Ancient Asteroids Enriched in Refractory Inclusions

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Calcium- and aluminum-rich inclusions (CAIs) occur in all classes of chondritic meteorites and contain refractory minerals predicted to be the first condensates from the solar nebula. Near-infrared spectra of CAIs have strong 2-micrometer absorptions, attributed to iron oxide-bearing aluminous spinel. Similar absorptions are present in the telescopic spectra of several asteroids; modeling indicates that these contain ~30 ± 10% CAIs (two to three times that of any meteorite). Survival of these undifferentiated, large (50- to 100-kilometer diameter) CAI-rich bodies suggests that they may have formed before the injection of radiogenic 26Al into the solar system. They have also experienced only modest post-accretionary alteration. Thus, these asteroids have higher concentrations of CAI material, appear less altered, and are more ancient than any known sample in our meteorite collection, making them prime candidates for sample return.

Calcium- and aluminum-rich inclusions (CAIs) found within all chondritic meteorites are arguably the oldest rocks in our collections and are used to define the start of the solar system (1). These millimeter-to-centimeter size objects contain refractory minerals that are the first phases predicted to condense from a gas of solar (or enhanced solar) composition. The highest abundance of CAIs is found in CO chondrites (~13 volume %), but CV3 chondrites contain the most diverse range of CAI types with abundances of up to 10% (2). Burbine et al. (3) identified CAIs on two dynamically related asteroids, 387 Aquitania and 980 Anacostia, that they argued contain CAI abundances of 5 to 10%, similar to that observed in CV3 meteorites. Because the early solar nebula evolved quickly and was spatially heterogeneous, it is reasonable to assume that asteroids with higher concentrations of CAIs should exist. Here, we provide evidence for the existence of several such CAI-rich asteroids from multiple parent bodies.

Near-infrared telescopic spectral surveys have widely been used to identify mafic silicates on the surfaces of asteroids and to infer the composition of the asteroid population as a whole. The only mineral contained in CAIs that has strong absorptions in the 1- to 2-μm region is aluminous spinel (MgAl2O4, sensu stricto). If aluminous spinel (in solid solution with hibonite, FeAl2O4) contains as little as tenths of a weight percent of FeO, its spectrum includes a strong, characteristic 2-μm absorption feature. In the absence of abundant mafic minerals, CAIs can thereby be remotely identified on asteroid surfaces (4).

CAIs are generally classified, on the basis of petrography and geochemistry, into three major groups: type As, Bs, and Cs (5). Of these, only fluff type As (FTAs) were not melted by a transient heating event before accretion (6). Type As and related inclusions are found in all classes of chondrites and are therefore thought to have been well dispersed within the asteroid accretion zone. Refractory minerals similar to those found in FTAs have also been identified in a Stardust sample collected from comet 81P/Wild 2, providing evidence that these materials were widely distributed throughout the solar system (7). Recent models of the evolution of protoplanetary disks predict widespread, outward transport of such high-temperature materials around the midplane (8). In contrast, type Bs and Cs are restricted to CV3 meteorites and more likely represent localized processing of minerals within restricted portions of the nebula (9).

To support our analysis of asteroid spectra, we collected representative spectra from CAIs within the Allende CV3 meteorite (Fig. 1) (10). Spectra of three type Bs, three FTAs, and one amoeboid olivine aggregate (AOA) were collected (Fig. 2). The major minerals in FTAs are melilite and spinel, often with abundant alteration phases such as nepheline and hedenbergite, whereas type Bs contain spinel, melilite, fassaite, anorthite, and minor amounts of alteration phases. Both types have minor and varying amounts of perovskite, hibonite, and metal phases. The spectra of both FTAs and type B CAIs are dominated by absorptions at 2 μm. However, the spectra of FTAs exhibit much stronger 2-μm absorption features than do the spectra of type Bs. This stronger absorption is consistent with the higher FeO concentrations in aluminous spinels in FTAs: ~3 to 14 weight percent (wt %) compared with <0.4 wt % in type Bs. Given that abundant FeO is effectively excluded from CAI minerals during condensation, the FeO must have been introduced into the CAIs during an alteration event. Although some FeO can be introduced into type A and B CAIs through gas/solid exchange within the nebula, the observed correlation between FeO content in spinel and the abundance of alteration phases between CAI-types implies that the FeO enrichment is dominantly post-accretionary.

