Recipes for making synthetic CAIs, refractory residues, and minerals for rim-forming experiments

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Abstract—Recipes are presented for synthesizing various type A and type B Ca-Al-rich inclusions (CAIs), refractory volatilization residues, and the minerals forsterite and melilite that are required for experiments. These experiments (described in other works) aim to make two determinations: 1) the conditions under which the surfaces of CAIs were either “flash-heated” or “volatilized subsolidus” to form a temporary ultra-refractory residue, and 2) the conditions under which the residue was then metasomatized to form the mineral layers making up Wark-Lovering (WL) rims on CAIs.

INTRODUCTION

Rationale for the Work

CAIs are among the oldest known materials in the solar system, so the conditions under which they formed and evolved should reveal much about the environment in the protosolar nebula (e.g., MacPherson et al. 1988) and, by implication, in other star-forming systems. Wark-Lovering (WL) rims are found on virtually all coarse-grained CAIs of types A, B, and C (Wark and Lovering 1977; Wark and Boynton 2001), so rim-forming events were an integral part of the history of these CAIs. However, rim formation is not well understood, therefore, experiments must be performed to determine how they formed.

CAIs are enclosed in WL rims that have the same refractory element abundance pattern as the underlying CAI, but are approximately four times richer in refractories. The refractory enrichment in the rims was thus derived from the CAI by the volatilization of the outer CAIs’ more volatile Mg and Si as well as other constituents (Wark and Boynton 2001). The mechanisms proposed for the volatilization are: 1) flash heating (Boynton 1988) of \textasciitilde 3000 °C for only 1–2 sec, or 2) subsolidus volatilization (Wark 2004) at lower, subsolidus temperatures for longer times of perhaps days. The volatilization (the first step of rim formation) would have created an aluminous refractory residue at the surface of the CAI. This residue was then metasomatized (the second step of rim formation) by an influx of Mg, Si, and Ca that converted the residue into three parallel mineral layers of spinel + perovskite, melilite, and pyroxene.

The questions which these synthetic recipe samples were created to answer include: Was the first step of rim formation flash heating or subsolidus volatilization? And then, under what conditions did the second (metasomatism) step occur?

Approach to the Work

The furnaces available for this work were: 1) a MoSi\textsubscript{2}-element, muffle furnace with controlled temperature-stepping and dwell times, capable of \textasciitilde 1650 °C in air, and 2) horizontal, mixed gas flow furnaces with alumina tubes and controllers as above, capable of \textasciitilde 1400 °C. The recipes were therefore based on sintering mixtures of finely ground, pelletized powders standing in alumina boats and on melts crystallizing in alumina or Pt crucibles in air or controlled atmospheres.

The textures of natural CAIs (formed by condensation, evaporation, or melt crystallization) differ from those of the sintered synthetic CAIs. However, the failure of the recipes to produce natural CAI textures is not a major impediment, since the chief objective in making the synthetic recipe materials was to have samples that could be subjected to both flash heating/volatilization to produce a refractory substrate, an experiment that would destroy pre-existing texture and mineralogy, and to formation of rim layers on the refractory substrate, a process that would completely...
reorganize (metasomatize) the structure, mineralogy, and chemistry of the substrate.

The recipes for these synthetic samples are therefore fundamentally different in purpose from the experiments designed to create type B1 and B2 CAIs (Richter et al. 2002a; Grossman et al. 2000; Beckett et al. 2004; Mendybaev et al. 2003), to produce mantles on type B1 CAIs (Richter et al. 2002b; Mendybaev et al. 2004), to explore the effects of fO2 and sample size on the formation of CAIs (Mendybaev et al. 2002; Connolly and Burnett 2003), or to investigate the formation of hibonite-bearing, largely type A CAIs (Beckett and Stolper 1994).

**The Evidence: How Did Rims Form?**

At present there is evidence for both flash heating and subsolidus volatilization as the first step in rim formation, and for formation of WL rims more than 10^5 years later than CAI formation (Liu 2005; Tonui 2005; Simon 2005; Taylor 2005; Cosarinsky 2005), though this latter information does not resolve the question of how rims formed.

In favor of flash heating are the following lines of evidence:

- The outer Al-rich mantle, though not the interior, of CAI 1623-5 was strongly reheated and partly volatilized while ^26Al was still alive and the CAI was in the nebula (McKeegan et al. 2005).
- Two CAIs of type C, ABC and TS26, contain partly resorbed chondrules from a late, strong heating event in the nebula that caused exchange with 16O-poor nebular gas and loss of the WL rims on the CAIs (Krot et al. 2005).
- Data from Ti^3+/Ti^4+ in the rim pyroxene indicates that the rims formed under high fO2, possibly due to a dusty shock wave in the nebula (Dyl et al. 2005).
- Volatilization of Eu from the rim to produce the negative Eu anomalies requires rapid heating to ~1450 °C to volatilize hibonite, followed by fast cooling to prevent re-condensation of Eu onto the rim (Russell et al. 2001).

