAIs were present. Evidence supporting this conclusion is the fact that the rare compound CAI-chondrule objects that have been described contain spinel, pyroxene, anorthite, hibonite, and grossite as their principal CAI minerals (Misawa & Fujita 1994; Maruyama, Yurimoto & Sueno 1999; Krot & Keil 2002; Krot, Hutcheon, & Keil 2002; Itoh & Yurimoto 2003; Krot et al. 2005a; Russell et al. , this volume). Again, the missing component is melilite. MacPherson & Huss (2005) suggested that somehow CAIs became separated into two populations, one of which became isolated from the solar nebula until just prior to accretion (these retained their melilite) and the other remained in contact with the gas and consequently continued to react with it (these lost their melilite to the reactions). But whatever the reason, solving the puzzle of the missing melilite will be critical to ultimately understanding the spatial and temporal relationship between chondrules and CAIs.

4.4. Why are CAIs and Chondrules Sorted into Different Size and Type Populations Within Different Chondrite Types?

The discoveries that most or all CAIs formed out of a uniform oxygen isotopic reservoir, and that CAIs contained live ^{10}Be at the time of their formation, led to the idea (e.g., McKeegan et al. 1998; Guan et al. 2000; Fagan et al. 2001) that CAIs formed in a single restricted spatial region of the solar nebula, near the protosun, and were later dispersed outwards into the diverse chondrite-accretion regions by, for example, bipolar outflow such as that described by Shu, Shang, & Lee (1996). One problem for this model is that the CAI populations of the different chondrite varieties differ. Why should grossite-rich CAIs be common only in the CR and CH chondrites and yet be so rare in others? One suggestion is that locally high dust/gas ratios stabilize grossite (Ivanova et al. 2002), but this needs to be tested. Equally, why are very large CAIs and Type B CAIs restricted to CV3 chondrites? Why are inclusions in CM chondrites so deficient in melilite? These effects cannot be attributed to size sorting: with the exception of the large CAIs in the CV3s, those in other chondrite groups are all of roughly comparable sizes.

There is a qualitative decoupling of size sorting between chondrules and CAIs with respect to their host chondrites. Although it is true that the largest CAIs occur in the CV chondrites, which also have very large chondrules, all other chondrites have comparably small CAIs regardless of the average chondrule sizes. And the LL chondrites represent a counterexample to the CV3s: chondrules in the LL chondrites are similar in size to those in CV3s, but the LL CAIs are far smaller than those of the CVs. To our knowledge no correlated, systematic quantitative study of size sorting of chondrules and CAIs in each of the major chondrite types has ever been conducted; only chondrules have been considered. A beginning of such a study can be found in May et al (1999), who studied only CV and CO chondrites and found that CVs have both larger chondrules and larger CAIs than do the COs. Clearly, a quantitative understanding of the decoupling of chondrule vs. CAI size sorting will provide a fundamental constraint on how and where each of these populations of objects formed.