To verify the identifications of Burbine et al. (3) and locate additional spinel-rich asteroids, we combined visible spectra (11, 12) and near-infrared data obtained with the SpeX instrument at the NASA Infrared Telescope Facility (13). SpeX data of Aquitania and Anacostia are

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Fig. 1. Smithsonian sample 3509 of the CV3 meteorite Allende sawed into ~1-cm-thick slabs (a centimeter-sized cube marked “T” is included for scale). Refractory inclusions suitable for both thin sectioning and crushing into powders were identified as shown here for slabs 5 and 6. After recording their locations, CAIs were cored out from slabs, and both thin sections and thick butts were produced. Part of the remaining sample was carefully excavated to avoid contamination from matrix materials and crushed into powders for spectral measurements.
dominated by a strong 2-μm absorption feature and confirm the previous data (Fig. 3A). On the basis of their unique compositions and general location, it was suggested that these two asteroids (100- and 85-km diameter, respectively) are genetically related (3). Shortward of 0.75 μm, the spectra of these two asteroids are also strongly red-sloped, as are a larger number of nearby objects (14). This cluster of asteroids, including Aquitania and Anacostia, was proposed as the Watsonia family (15). We measured the near-infrared spectra of other members of the Watsonia family. Some, in particular 599 Luisa (Fig. 3B), have spectra that include strong 2-μm absorptions, supporting the hypothesis of a breakup of a larger body.

Visible data also suggest a second group of strongly sloped asteroids, the Henan family (15), which was originally identified dynamically (16). Near-infrared SpeX data of ~10 much smaller (10 to 15 km), and thus fainter, Henan family asteroids also contain 2-μm absorptions (Fig. 3B), suggesting the existence of a second spinel-rich asteroid family. In addition, we have identified a third spinel-rich body, the 45-km diameter asteroid 234 Barbara (17). The spectrum of Barbara is dominated by a strong 2-μm absorption, similar to those of Anacostia and Aquitania (Fig. 3B).

Although they favored a link between spinel-rich asteroids and CAIs, Burbine et al. (3) could not definitively rule out an alternative spectral interpretation: that the spinel was igneous in origin and due to the spinel group mineral chromite (FelO). Spectra of FeO-bearing aluminous spinels are distinct from that of chromites (18, 19). Chromite spectra include a strong absorption at 1.3 μm, and the reflectance is lower from 2 to 2.5 μm than it is for FeO-bearing aluminous spinels. Spectra of Watsonia and Henan family members and Barbara lack strong 1.3-μm features and increase in reflectance beyond 2.1 μm. Therefore, we conclude that the asteroids contain FeO in aluminous spinel rather than chromite. The strong 2-μm absorptions in these asteroid spectra do not require that the asteroids are dominated by aluminous spinel but rather that spinel is the only mineral with significant near-infrared absorptions. In meteorites, abundant aluminous spinels are only observed in CAIs, and spinel is the only phase in CAIs that has strong near-infrared absorption features (20); yet in Allende, CAIs contain only 10 to 30 volume % aluminous spinels.

To further test the link between CAIs and aluminous spinel-rich asteroids and to determine the abundance of CAI materials on these asteroids, we modeled the asteroid spectra using endmembers collected from Allende. In addition to the spectra of FTAs and type B CAIs (Fig. 2), we measured spectra of a sample of matrix materials extracted from Allende. We first used these CAIs and CAI-free matrix spectral endmembers to model the spectrum of an aliquot taken from the Allende standard reference powder, a homogenized 2.6-kg sample of the bulk meteorite (21). Modeling the bulk Allende powder requires the use of radiative transfer theory to account for the multiple scattering among particles that are intimately mixed. This nonlinear effect is addressed with Hapke radiative transfer theory (22), which can be used to convert reflectance spectra to single-scattering albedo (23). As shown in Fig. 4, we were able to reproduce the spectrum of the Allende bulk powder as a combination of CAI-free matrix and either FTA or type B CAIs (or more likely a combination of both). In the least-squares solution, the bulk Allende spectrum can be modeled with 11% FTA and 89% CAI-free matrix or 10% type B CAIs and 90% CAI-free matrix. These derived abundances of ~10% CAIs are in excellent agreement with the known abundance of CAIs in CV3 meteorites (2).

Burbine et al. (3) argued that the regoliths of Aquitania and Anacostia are relatively immature and that intact CAIs would thus be preserved on their surfaces. With these assumptions, they modeled their asteroid spectra as linear combinations of a CAI and bulk Allende and derived a CAI abundance of 5 to 10%. Recent flybys of several asteroids indicate that a modern regolith is likely to be composed of a highly comminuted mixture of all materials (24–26). Furthermore, given the similarity in the strengths of CAIs and matrix materials, it is unlikely that intact CAIs could exist in

**Fig. 2.** Spectra of Allende components. CAIs include FTAs (red), type Bs (blue), and an AOA (green). Spectra of CAI-free matrix materials (orange) and a bulk Allende sample (black) are also shown. All samples are of <38-μm powders and were measured at RELAB, Brown University’s NASA-Keck facility (40).