In favor of subsolidus volatilization are the following lines of evidence:

- Experiments by Richter et al. (2005) and by Mendybaev et al. (2003, 2004) on the vaporization of type B CAIs in a H2-rich (nebular) atmosphere show that Mg continues to vaporize from the CAIs down to temperatures of ~1250 °C, where the outer CAI is almost completely solid.
- “Fluffy type A” CAI 20A1J-B shows no signs of melting just below the rim, as might perhaps be expected from a flash heating event (Wark et al. 2005).

**Arrangement of the Recipes**

It is not possible to give one “typical” recipe for type A CAIs and one for type B because type As have at least four different varieties, and type Bs at least six, which give rise to their overlapping chemical and petrological classifications. The recipes therefore begin with a summary of the classifications and then the average bulk chemical compositions of each variety. Detailed recipes are then given for the preparation of one or two of the most common varieties of that type of CAI. Interested workers can, of course, use the bulk compositions given in the tables to prepare samples of the less common varieties, but they would need to pay careful attention to the phase diagram to avoid possible problems in the furnace. In a similar way, there are many possible refractory residues, depending on the degree of volatilization. Recipes are given for two residues: one having a low degree of refractory enrichment and the other a high degree of refractory enrichment. A recipe is given for forsterite because it is the major phase in the accretionary rims outside the WL rims, and because it is a common source/sink for Mg, Si, and O in the nebula. Finally, a recipe is also given for one variety of melilite (akermanite 5%), which is common in the outer parts of CAIs.

**Classification**

CAIs fall in two overlapping classifications: chemical and petrological.

Six chemical groups were defined by Mason and Taylor (1982), based chiefly on rare earth element (REE) patterns. Coarse-grained CAI groups I, V, and VI have flat patterns with unfractionated REE abundances, except for positive Eu and Yb anomalies in groups I and VI. Eu and Yb are the two least refractory REE in nebular gas, so their +ve anomalies could be due to an addition of an uncondensed REE residue to their parental gas. Otherwise, groups I, V, and VI are so similar that they are lumped together here for simplicity as unfracti onated “group I.” They have mostly “normal” solar system isotopic abundances, except oxygen (Clayton et al. 1977), and lack marked mass fractionation.

Group II CAIs, in stark contrast, are highly fractionated with negative anomalies of Eu and Yb, abundant light REE and Tm, and low abundances of the remaining heavier REE. Group II CAIs are common as both so-called coarse-grained and fine-grained CAIs. They are depleted in ultra-refractory trace elements, especially the ultra-refractory REE and metals. The parental material from which group II CAIs formed, though not necessarily the present CAIs, must therefore have condensed from gas (Boynton 1975). They have mass fractionated Mg, Si, and Cr, favoring the lighter isotopes (Clayton et al. 1999; Birck and Allegre 1984; Esat 1988; Esat and Taylor 1990).

Group III CAIs are uncommon, but are refractory-rich, occur as both coarse-grained and fine-grained types, and have negative Eu and Yb anomalies. Group IV objects are olivine-rich rather than CAIs, and have low, flat REE abundances.

Groups I and II also differ from one another by their mineral abundances and bulk chemistry (Wark 1984). For
example, in type A CAIs, group I has 5–10 vol% primary spinel and 86–94 vol% primary melilite, with 20–26% SiO$_2$, 30–39% Al$_2$O$_3$, 2–6% MgO, and 35–39% CaO. Group II has 14–25 vol% primary spinel, 64–84 vol% primary melilite, with 14–22% SiO$_2$, 39–53% Al$_2$O$_3$, 5–9% MgO, and 26–34% CaO.

The main petrological classification features of CAIs will be presented later with the recipes of each type.

**TYPE A CAIs**

**Mineralogical Compositions**

Type A CAIs (MacPherson et al. 1988) are white to pinkish bodies of 5–20 mm that are composed mainly of gehlenitic melilite containing poikilitic inclusions of spinel (up to 25 vol%), perovskite (a few %), possibly hibonite (Ca hexaluminate CaAl$_{12}$O$_{19}$ with some substitutions of Mg, Ti, and Si), grossite (Ca dialuminate Ca$_2$Al$_4$O$_7$) and Ti-Al-pyroxene, together with traces of micron-sized NiFe and refractory/platinum metal (RPM) alloy nuggets (FeNiPtRuOsIrMoWReRhGe) (Wark and Lovering 1976). The group II type As have very sparse metal grains that are generally micrometer-sized, FeNi-rich, and that sometimes include Cu and Zn (Wark 1984). The melilite from Allende type As typically has very extensive veins and patches, especially in “fluffy type As” (FTAs), of alteration due to influx of alkalis, halogens, Si and Fe, and loss of Ca, forming the secondary phases anorthite, nepheline, sodalite, grossular, hedenbergite, andradite, and Fe-bearing spinel (Wark 1981a).