4.5. Why are ^{26}Al and Nuclear Isotope Anomalies Mutually Exclusive?

One of the originally defined characteristics of FUN CAIs is their general lack of ^{26}Al at the time of formation, in contrast with other CAIs (see above). However, what really brought this observation into focus was a diagram published in Clayton et al. (1988), reproduced here in Figure 7. The graph plots titanium isotope compositions ($\delta^{50}\text{Ti}$) versus the inferred initial $^{26}\text{Al}/^{27}\text{Al}$ ratios measured in a variety of CAIs (mostly from CV and CM meteorites; see Clayton et al. 1988 for data sources). It shows that, to first order, the two components are mutually exclusive. FUN and the related UN CAIs have large $\delta^{50}\text{Ti}$ anomalies but little or no ^{26}Al , whereas other CAIs have just the reverse. The implication of this remarkable observation is that the two isotopic signatures remained largely separated during CAI formation. Either FUN/UN CAIs formed in a completely different place and/or time from other CAIs, from different material, and yet by parallel processes that rendered the two groups of CAIs otherwise indistinguishable from each other, or else the precursor grains for the two groups of objects simply did not mix during a single process. This mystery lies at the heart of understanding both what FUN CAIs are and, also, the very nature of isotopic reservoirs in the solar nebula. It also bears on the question of the origin of ^{26}Al : was it produced locally within the solar system (e.g., Shu et al. 1996) or was it produced in a nearby supernova shortly before solar system formation? Also relevant is the origin of the ^{50}Ti anomalies, as these can arise in Type Ia or Type II supernovae (Wallerstein et al. 1997). Obtaining an absolute radiometric age date of a FUN (or UN) CAI will be one necessary step in resolving the mystery. Studies of nuclear anomalies in new FUN/UN inclusions would also be a significant advance. It is interesting and frustrating to note that no presolar grains ever been found (or at least recognized) in a CAI, not even the most primitive unmelted aggregates, and this remains a mystery.

4.6. What is the Origin of the Internal Oxygen Isotopic Heterogeneity in CV3 CAIs?

Clayton *et al.* (1977) showed that the phases within individual CAIs in Allende disperse along the same slope ~ 1 line as do the data for bulk CAIs. A wealth of ion microprobe data obtained subsequently by many workers has refined the details somewhat but the basic pattern is the same; an illustrative data set from one such CAI is shown in Figure 8. Spinel and pyroxene are consistently ^{16}O -rich, and anorthite and melilite are ^{16}O -poor. This pattern is not the result of simple igneous fractionation. The original explanation is that the CAIs originally formed with homogeneous internal isotopic compositions at the extreme ^{16}O -rich (lower left) end of the line, but that later solid-state exchange with a different and ^{16}O -poor reservoir caused those minerals with the fastest oxygen diffusion rates to exchange more completely than phases with much slower diffusion rates. This model is supported in part by the fact that CAIs from other chondrite types tend to have more uniform—and in many cases uniformly ^{16}O -rich—internal compositions, including even melilite. However, this same observation implies that the CV CAIs have had some kind of unusual history that is possibly related to secondary processes. An unresolved problem with this model is that experimentally determined diffusion rates do not entirely support the model (Ryerson & McKeegan 1994). Alternative models, such as dynamic crystallization during isotopic exchange of molten ^{16}O -rich droplets in a ^{16}O -poor gaseous reservoir, tend to be inconsistent with the CAI crystallization sequences (especially for the Type Bs, where such a model would predict that spinel and melilite should be ^{16}O -rich relative to pyroxene and anorthite).

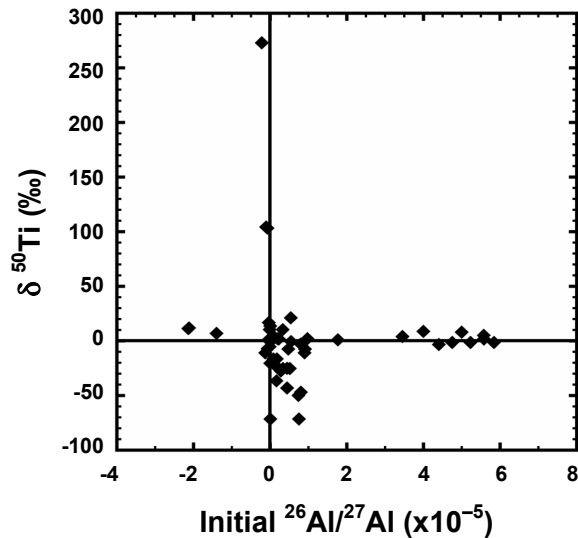


Figure 7. Measured $\delta^{50}\text{Ti}$ anomalies vs. calculated initial $^{26}\text{Al}/^{27}\text{Al}$ ratios in CAIs, showing that CAIs with $\delta^{50}\text{Ti} > \sim 10$ have $^{26}\text{Al}/^{27}\text{Al} < 1 \times 10^{-5}$. Essentially, the points plot on one axis or the other but not in between.