**Fig. 3.** (A) Visible near-infrared spectra of asteroids 387 Aquitania (red) and 980 Anacostia (orange) from Burbine et al. (3) compared with the current higher–spectral resolution Small Main-Belt Asteroid Spectroscopic Survey (SMASII) (visible) (12) and SpeX (near-infrared) (13) data. (B) Combined SMASII and SpeX data for the asteroid 234 Barbara (green) and representative asteroids from the Watsonia and Henan families (table S1). All spectra are dominated by strong 2-μm absorptions. The observing conditions for these data and other members of the Watsonia and Henan families are given in table S1.
present-day regoliths. Therefore, to model spectra of asteroids covered in mature intimately mixed regoliths, we used nonlinear radiative transfer theory (22), as we did for our laboratory data of Allende (23). We estimated the absolute albedos for Barbara, Aquitania, and Anacostia from measurements made by the Infrared Astronomical Satellite (27). The relatively small Henan family asteroids have unknown albedos, and thus the abundance of CAIs on their surfaces cannot be reliably determined with radiative transfer theory.

We initially modeled the asteroid data as nonlinear combinations of CAI-free matrix and either FTAs or type B CAIs. However, it is clear even from visual comparisons (Figs. 2 and 3) that the asteroid spectra are sloped relative to the laboratory data (26). To account for this slope in our modeling, we used the spectrum of asteroid 2448 Sholokhov, a member of the Watsonia family, which has a generally featureless but sloped spectrum (fig. S1) (29). In addition, it is evident that more olivine is needed (compared with Allende) to explain the 1-μm absorptions in the spectra of the asteroids and to brighten the spectra in the 2-μm region. Despite these additional components, no satisfactory fits to the asteroid spectra are achievable with the use of any combination of materials and type B CAIs (Fig. 5A). With type B CAIs, models for all three asteroid spectra include absorptions at 2 μm that are too weak.

Reasonable matches to the spectra of Barbara, Aquitania, and Anacostia—particularly in the near infrared—are achieved with models that include FTAs (Fig. 5B and Table 1). Models of all three asteroid spectra require greater slopes than in the Allende spectra. The relative differences in the slope components among these asteroids, generally well modeled by the spectrum of Sholokhov, probably represent different degrees of space weathering (28). The MgO-rich olivine and CAI-free matrix abundances also vary substantially among the asteroids: Barbara has a substantial olivine component, Aquitania requires only CAI-free matrix, and Anacostia has both. Alteration is widespread in almost all primitive planetary materials (2), and the variation in olivine content among the asteroids probably reflects differences in their alteration histories. Enrichment in olivine relative to Allende suggests that the asteroids Barbara and Aquitania have experienced less alteration than Allende, whereas Anacostia may be as altered as Allende.

Alteration of most chondrites, which occurs dominantly in accreted bodies and to a lesser extent in gas/solid exchange in the nebula, is also responsible for the enrichments in FeO observed within aluminous spinels in CAIs. FeO in aluminous spinels is essential for producing the observed 2-μm absorptions in their spectra. Whereas the mechanism that mobilized FeO within these apparently unmetamorphosed chondrites remains a mystery, a likely source is the ubiquitous olivine in chondrites that accreted along with CAIs. The specific materials and the timing of accretion affect the extent of such reactions and may explain the variability observed between individual meteorites, even within meteorite groups. This variability also provides a reasonable explanation for the inferred differences in olivine abundance among the CAI-rich asteroids. The FeO enrichment in the CAI minerals within these asteroids is evidence that these objects were aqueously altered and/or thermally metamorphosed, although the activity was short-lived and alteration was modest compared with that observed in many chondrites.

Despite these variations in alteration histories that manifest as differences in other spectral components, the near-infrared absorption features of all three asteroids are well modeled with 22 to 39% FTAs. Our modeling therefore indicates that these asteroids contain 30 ± 10% CAIs, substantially more than the 10% seen in CV3 meteorites. Spectrally, these asteroids rich in CAI materials are inconsistent with type B inclusions, which are unique to CV3 meteorites and probably represent localized events in the nebula. Instead, the asteroids appear to be dominated by the minerals contained in type A inclusions, which are ubiquitous in all chondritic classes. The CAI-rich asteroids thus contain both a different distribution and a higher abundance of CAI minerals than CV3 meteorites. Furthermore, we have identified three different CAI-rich parent bodies, including asteroids with diameters of ~50
to 100 km. The CAI-rich asteroids are thus a distinct group of bodies that likely are not represented in our meteorite collection.