The petrological classification of type A CAIs recognizes two types:

- Condensates (so-called “fluffy type As” or FTAs)
- CAIs that crystallized from melts (so-called “compact type As” or CTAs).

FTAs and CTAs differ in texture from each other.

FTAs typically have convoluted shapes and brecciated textures with broken fragments of CAI irregularly welded together (MacPherson and Grossman 1984). Many grains within each piece of CAI have microscopic voids between them and a random distribution of melilite compositions within each CAI fragment, except for a radial gradient of increasing gehlenite content from ∼0.5 mm up to the rim. Individual melilite crystals are often reverse-zoned with more refractory exteriors than interiors. FTAs are typically more altered than CTAs, with pervasive alteration through the pore space of the CAI compared to the radially-decreasing alteration patches of solidly-textured CTAs.

CTAs are subrounded and have the compact, void-free textures of igneously crystallized rocks (Simon et al. 1999). They usually have a spinel-poor, melilite mantle several mm wide, across which melilite becomes increasingly gehlenitic (Al-rich) towards the rim, as in type B1 CAI mantles. The CAI interiors sometimes also possess grains of Ti-Al-pyroxene and anorthite, again as in type B1 CAIs. Melilite crystals are typically normally-zoned (i.e., higher melting point, more gehlenitic cores and lower m.p., more akermanitic grain exteriors).

Type A CAIs may thus be one of four varieties: group I FTA, group I CTA, group II FTA, or group II CTA.

**Recipe for Type A Group I CTA**

Sintering the average major element primary composition (Table 1) for synthetic type A CAIs creates the approximate mineralogy of a group I CAI. The pre-alteration bulk compositions were used as estimated by Wark (1981a, 1981b) and shown in Wark (1984).

**TYPE B CAIs**

**Mineralogical Compositions**

Type B CAIs (Grossman 1975; Wark and Lovering 1982) are subrounded, whitish pieces of igneous rock 5–20 mm in diameter that are composed (Table 2) of Ti-Al-fassaitic pyroxene (“Tpx,” 30–60 vol%), melilite (30–50 vol%), anorthite (5–25 vol%) and forsterite (absent to abundant). These phases contain poikilitic inclusions of spinel, and inclusions up to 20 microns or more of FeNi metal, FeNi sulfides, magnetite Fe$_3$O$_4$, a few-micron-sized grains of

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**Table 1. Proportions of components for approximate average group I type A CAI.**

<table>
<thead>
<tr>
<th>Type A components</th>
<th>Wt%</th>
<th>Components</th>
<th>Mass (g) to weigh</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>22.5%</td>
<td>SiO$_2$</td>
<td>22.5 g</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>1.25%</td>
<td>TiO$_2$</td>
<td>1.25 g</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>34.7%</td>
<td>Al$_2$O$_3$</td>
<td>34.7 g</td>
</tr>
<tr>
<td>MgO</td>
<td>3.9%</td>
<td>MgO</td>
<td>3.9 g</td>
</tr>
<tr>
<td>CaO</td>
<td>37.2%</td>
<td>CaCO$_3$</td>
<td>66.4 g</td>
</tr>
<tr>
<td>Sc, La, Ce, Eu, Yb, Lu, Zr elements</td>
<td>0.035%</td>
<td>Sc$_2$(SO$_4$)$_3$ (or suitable source)</td>
<td>0.021 g Sc$_2$(SO$_4$)$_3$</td>
</tr>
<tr>
<td></td>
<td>(50 ppm each)</td>
<td>La, Ce, Eu, Yb, Lu, Zr oxides (or suitable sources)</td>
<td>~0.006 g each La-Zr oxide</td>
</tr>
<tr>
<td>Sr, Cr, V elements</td>
<td>0.090%</td>
<td>Sr(NO$_3$)$_2$ (or suitable source)</td>
<td>0.081 g Sr(NO$_3$)$_2$</td>
</tr>
<tr>
<td></td>
<td>(300 ppm each)</td>
<td>Cr(NO$_3$)$_3$.9H$_2$O (or suitable source)</td>
<td>0.231 g Cr(NO$_3$)$_3$.9H$_2$O</td>
</tr>
<tr>
<td></td>
<td></td>
<td>NH$_4$VO$_3$ (or suitable source)</td>
<td>0.069 g NH$_4$VO$_3$</td>
</tr>
<tr>
<td>Total%</td>
<td>100.0%</td>
<td>Total mass</td>
<td>129.2 g</td>
</tr>
</tbody>
</table>
D. Wark