4.7. Where and When Did Secondary Processing of CAIs Occur?

CAIs in virtually all chondrite types show evidence of secondary alteration; that is, primary phases (especially melilite and anorthite) are partially replaced by a different suite of minerals that rim, vein, texturally corrode, or even pseudomorph the primary phases. Some secondary phases such as nepheline, sodalite, hedenbergite, andradite, and phyllosilicates, are highly enriched in components (alkalis, oxidized iron, water) that are lacking in the primary phases. Other secondary phases such as monticellite, wollastonite and grossular differ from the primary ones mainly in having higher silica contents.

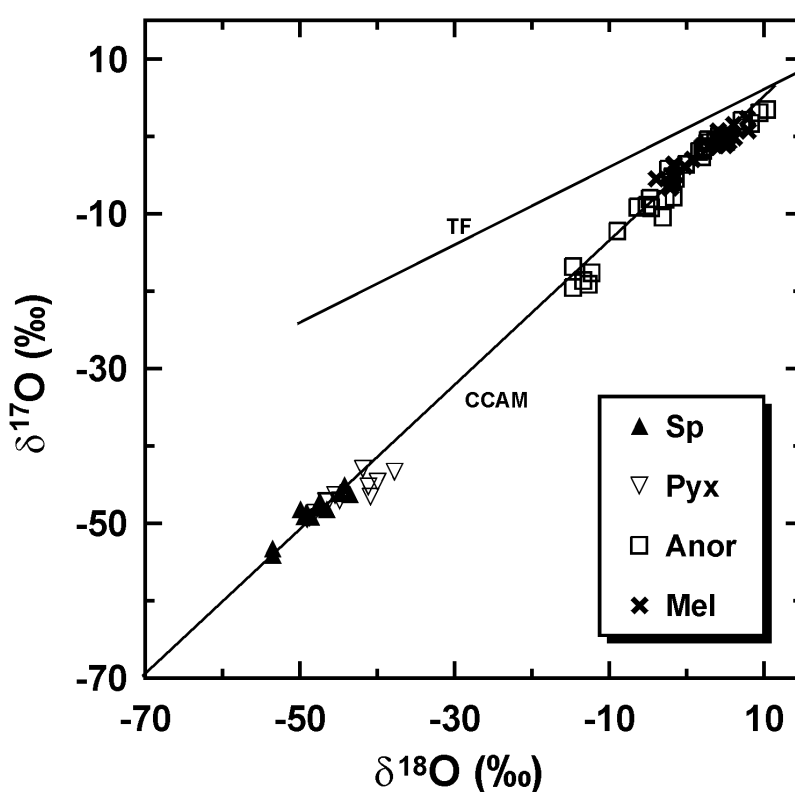


Figure 8. A three-isotope plot for oxygen in a single Type B Allende CAI. Spinel and pyroxene are highly enriched in ^{16}O , whereas anorthite and melilite are not. Data from McKeegan et al. (1996). Abbreviations: TF—terrestrial fractionation line; CCAM—carbonaceous chondrite anhydrous minerals line.

The most advanced examples are in the oxidized subgroup CV3 chondrites and many of the CO3s, where both oxidized-iron-bearing and alkali-rich phases are abundant in most CAIs; veins containing grossular, fine-grained anorthite, aluminous diopside, and monticellite cross-cut many Type B CAIs. In the reduced-subgroup

CV3 meteorites, oxidized-iron-bearing and alkali-rich phases are either lacking (Efremovka and Leoville) or in very low abundance (Vigarano). Veins are less common than in the oxidized CV3s, but where present contain fine-grained anorthite and aluminous diopside. Some phases in CAIs in the CM meteorites have been partially replaced with hydrous phyllosilicates.