The existence of these objects allows us to test hypotheses for the timing of events in the early solar system. If these asteroids had accreted during the first few half-lives of $^{26}$Al (~720,000 years) with ~30% CAI material that contains canonical $^{26}$Al/$^{27}$Al ratios, these asteroids would have melted (30). Yet melting experiments of carbonaceous chondrites (37) show no evidence that aluminous spinel is substantially enriched during melting. This strongly suggests that the CAI-rich asteroids have not undergone substantial melting or differentiation, consistent with their affinity to FTAs. We cannot rule out the possibility that these asteroids accreted with additional materials that prevented igneous differentiation [e.g., abundant ice (32)], as the 3-µm spectra of at least one of the asteroids is indicative of minor hydration (33). It is also possible that these asteroids experienced an anomalous thermal history related to collisional breakup and reassembly, yet this seems improbable given the number and size of CAI-rich asteroids.

A plausible explanation for the survival of CAI-rich asteroids is that they do not contain canonical $^{26}$Al/$^{27}$Al abundances. Indeed, some refractory inclusions in meteorites contain substantial lower-than-canonical $^{26}$Al values or are even devoid of $^{26}$Al (34), suggesting that $^{26}$Al may have been injected into the solar nebula some time after the onset of CAI formation (35).

The alternative explanation—that the injection of $^{26}$Al was spatially variable—is inconsistent with the occurrence of CAI-rich asteroids across the inner mainbelt and the dominance of the ubiquitous FTA-like CAI minerals in these asteroids. If these CAI-rich asteroids accreted from $^{26}$Al-poor materials, they may record an early period of solar system history when refractory materials were prevalent but before the injection of $^{26}$Al into the solar system. Thus, these asteroids have two to three times more CAI material, appear less altered, and are more ancient than any known sample in our meteorite collection, making them prime candidates for sample return.

### Table 1. Abundances derived from modeling the spectra of CAI-rich asteroids.

<table>
<thead>
<tr>
<th>Modeled asteroid</th>
<th>Fluffy type A</th>
<th>CAI-free Allende matrix</th>
<th>MgO-rich olivine</th>
<th>Slope (2448 Shokhkov)</th>
</tr>
</thead>
<tbody>
<tr>
<td>234 Barbara</td>
<td>22%</td>
<td>0%</td>
<td>40%</td>
<td>38%</td>
</tr>
<tr>
<td>387 Aquitania</td>
<td>25%</td>
<td>11%</td>
<td>26%</td>
<td>33%</td>
</tr>
<tr>
<td>980 Anacostia</td>
<td>39%</td>
<td>0%</td>
<td>0%</td>
<td>50%</td>
</tr>
</tbody>
</table>

4. Other common Fe-bearing silicates that have strong absorptions in the near infrared (38). Although pyroxene spectra have absorptions in the 2-µm region, they have even stronger features near 1 µm. Conversely, olivine spectra lack 2-µm absorptions and are instead characterized by a complex feature at 1 µm. It is on this basis (a strong 2-µm absorption in the absence of a stronger 1-µm feature) that spinel is spectrally identified.

5. This nomenclature was primarily designed for use in classifying CAIs from CV3 meteorites. Over the last three decades other descriptive terminology has been developed for other chondrite types (9, 39).


10. The Smithsonian Allende sample USNM 3509 was sectioned into large slices, and refractory inclusions were identified and cored. Thin and thick sections were made from half of the objects, and reference materials were preserved for future study. Thin sections were analyzed by the Cameca SX50 electron microprobe at the Lunar and Planetary Laboratory at the University of Arizona to quantify major and minor element abundances. While avoiding contamination from the matrix, material from the other half of the objects was cored out, ground into 3-µm-size powders, and sent to Brown University for spectral measurements at the NASA-Keck Reflectance Experiment Laboratory (RELAB) facility (40). All spectra were measured with a 75° resolution at a standard viewing geometry of 30° incidence, 0° emission.


14. In the Bus visible asteroid taxonomy, objects with a steep red spectral slope at wavelengths up to 0.75 µm, which are then relatively flat, are classified as types (42).


17. Whereas the Henan and Watsonia families are roughly the same distance from the sun, the mean orbits of asteroids making up these two families are markedly different in both eccentricity and inclination. The mean proper elements for the Henan family are $2.73 \pm 0.07$ astronomical units (AU) (ranging from 2.69 to 2.76 AU), $e = 0.16 \pm 0.06$ (where $e$ is eccentricity and $i$ is inclination), compared with the Watsonia family at $2.77 \pm 0.07$ AU (ranging from 2.74 to 2.80 AU), $e = 0.19 \pm 0.08$, and $i = 0.29$. This corresponds to a difference in orbital eccentricity of 0.07, and $i = 0.29$. This corresponds to a difference in orbital period of 0.07, and $i = 0.29$. This corresponds to a difference in orbital period.