(often U-rich) accessory phases (pyrochlore Ca niobate, zirconolite CaZrTi$_2$O$_7$, baddeleyite ZrO$_2$, thorianite ThO$_2$, Ca phosphates, Ca molybdate, beekelite CaREE silicate, perovskite CaTiO$_3$ and celsian Ba feldspar) (Lovering et al. 1979; Wlotzka and Wark 1982) and "fremdlinge" (complex intergrowths of FeNi metal, sulfides, phosphates, silicates, and refractory metal nuggets) (Wark and Lovering 1978; El Goresy et al. 1978). The melilite typically has patches and veins of alteration similar to those in CTAs. The compositions used to make up the synthetic CAIs are the pre-alteration bulk compositions as estimated by Wark (1981a, 1981b) and shown in Wark (1984). For type B CAIs, however, the primary and altered compositions are much closer than in type A CAIs, so little correction for alteration is usually needed.

Classification

Type B CAIs fall in two overlapping classifications:

Chemical Groups

There are two main chemical groups, described above, of which group I is the most common (unfractionated refractory trace elements and lacking marked mass fractionation, except for Mg and Si in the mantles of type B1 CAIs, which become more isotopically "heavy" inwards [e.g., Goswami et al. 1994]) and group II (fractionated, as above). These two groups are also distinguished from one another by their mineral abundances and bulk chemistry, analogous to the differences for type A CAIs. In particular, group II CAIs are spinel-rich.

Petrological/Textural Types

Type B1 CAIs are zoned, subrounded bodies with wrinkled rims. Below their rim they have a ~1 mm-wide, spinel-poor melilite mantle varying from ~ak 5% at the rim to ~ak 35% at the boundary to the core of Tpx, melilite, spinel, and anorthite. Typical grain sizes are relatively coarse, from 0.5–2.0 mm (Wark and Lovering 1982a).

Type B2 CAIs are unzoned, smooth, rounded bodies without a melilite mantle. They have finer (0.1–0.5 mm), more equant grains than type B1, with compositions that are randomly, not radially, distributed. Modal abundances differ from those of type B1, mineral phases have a narrower range of compositions in type B2 (Table 2), and type B2s possess spinel frambooids and ‘palisade bodies’ (Wark and Lovering 1982b).

Type B3 CAIs (forsterite-bearing type Bs) fall on a continuum from B1–B3 of increasing Mg and Si contents, lower melilite, and high forsterite modal abundances, and lower refractory element enrichments (Wark et al. 1987).

Type B CAIs may thus be group I type B1, B2, or B3, or group II type B1, B2, or B3.

All type B CAIs share a common origin from partially molten material (Stolper and Paque 1986), with the degree of melting and crystallization temperature decreasing from B1 to B2 (Wark and Lovering 1982a).

Recipe for Group I Type B1 and B2

The recipes below for synthetic sintered/melt crystallized type B1 and B2 CAIs use the average major element compositions for types B1 and B2 CAIs (Table 3) and create a mineralogy similar to, though with a finer-grained, more uniform texture, than that in natural type B CAIs.

<table>
<thead>
<tr>
<th>Range of property</th>
<th>B1</th>
<th>B2</th>
<th>B3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melilite (vol%)</td>
<td>32–63</td>
<td>38–59</td>
<td>3–26</td>
</tr>
<tr>
<td>Ti-Al-pyroxene (vol%)</td>
<td>15–32</td>
<td>23–30</td>
<td>30–65</td>
</tr>
<tr>
<td>Spinel (vol%)</td>
<td>10–19</td>
<td>10–13</td>
<td>&gt;20</td>
</tr>
<tr>
<td>Anorthite (vol%)</td>
<td>1–21</td>
<td>6–21</td>
<td>2–5</td>
</tr>
<tr>
<td>Forsterite (vol%)</td>
<td>–</td>
<td>–</td>
<td>&gt;20</td>
</tr>
<tr>
<td>Melilite (ak%)</td>
<td>15–60</td>
<td>47–85</td>
<td>50–90</td>
</tr>
<tr>
<td>Ti-Al-pyroxene (TiO$_2$ wt%)</td>
<td>5–11</td>
<td>3–6</td>
<td>0.3–6</td>
</tr>
</tbody>
</table>

Table 2. Modal abundances and major mineral compositions of type B CAIs.
the powder in a covered alumina beaker to not more than half full. This prevents loss of powder, as it puffs up on decarbonation. Leave a gap below the lid for the escape of CO$_2$ gas but to prevent entry of MoSi$_2$ or other material from roof and walls of furnace.