A lively debate has continued for more than ten years about the origin of this secondary alteration (see Krot, Scott, & Zolensky 1995; review by Brearley 2003), basically dividing into the nebular vs. asteroidal parent body camps. The debate has especially focused on the CV and CM chondrite groups, and not just on their CAIs but also on the meteorites as a whole. Good arguments are made on both sides (Brearley's 2003 review gives a good summary). Increasingly, however, there is evidence that not only did secondary processing extend over a significant time period (several My) but, also, multiple processes may have been involved that occurred in different settings or, at least, under very different conditions. Specifically, the event that introduced oxidized iron and alkalis may have been separate from the ones that produced fine-grained anorthite + aluminous diopside and grossular + monticellite + wollastonite. In general, secondary minerals show no evidence for the presence of live ^{26}Al at the time they formed, even though the primary phases they replace commonly show "canonical" initial $^{26}\text{Al}/^{27}\text{Al}$ ratios of $\sim 5 \times 10^{-5}$; this suggests that secondary alteration occurred 2 My or more after formation of the primary phases. However, clear excesses of ^{26}Mg have been reported in sodalite and nepheline from one Allende CAI (Brigham et al. 1986), in sodalite from a CAI in Semarkona (LL3; Huss et al. 2001), and in grossular from another Allende CAI (Fagan et al. 2005); in all three cases, the initial $^{26}\text{Al}/^{27}\text{Al}$ ratios are close to 5×10^{-5} . In the Allende CAI in which grossular shows evidence for ^{26}Al , nepheline and secondary anorthite in the same CAI show no such ^{26}Mg excesses; this argues against the isotopic signature of the grossular simply being an inherited relict from the precursor melilite. Therefore, secondary alteration phases apparently formed over very extended periods of time and possibly in multiple episodes, starting almost contemporaneously with primary CAI formation and extending (even within individual CAIs) over at least 2 My. *It is difficult to reconcile the entire data set with either a nebular setting or a parent body setting alone.* Much more work on the isotopic signatures of secondary phases is required to constrain the timing and setting(s) of secondary processing, and the different types involved.

The multilayered rim sequences (Wark & Lovering 1977) that surround most CAIs are a special case here, because although they must be later than the CAIs they enclose, they consist of the same primary high temperature minerals as the CAI interiors. They represent later reprocessing of the CAIs, but clearly are unrelated to the secondary alteration described above. Indeed, the rim sequences must have formed relatively early because they are ^{16}O -rich, but the rims themselves were subjected to the same secondary mineralization as affected the CAIs they mantle. Wark-Lovering rims clearly mark a fundamental event in the history of most CAIs, but after 25+ years of studying them we still basically do not understand what the nature of the event was (see review in MacPherson 2003).

4.8. Do Oxygen and Beryllium Isotopes Correlate?

Among the short-lived radionuclides now known to have been present in CAIs at the time of their formation, ^{10}Be is a special case because it is likely to have been produced locally within the solar nebula by energetic particle bombardment from the early sun (although Desch, Connolly, & Srinivasan 2004 and Cameron 2001 propose alternative models). If the local-origin model is correct, then distance from the sun is one critical parameter in CAI formation. An analogous situation might exist with oxygen. Although the enrichment in ^{16}O that characterizes most CAIs is now believed to simply reflect the bulk composition of the sun (Yurimoto & Kuramoto 2004; Hashizume & Chaussidon 2005; Krot et al. 2005b), the location where the ^{16}O -poor component was produced and introduced into later materials such as chondrules remains unknown. In one class of models, the ^{16}O -poor component is produced by self-shielding very near the protosun (Clayton 2002).

If ^{16}O and ^{10}Be both were in fact produced near the protosun, then the abundances of these isotopes might conceivably correlate when compared across objects as different as CAIs and chondrules. Some ferromagnesian and aluminum-rich chondrules do show enrichment in ^{16}O , but at much lower levels than in the CAIs (e.g., Russell et al. 2000; Krot et al. 2005b). Evidence for ^{10}Be has been searched for in chondrules (Sugiura 2001) but the evidence is inconclusive; this is in part an analytical sensitivity problem. If there is a correlation, this would serve as a test of the Clayton (2002) model for production of the ^{16}O -poor isotopic component. In the event that such a correlation is found, a heliocentric yardstick might result that would apply to the innermost solar system and possibly provide a test for the idea that CAIs and chondrules originated at different heliocentric distances.

Determining whether there is or is not a correlation will require solving the analytical problem of measuring boron and beryllium isotopes in chondrules. This may require a technique intrinsically more sensitive and precise than SIMS, such as laser resonance ionization.

Acknowledgments. This manuscript benefited greatly from reviews by Drs. Sara Russell, Associate Editor Matthieu Guenelle, and Ed Scott. This work was supported by NASA grants NAG5-10468 (G. J. MacPherson, P.I.), NAG5-13131 (A. N. Krot, P.I.), NAG5-11588 (L. Grossman, P.I.), NAG5-12997 (A. Davis, P.I.), and NAG5-11591 (K. Keil, P.I.).

References

- Amelin, Y., Krot, A. N., Hutcheon, I. D., & Ulyanov, A. A. 2002, *Science*, 297, 1678
Amelin, Y., Krot, A. N., & Twelker, E. 2004, *Geochim. Cosmochim. Acta*, 68, A759
Beckett, J. R. 1986, PhD Dissertation, Univ. Chicago, 373
Birck, J.-L., & Allègre, C. J. 1985, *Geophys. Res. Lett.*, 11, 745
Bizzarro, M., Baker, J. A., & Haack, H. 2004, *Nature*, 431, 275
Boynton, W.V. 1975, *Geochim. Cosmochim. Acta*, 39, 569
Brearley, A. J. 2003, in *Meteorites, Planets, and Comets*, ed. A. M. Davis, Vol. 1, Treatise on Geochemistry, eds. H. D. Holland, & K. K. Turekian (Oxford: Elsevier-Pergamon), 247
Brearley, A. J., & Jones, R. H. 1998, in *Planetary Materials*, ed. J. J. Papike, Reviews in