Decarbonate and react in muffle furnace as follows:

- Heat for 6 hr at 1000 °C (CaCO$_3$ starts to decarbonate at ~900 °C), then for 18 hr at 1150 °C.
- Cool and break up the friable “cake,” then regrind in a mortar and pestle.
- React for 24 hr at 1200 °C.
- Cool and break up the friable “cake,” then regrind in a mortar and pestle.
- For type A CAIs only, react again for 24 hr at 1300 °C.
- Cool and break up the friable “cake,” then regrind the reacted mix in a mortar and pestle.

**BALL MILLING**

Ball mill the reacted mixture down to roughly micron-sized powder, which will make uniform, well-bound, pressed pellets.

Place ~30 g of reacted powder, ~50–70 Y-stabilized zirconia balls (~1 cm in diameter) and ~100 ml dry, high-purity isopropanol (the presence of water destroys the balls, which react with water) into a screw-capped PET or PP container with about half of the remaining space free for shake action.

Shake in a tumbler ball mill for approximately 2 days, pour out the slurry into a wide-mouthed beaker through a coarse sieve to remove 1 cm balls, rinsing the residual slurry off the balls with propanol into the beaker. Clean balls with isopropanol, then dry and store in a closed container.

Let the slurry settle (~12 h), then decant off the clear isopropanol. Slowly evaporate off the remaining isopropanol in a fume hood over a gentle hot plate, covering the mouth of the beaker with a tilted watchglass to allow the escape of fumes but not the loss of spitting slurry.

When it is thoroughly dry, store synthetic type A mix.

### Table 3. Average compositions and ranges for group I type B1, B2, and B3 CAIs, and masses to weigh out.

<table>
<thead>
<tr>
<th>Type B component</th>
<th>Type B1 wt%</th>
<th>Type B1 mass (g) to weigh</th>
<th>Type B2 wt%</th>
<th>Type B2 mass (g) to weigh</th>
<th>Type B3 wt%</th>
<th>Type B3 mass (g) to weigh</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>28.7% (25–32)</td>
<td>28.7 g</td>
<td>33.2% (30–35)</td>
<td>33.2 g</td>
<td>~35%</td>
<td>34.5 g</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>1.3% (0.9–1.9)</td>
<td>1.3 g</td>
<td>1.5% (1.2–1.6)</td>
<td>1.5 g</td>
<td>~1.2%</td>
<td>1.2 g</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>30.1% (27–34)</td>
<td>30.1 g</td>
<td>27.0% (25–28)</td>
<td>27.0 g</td>
<td>~22%</td>
<td>21.6 g</td>
</tr>
<tr>
<td>MgO</td>
<td>10.2% (9–12)</td>
<td>10.2 g</td>
<td>11.7% (10–16)</td>
<td>11.7 g</td>
<td>~26%</td>
<td>25.6 g</td>
</tr>
<tr>
<td>CaO for wt%</td>
<td>29.3% (24–32)</td>
<td>52.3 g CaCO$_3$</td>
<td>26.2% (22–28)</td>
<td>46.8 g CaCO$_3$</td>
<td>~17% CaO</td>
<td>29.8 g CaCO$_3$</td>
</tr>
<tr>
<td>CaCO$_3$ for mass</td>
<td>CaO</td>
<td>CaO</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sc, La, Ce, Pu, Ru, Zr &amp; elements</td>
<td>0.035% (50 ppm, each Sc-Zr)</td>
<td>0.021 g Sc$^a$</td>
<td>0.035% (50 ppm, each Sc-Zr)</td>
<td>0.021 g Sc$^a$</td>
<td>0.035%</td>
<td>0.021 g Sc$^a$</td>
</tr>
<tr>
<td>Eu, Yb, Lu, Zr &amp; elements</td>
<td>0.006 g each La-Zr$^a$</td>
<td>0.006 g each Sc-Zr$^a$</td>
<td>0.006 g each La-Zr$^a$</td>
<td>0.006 g each Sc-Zr$^a$</td>
<td>0.035%</td>
<td>0.006 g each La-Zr$^a$</td>
</tr>
<tr>
<td>Sr, Cr, V &amp; elements</td>
<td>0.090% (300 ppm, each)</td>
<td>0.081 g Sr$^a$</td>
<td>0.090% (300 ppm, each)</td>
<td>0.081 g Sr$^a$</td>
<td>0.090%</td>
<td>0.081 g Sr$^a$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.231 g Cr$^a$</td>
<td></td>
<td></td>
<td></td>
<td>0.231 g Cr$^a$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.069 g V$^a$</td>
<td></td>
<td></td>
<td></td>
<td>0.069 g V$^a$</td>
</tr>
<tr>
<td>Total</td>
<td>100.0%</td>
<td>123.0 g</td>
<td>100.0%</td>
<td>120.6 g</td>
<td>100.0%</td>
<td>113.1 g</td>
</tr>
</tbody>
</table>

$^a$Sources of traces elements are the same as in Table 1.