- Mineralogy, Vol. 36, (Washington, DC: Mineralogical Society of America), 3-1
- Brigham, C. A., Hutcheon, I. D., Papanastassiou, D. A., & Wasserburg, G. J. 1986, *Lunar Planet. Sci.*, 17, 85.
- Burns, R. G., & Huggins, F. E. 1973, *Amer. Mineral.*, 58, 955
- Cameron, A. G. W. 2001, *ApJ*, 562, 456
- Cameron, A. G. W., & Truran, J. W. 1977, *Icarus*, 30, 447
- Christophe Michel-Lévy, M. 1968, *Bull. Soc. Fr. Minéral. Cristallogr.*, 91, 212
- Clayton, R. N. 2002, *Nature*, 415, 860
- Clayton, R. N., & Mayeda, T. K. 1977, *Geophys. Res. Lett.*, 4, 295
- Clayton, R. N., Grossman, L., & Mayeda, T. K. 1973, *Science*, 182, 485
- Clayton, R. N., Hinton, R. W., & Davis, A. M. 1988, *Phil. Trans. R. Soc. Lond.*, 325, 483
- Clayton, R. N., Onuma, N., Grossman, L., & Mayeda, T. K. 1977, *Earth Planet. Sci. Lett.*, 34, 209
- Davis, A. M., & Richter, F. M. 2004, in *Meteorites, Planets, and Comets*, ed. A. M. Davis, Vol. 1, *Treatise on Geochemistry*, eds. H. D. Holland, & K. K. Turekian (Oxford: Elsevier-Pergamon), 407
- Davis, A. M., Tanaka, T., Grossman, L., Lee, T. & Wasserburg, G. J. 1982, *Geochim. Cosmochim. Acta*, 46 1627
- Davis, A. M. & Grossman, L. 1979, *Geochim. Cosmochim. Acta*, 43, 1611
- Davis, A. M., MacPherson, G. J., Clayton, R. N., Mayeda, T. K., Sylvester, P., Grossman, L., Hinton, R. W., & Laughlin, J. R. 1991, *Geochim. Cosmochim. Acta*, 55, 621
- Davis, A. M., Richter, F. M., Mendybaev, R. A., Janney, P. E., Wadhwa, M., & McKeegan, K. D. 2005, *Lunar Planet. Sci.*, 36, 2334
- Desch, S. J., Connolly, H. C. Jr., & Srinivasan, G. 2004, *ApJ*, 602, 528
- Dowty, E., & Clarke, R. S. Jr. 1973, *Amer. Mineral.*, 58, 230
- Fagan, T. J., McKeegan, K. D., Krot, A. N., & Keil, K. 2001, *Meteorit. Planet. Sci.*, 36, 223
- Fagan, T. J., Guan, Y., MacPherson, G. J., & Huss, G. R. 2005, *Lunar Planet Sci.*, 36, 1820
- Floss, C., El Goresy, A., Zinner, E., Kransel, G., Rammensee, W., & Palme H. 1996, *Geochim. Cosmochim. Acta*, 60, 1975
- Galy, A., Hutcheon, I. D., & Grossman, L. 2004, *Lunar Planet. Sci.*, 35, 1790
- Gray, C. M., Papanastassiou, D. A., & Wasserburg, G. J. 1973, *Icarus*, 20, 213
- Grossman, L. 1972, *Geochim. Cosmochim. Acta*, 36, 597
- Grossman, L. 1975, *Geochim. Cosmochim. Acta*, 39, 433
- Grossman, L. 1980, *Ann. Rev. Earth Planet. Sci.*, 8, 559
- Grossman, L., & Steele I. M. 1976, *Geochim. Cosmochim. Acta*, 40, 149
- Grossman, L., Ebel, D. S., Simon, S. B., Davis, A. M., Richter, F. M., & Parsad, P. M. 2000, *Geochim. Cosmochim. Acta*, 64, 2879
- Grossman, L., Ebel, D. S., & Simon, S. B. 2002, *Geochim. Cosmochim. Acta*, 66, 145
- Guan, Y., McKeegan, K. D., & MacPherson, G. J. 2000, *Earth Planet. Sci. Lett.*, 181, 271
- Hashizume, K., & Chaussidon, M. 2005, *Nature*, 434, 619
- Huss, G. R., Fahey, A. J., Russell, S. S., & Wasserburg, G. J. 1995, *Lunar Planet Sci.*, 26, 641
- Huss, G. R., MacPherson, G. J., Wasserburg, G. J., Russell, S. S., & Srinivasan, G. 2001, *Meteorit. Planet. Sci.*, 36, 975
- Ireland, T.R. 1988, *Geochim. Cosmochim. Acta*, 52, 2827
- Ireland, T. R., & Fegley, B. Jr. 2000, *Int. Geol. Rev.*, 42, 865
- Ireland, T. R., Fahey, A. J., & Zinner, E. K. 1988, *Geochim. Cosmochim. Acta*, 52, 2841
- Ireland, T. R., Zinner, E. K., Fahey, A. J., & Esat, T. M. 1992, *Geochim. Cosmochim. Acta*, 56, 2503
- Itoh, S., & Yurimoto, H. 2003, *Nature*, 423, 728
- Ivanova, M. A., Petaev, M. I., MacPherson, G. J., Nazarov, M. A., Taylor, L. A., & Wood J. A. 2002, *Meteorit. Planet. Sci.*, 37, 1337

- Jones, R. H., Lee, T., Connolly, H. C. Jr., Love, S. G., & Shang, H. 2000, in *Protostars and Planets IV*, eds. V. Mannings, A. P. Boss, & S. S. Russell, (Tucson: Univ. Arizona Press), 927
- Krot, A. N., & Keil, K. 2002, *Meteorit. Planet. Sci.*, 37, 91
- Krot, A. N., Scott, E. R. D., & Zolensky, M. E., 1995, *Meteoritics*, 30, 748
- Krot, A. N., Hutcheon, I. D., & Keil, K. 2002, *Meteorit. Planet. Sci.*, 37, 155
- Krot, A. N., Petaev, M. I., Russell, S. S., Itoh, S. J., Fagan, T. J., Yurimoto, H., Chizmadia, L., Weisberg, M. K., Komatsu, M., Ulyanov, A. A., & Keil, K. 2004a, *Chem. Erde*, 64, 185
- Krot, A. N., MacPherson, G. J., Ulyanov, A. A., & Petaev M. I., 2004b, *Meteorit. Planet. Sci.*, 39, 1517
- Krot, A. N., Yurimoto, H., Hutcheon, I. D., & MacPherson, G. J. 2005a, *Nature*, 434, 998
- Krot, A. N., Hutcheon, I. D., Yurimoto, H., Cuzzi, J. N., McKeegan, K. D., Scott, E. R. D., Libourel, G., Chaussidon, M., Aléon, J., & Petaev, M. I. 2005b, *ApJ*, 622, 1333
- Lee, T. 1978, *ApJ*, 224, 217
- Lee T., Papanastassiou D.A. & Wasserburg G.J. 1976, *Geophys. Res. Lett.*, 3, 109
- Loss, R. D., Lugmair, G. W., Davis, A. M., & MacPherson, G. J. 1994, *ApJ*, 436, L193
- Lyons, J. R., & Young, E. D. 2005, *Nature*, 435, 317
- MacPherson, G. J., 2003, in *Meteorites, Planets, and Comets*, ed. A. M. Davis, Vol. 1, *Treatise on Geochemistry*, eds. H. D. Holland, & K. K. Turekian (Oxford: Elsevier-Pergamon), 201
- MacPherson, G. J., & Grossman, L. 1984, *Geochim. Cosmochim. Acta*, 48, 29
- MacPherson, G. J., & Huss, G. R. 2005, *Geochim. Cosmochim. Acta*, in press
- MacPherson, G.J., Paque, J.M., Stolper, E. & Grossman, L. 1984, *J. Geol.*, 92, 289
- MacPherson, G. J., Petaev, M. I., & Krot, A. N. 2004, *Lunar Planet. Sci.*, 35, 1838
- MacPherson, G. J., Bar-Matthews, M., Tanaka, T., Olsen, E., & Grossman L. 1983, *Geochim. Cosmochim. Acta*, 47, 823
- MacPherson, G. J., Wark, D. A., & Armstrong, A. 1988, in *Meteorites and the Early Solar System*, eds. J. F. Kerridge, & M. S. Matthews (Tucson: Univ. Arizona Press), 746
- MacPherson, G. J., Davis, A. M., & Zinner, E. 1995, *Meteoritics*, 30, 365
- MacPherson, G. J., Huss, G. R., & Davis, A. M. 2003, *Geochim. Cosmochim. Acta*, 67, 3165
- Maruyama, S., Yurimoto, H., & Sueno, S. 1999, *Earth Planet. Sci. Lett.*, 169, 165
- May, C., Russell, S. S., & Grady, M. M. 1999, *Lunar Planet. Sci.*, 30, 1688.
- McKeegan, K. D., & Davis, A. M. 2003, in *Meteorites, Planets, and Comets*, ed. A. M. Davis, Vol. 1, *Treatise on Geochemistry*, eds. H. D. Holland, & K. K. Turekian (Oxford: Elsevier-Pergamon), 431
- McKeegan, K. D., Chaussidon, M., & Robert, F. 2000, *Science*, 289, 1334
- McKeegan, K. D., Leshin, L. A., Russell, S. S., & MacPherson, G. J. 1998, *Science*, 280, 414
- McKeegan, K. D., Davis, A. M., Taylor, D. J., & MacPherson, G. J. 2005, *Lunar Planet. Sci.*, 36, 2077
- Mendybaev, R. A., Richter, F. M., & Davis, A. M. 2003, *Lunar Planet. Sci.*, 34, 2062
- Misawa, K., & Fujita, T. 1994, *Nature*, 368, 723
- Niederer, F. R., & Papanastassiou, D.A. 1984, *Geochim. Cosmochim. Acta*, 48, 1279
- Notsu, K., Onuma, N., Nishida, N. & Nagasawa, H. 1978, *Geochim. Cosmochim. Acta*, 42, 903
- Petaev, M. I., & Wood, J. A. 1998a, *Meteorit. Planet. Sci.*, 33 Suppl., A122
- Petaev, M. I., & Wood, J. A. 1998b *Meteorit. Planet. Sci.*, 33, 1123
- Podosek, F. A., Zinner, E. K., MacPherson, G. J., Lundberg, L. L., Brannon, J. C., & Fahey, A. J. 1991, *Geochim. Cosmochim. Acta*, 55, 1083
- Richter, F. M. 2004, *Geochim. Cosmochim. Acta*, 68, 4971
- Richter, F. M., Davis, A. M., Ebel, D. S., & Hashimoto, A. 2002, *Geochim. Cosmochim.*