**MICROSCOPIC METAL ALLOY GRAINS**

An artificial RPM alloy (Table 4) was made by multiple arc melting of pelletized metal powders at Monash University. The composition was the same as the average of RPM nuggets found in some FTA CAIs, and has close to chondritic ratios of the refractory metals to one another.

The FeNiVRPM alloy (Table 4) was produced by taking 10.0% of the RPM alloy powder and mixing it with 4.0% V metal powder and 43.0% each of Fe and Ni metal powders, then pelletizing and melting under argon in a levitation-induction furnace at Caltech (Wark 1984).

Rub a flat surface on a lump of Fe-Ni-V-RPM metal alloy quickly but gently under alcohol on a clean sheet of the finest AlO$_x$ abrasive paper (at least 1200 grade), or, separately, a flat face of a lump of RPM alloy (refractory platinum metal). Do not use tungsten carbide paper or you will get W contamination. With alcohol, wash the metal filings and rubbed-off alumina grains into two dishes, one for each type of metal.

In order to see several metal grains of each type per microscope field of view on the synthetic CAI, you will need approximately 0.30 g of RPM alloy (1–5 micron grains) and approximately 0.50 g of FeNiVRPM alloy (slightly coarser in typical CAIs, 1–10 micron grains) for approximately 100 g of synthetic mixture. These masses of metal yield modal abundances of metal of approximately 1 in 1000, since a given mass of metal, being denser than oxide and silicate, has only one-third to one-fourth of the volume of oxide and silicate. Thus, a 30 × 30 grid on the CAI surface would have metal filling only 1 grid square on average (or several grains smaller than 1 grid square), similar to the abundance in many natural CAIs.

Filter each slurry of metal and alcohol through the finest nylon mesh (~30–40 micron mesh) in order to remove coarse metal grains and some alumina grains.

Next, filter each slurry of this finer metal through two “nuclepore” filters in series.
For the RPM grains, first use a 20 micron, then a 5 micron filter to get <5 micron grains. For the FeNiVRPM grains, first use a 20 micron, then a 10 micron filter to get <10 micron grains.

Gently dry the grains without heating and avoid oxidation of the metal.

Weigh the metal grains produced. This is a slow process and patience is required! Make sure you rub off more than enough metal so that you won’t have to repeat the filtration process. Weigh each lump before and after rubbing to find how much metal has been removed.

Weigh the required masses of metal grains into the ball milled, reacted CAI mixture. It may be desirable to add extremely fine-grained “iridium black” and “rhodium black” to the mixture as well. (NB these fine powders are pyrophoric and the containers should be opened under nitrogen or argon). Iridium is ultra-refractory and will probably survive the flash heating, whereas the rhodium is less refractory and will probably survive only at some depth below the surface where the temperature is lower, revealing information about the temperature gradient in the flash heated surface.

In order to mix the metal grains well with the synthetic CAI powder, ball mill the powder + metal again with isopropanol for 2 hr, then sieve out, rinse, and dry the balls, then dry the powder gently to avoid oxidizing the metal.

PRESSING CYLINDRICAL PELLETS OF SAMPLES

Select a press that will produce cylindrical pellets of the desired diameter after allowing for ~20% shrinkage during firing. Suitable presses for various purposes have been found to be ~10 mm in diameter. Fill the cylindrical hole in the press to ~1.5 times deeper than the desired pellet to allow for compression and shrinkage. Use a funnel to make all the powder go into the bottom of the hole, tapping after each addition to compact the powder. When filled, wipe out the empty upper part inside the hole to remove powder, which will tend to make the pressing cylinder bind to the die. No binding medium must be used. The fine dry powder binds well.

Press very slowly over about 1 min to no more than ~1000 lb weight. Increase the pressure in small increments over 1–2 min, then let the press stabilize for ~1 min before very slowly releasing the pressure in small increments. This is the critical part, because too rapid a release of pressure will cause the pellet to fracture. If available, a vacuum press is desirable to remove air from between the grains and produce a more compact pellet.

Gently use the press to push out the pellet onto clean alfoil inside a ring. Do not let the pellet fall far. Transfer the pellet on the alfoil to a large sheet of clean paper on a smooth, flat bench with barriers to prevent the pellet from rolling off. Use a camel hair brush to move the pellet around and orient it on edge (like a wheel).

Clean the metal scraped from the die onto the curved surface of the pellet.