- Acta, 66, 521
- Richter, F. M., Mendybaev, R. A., & Davis, A. M. 2005, *Meteorit. Planet. Sci.*, in press
- Russell, S. S., MacPherson, G. J., Leshin, L. A., & McKeegan, K. D. 2000, *Earth Planet. Sci. Lett.*, 184, 57
- Shu, F., Shang, H., & Lee, T. 1996, *Science*, 271, 1545
- Simon, S. B., Yoneda, S., Grossman, L., & Davis, A. M. 1994, *Geochim. Cosmochim. Acta*, 58, 1937
- Srinivasan, G., Ulyanov, A. A., & Goswami, J. N. 1994, *ApJ*, 431, L67
- Stolper, E. 1982, *Geochim. Cosmochim. Acta*, 46, 2159
- Stolper, E., & Paque, J. M. 1986, *Geochim. Cosmochim. Acta*, 50, 1785
- Sugiura, N. 2001, *Lunar Planet. Sci.*, 32, 1277
- Thiemens, M. H. 1999, *Science*, 283, 341
- Wallerstein, G. et al. 1997, *Rev. Mod. Phys.*, 69, 995
- Wang, J., Davis, A. M., Clayton, R. N., Mayeda, T. K., & Hashimoto, A. 2001, *Geochim. Cosmochim. Acta*, 65, 479
- Wark, D. A., & Lovering, J. F. 1977, *Proc. Lunar Sci. Conf.*, 8, 95
- Wasserburg, G. J., Lee, T., & Papanastassiou, D. A. 1977, *Geophys. Res. Lett.*, 4, 299
- Weber, D., Zinner, E., & Bischoff, A. 1995, *Geochim. Cosmochim. Acta* 59, 803
- Wood, J. A. 1996, in *Chondrules and the Protoplanetary Disk*, eds. R. H. Hewins, R. H. Jones, & E. R. D. Scott (Cambridge: Cambridge Univ. Press), 55
- Yoneda, S., & Grossman, L. 1995, *Geochim. Cosmochim. Acta*, 59, 3413
- Young, E. D., Simon, J. I., Galy, A., Russell, S. S., Tonui, E., & Lovera, O. 2005, *Science*, 308, 203
- Yurimoto, H., & Kuramoto, K. 2004, *Science*, 305, 1763