Pull off a strip of 2-cm-wide Magic Tape approximately 15 cm long. Hold the tape taut at each end, sticky side down, and gently press one end onto the grey (metal contaminated) surface of the “wheel.” Pull the tape sideways to roll the “wheel” along, making sure the tape stays in gentle contact with the full width of the “wheel.” The grey metal from the die will adhere to the Magic Tape, thus cleaning the pellet. Keep doing this with fresh pieces of tape until the “wheel” is completely clean. The circular top and bottom can also be cleaned. Blow the loose dust off the pellets with a photographic blower and stack them on the flat surface with tissue spacers top, bottom and sides inside a screw-capped Perspex jar no more than twice the diameter of the pellets (to minimize damaging movements).

FIRING PELLETS

Using foil or paper scoops and a camel hair brush, gently place the pellets on edge, like “wheels,” on a thin layer of calcined, coarse alumina powder in the base of an alumina boat. Separate the pellets by 2–3 mm. Place into the end of an alumina tube furnace, seal the end, then very gradually, so as not to explode the pellets with the compressed gas inside them, pump out and backfill with high purity argon containing some H₂ (but not air, which would oxidize the metal and cause loss of V). I used He + 0.1 vol% H₂. Gradually push the boat into the middle of an alumina tube furnace at ~400 °C (the temperature should not rise more than 100 °C/hr or the pellet is likely to be blown apart by the increased gas pressure).

If metal grains are not included in the pellets, the use of reducing or inert gases in a tube furnace can be avoided and the pellets heated in air in a muffle furnace in an alumina boat—provided some sort of non-oxidizable (i.e., not Mo) cover is placed over the top of the boat to keep MoSi₂ flakes from the heating element out of the CAI pellets.

Type A CAIs

From ~400 °C, the temperature can be programmed to
rise by \( \sim 200 \) °C/hr to 1470 °C. If the temperature rises to 1480 °C, the pellet melts too much and slumps, with a green liquid flowing out of the pores and sticking the pellet to the crucible. Dwell at 1470 °C for \( \sim 30 \) min to help sinter the pellet compactly, then cool at \( \sim 100 °C \) to 1420 °C, dwell for 1 hr, then cool at \( \sim 100 °C \) to 1400 °C, dwell for 1 hr, then cool at 100 °C/hr to room temperature. The pale grey CAI pellets are strong and hard with \( \sim 30\% \) small pores.

**Type B CAIs**

From \( \sim 400 °C \), the temperature can be programmed to rise by \( \sim 200 °C/hr \) to 1320 °C. If the temperature rises much above this, the pellet melts too much and slumps, with a green liquid flowing out of the pores and sticking the pellet to the crucible. Dwell at 1320 °C for \( \sim 3 \) hr to help sinter the pellet compactly, then cool slowly at \( \sim 50 °C \) to 1000 °C, then cool at 100 °C/hr to room temperature. The pale grey CAI pellets are strong, hard and slightly rounded, with \( \sim 30\% \) small pores and some sub-millimeter crystals.

**ULTRA REFRACTORY RESIDUES**

Stage I of rim formation requires the volatilization of essentially all the Mg, Si, and more volatile elements, plus their stoichiometric amounts of O from a 200 micron-wide surface layer. In addition, substantial amounts of Ca, Sr, Eu, V, and similar moderately refractory elements (plus their O) must be volatilized to create the observed 2.4- to 5.6-fold enrichments of ultra-refractory elements in the WL rims (after allowing for re-entry of some Mg, Si, and O during metamorphism of the ultra-refractory residue to create the layers of spinel, melilite, and pyroxene), as discussed in Wark and Boynton (2001). To create rims that are even more highly enriched in ultra-refractory elements, virtually all the Ca and other elements must be volatilized.

The compositions of the refractory residues are based on the experiments of Hashimoto (1983), who volatilized chondrite starting material and measured the residual fractions (RF) and compositions of the residues as volatilization progressed through loss of S, Fe, alkalis, Mg, Si, Ca, Ti, and finally Al. He found that primary CAI compositions correspond to RF = 6.5–7.5 mol% (average 7.0 mol%) of the starting chondrite. At RF = 3 mol%, the CAI composition would have been distilled down to produce a refractory enrichment of 7/3 = 2.3 times. From Hashimoto’s data, this corresponds to a refractory residue composition of 85.4% Al\(_2\)O\(_3\), 12.0% CaO and 2.6% TiO\(_2\), which is refractory residue #1 in Table 5, the minimum observed in CAI rims (Wark and Boynton 2001). In Table 5, refractory residue #2, which contains only 1.0% CaO, corresponds to an ultra-refractory enrichment factor of \( \sim 5 \).

In order to perform diffusion experiments to find the conditions required for metamorphism to produce the spinel, melilite, and pyroxene layers, the above two ultra-refractory residues (#1 and #2) were synthesized.

**Residue Compositions**

Weigh the desired total mass of components in the proportions of columns 3 or 5 of Table 5. Mix well and grind in mortar and pestle, then place in a covered alumina beaker to not more than half full. This is to prevent loss of powder, as it puffs up on decarbonation. Leave a gap below the lid to allow the escape of gas.

Decarbonate and react in a muffle furnace as follows:
- Heat for 6 hr at 1000° (the CaCO\(_3\) starts to decarbonate at \( \sim 900 °C \)), then for 18 hr at 1200 °C.
- Cool and break up the friable “cake,” then regrind in a mortar and pestle.
- Ball mill the mixture as above.
- RPM metal grains only (not the more volatile FeNiVRPM metal) may, if desired, be weighed in the proportions given above to the ball milled, reacted CAI mixture. It may be desirable also to add extremely fine-grained “iridium black” and “rhodium black.”
- Press and clean the pellets of residues as above. Note that pellets of the high-alumina residue #2 crumble very easily and need to be pressed more gently, to a load of \( \sim 300 \) lb.
- Fire the pellets loaded like “wheels” in an alumina boat in a tube furnace under reducing or inert gas (above). If metal grains are not included in the mixture, the pellets can be fired in air. Follow the precautions above concerning de-pressurizing and heating the pellets up to \( \sim 400 °C \). Then ramp the temperature up at \( \sim 100 °C/hr \) to 1700 °C (or, if such a furnace is available, to 1800 °C for a more compact residue). The pellets heated to 1700 °C

---

**Table 5. Compositions of mixtures to make ultra-refractory residues and masses to weigh out.**

<table>
<thead>
<tr>
<th>Component of residue</th>
<th>Wt% #1 residue</th>
<th>Mass #1 residue (g)</th>
<th>Wt% #2 residue</th>
<th>Mass #2 residue (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al(_2)O(_3)</td>
<td>85.4%</td>
<td>85.4 g</td>
<td>97.1%</td>
<td>97.1 g</td>
</tr>
<tr>
<td>CaO (wt%)</td>
<td>12.0% CaO</td>
<td>21.4 g CaCO(_3)</td>
<td>1.0% CaO</td>
<td>1.8 g CaCO(_3)</td>
</tr>
<tr>
<td>CaCO(_3)(mass)</td>
<td>2.6%</td>
<td>2.6 g</td>
<td>1.9%</td>
<td>1.9 g</td>
</tr>
<tr>
<td>TiO(_2)</td>
<td>0.035%</td>
<td>0.021 g Ca(_3)</td>
<td>0.035%</td>
<td>0.021 g Se(_3)</td>
</tr>
<tr>
<td>Sc, La, Ce, Eu, Yb,</td>
<td>(50 ppm each Sc-Zr)</td>
<td>0.006 g each La-Zr(_3)</td>
<td>(50 ppm each Sc-Zr)</td>
<td>0.006 g each La-Zr(_3)</td>
</tr>
<tr>
<td>Total</td>
<td>100.0%</td>
<td>109.4 g</td>
<td>100.0%</td>
<td>118.0 g</td>
</tr>
</tbody>
</table>

*Sources of traces elements are the same as in Table 1.*
Table 6. Compositions of mixtures to make melilite (5% akermanite) and masses to weigh.

<table>
<thead>
<tr>
<th>Component</th>
<th>Weight%</th>
<th>Mass to weigh out (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>40.92%</td>
<td>73.07 g CaCO₃</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>35.32%</td>
<td>35.32 g</td>
</tr>
<tr>
<td>MgO</td>
<td>0.74%</td>
<td>0.74 g</td>
</tr>
<tr>
<td>SiO₂</td>
<td>23.02%</td>
<td>23.02 g</td>
</tr>
<tr>
<td>La₂O₃</td>
<td>0.028%</td>
<td>0.028 g</td>
</tr>
<tr>
<td>Total</td>
<td>100.0%</td>
<td>132.15 g</td>
</tr>
</tbody>
</table>

The powdered mixture was ball milled as described above, then dried and heated in air as follows:

- 1100 °C for 2 hr
- 1200 °C for 3 hr
- Cooled, reground in a mortar and pestle, and pelletized.

It is very important to check the phase diagram, since the m.p. of melilite changes rapidly (Deer et al. 1966) with small compositional changes near the gehlenite end-member. In this case, several pellets were stacked on top of one another in narrow alumina crucibles and fired in air at 1530 °C for ~1 hr, then cooled as rapidly as possible without damage to the furnace.

The pellets just melted to a pale greenish glassy material and stuck slightly to the crucible, from which they had to be broken away.

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