Formation of spinel-, hibonite-rich inclusions found in CM2 carbonaceous chondrites

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ABSTRACT

We report petrography, mineral chemistry, and bulk isotopic compositions of a suite of 40 spinel-rich inclusions from the Murchison (CM2) carbonaceous chondrite. Seven types of inclusions have been identified based on mineral assemblage: spinel-hibonite-perovskite; spinel-perovskite-pyroxene; spinel-perovskite-melilite; spinel-hibonite-perovskite-melilite; spinel-hibonite; spinel-pyroxene; and spinel-melilite-anorthite. Hibonite-bearing inclusions have Ti-poor spinel compared to the hibonite-free ones, and spinel-hibonite-perovskite inclusions have the highest average bulk TiO2 contents (7.8 wt%). The bulk CaO/Al2O3 ratios of the inclusions range from 0.005 to 0.21, well below the solar value of 0.79. Hibonite- and spinel-rich inclusions consist of phases that are not predicted by condensation calculations to coexist; in the equilibrium sequence, hibonite is followed by melilite, which is followed by spinel. Therefore, hibonite-melilite or melilite-spinel inclusions should be dominant instead. One explanation for the “missing melilite” is that it condensed as expected, but was lost due to evaporation of Mg and Ca during heating and melting of spherule precursors. If this theory were correct, melilite-poor spherules would have isotopically heavy Mg and Ca, assuming Rayleigh fractionation accompanied evaporation. Except for one inclusion with $F_{\text{Mg}} = 4.3 \pm 2.6\%$ per amu and another with isotopically light Ca ($F_{\text{Ca}} = -3.4 \pm 2.0\%$ per amu), however, all the inclusions we analyzed have normal isotopic compositions within their 2σ uncertainties. Thus, we found no evidence for significant mass-dependent fractionation. Conditions necessary for non-Rayleigh evaporation are unlikely if not unrealistic, and our preferred explanation for the general lack of melilite among hibonite- and spinel-bearing inclusions is kinetic inhibition of melilite condensation relative to spinel. Because of similarities between the crystal structures of hibonite and spinel, it should be easier for spinel than for melilite to form from hibonite.

Keywords: Spinel, refractory inclusions, melilite, hibonite, carbonaceous chondrites, mass fractionation

INTRODUCTION

One way in which the origin of refractory inclusions is investigated is by comparing observed assemblages to results of equilibrium condensation calculations for a gas of solar composition. Although many refractory inclusions have undergone melting, by definition they consist of phases predicted to condense at high temperatures from a gas of solar composition. Spinel-, hibonite-bearing spherules, a major type of inclusion common in CM2 chondrites, consist of phases that are predicted by thermodynamic calculations to condense, but they are not predicted to coexist. Melilite (specifically, the gehlenite end-member, Ca2Al2SiO7), should form by reaction between hibonite (CaAl2O4) and vapor after almost all Al is condensed into hibonite. Then, after melilite formation has consumed all the Ca remaining in the vapor, the remaining hibonite should react with the vapor to form spinel sensu stricto, MgAl2O4. Throughout updates and additions to the database over the years, calculations (e.g., Grossman 1972; Yoneda and Grossman 1995; Ebel and Grossman 2000) consistently have shown that melilite should condense after hibonite and before spinel. Contrary to these predictions, however, spinel- and melilite-free melilite-spinel inclusions have not been reported. Instead, spinel-, spinel-bearing inclusions that are melilite-free or very melilite-poor are abundant among the inclusions found in CM2 chondrites, consistent with formation of spinel before melilite. For inclusions that were once molten, we assume that if melilite is present, then it was among the precursor phases that were melted. Therefore, the origin of spinel-, hibonite-rich, melilite-free inclusions has puzzled researchers for years. Some fine-grained inclusions that consist of spinel-, hibonite-, perovskite nodules ± thin melilite rims also provide petrographic evidence for formation of spinel before melilite (Krot et al. 2004).

Explanations that have been offered to reconcile the observed assemblages with condensation calculations include: slower formation of melilite than spinel (MacPherson et al. 1983); preferential nucleation of spinel upon hibonite relative to melilite (Beckett and Stolper 1994); suppression of melilite condensation due to depletion of the vapor in Al as a result of prior condensation and removal of an Al-rich phase (Beckett and Stolper 1994); condensation under conditions of supersaturation (Petaev et al.
2005); and loss of melilite originally present due to evaporation of Ca, Si, and Mg during partial melting of the precursors (MacPherson et al. 1983). MacPherson and Davis (1994) argued that spinel would have been destabilized by evaporation of Mg during melting, but if melting occurred at a temperature at which spinel was stable, preferential evaporation of the liquid relative to spinel could enhance the evaporation rates of Si and Ca relative to Mg, possibly further stabilizing spinel. If evaporation occurred from partially molten inclusions, then they should be measurably enriched in the heavier isotopes of these elements (i.e., $F_{26Mg}, F_{24Mg}, F_{Ca} > 0$), assuming Rayleigh-type fractionation occurred. We might also expect that melt-free inclusions would be more fractionated than those with melilitic. Previous studies of Ca (Ireland 1990) and Mg (Ireland 1988) isotopes in Murchison inclusions showed some positive mass-fractionations greater than analytical uncertainty and no large, negative fractionations, providing a hint that Ca and Mg evaporation did take place. That work did not reveal any correlation between Mg and Ca isotopic compositions, or between isotopic and chemical compositions. We have undertaken a petrologic and ion-microprobe study of a variety of spinel-bearing inclusions from Murchison to see whether they are isotopically fractionated and if there are any correlations of isotopic composition with mineral assemblage. Preliminary results of this work were reported by Simon and Grossman (2004) and by Simon et al. (2005a).

**RESULTS**

**Petrography**

The first step in this study was a detailed, systematic petrographic classification of spinel-rich spherules. Also known as “blue spherules” (MacPherson et al. 1983) or “SHIBs” (spinel hibonite inclusions; Ireland 1988), spinel-rich refractory spherules from CM chondrites actually exhibit a variety of mineral assemblages and textures and should not all be grouped together. The 40 spherules or fragments thereof selected for this study are from Murchison and range from 50 to 200 μm across. They comprise 12 spinel (sp)-hibonite (hib)-perovskite (pv) inclusions; 9 sp-pv-pyroxyene (pxy); 8 sp-pv-mellite (mel); 6 sp-hib-pv-mel; 2 sp-hib; 2 sp-pxy; and one sp-mel-anorthite. Although intended to represent the range of inclusion types found in Murchison, this suite is not intended to represent their relative proportions. We are mainly interested in spinel-hibonite-mellite inclusions, and these dominate our suite. Few inclusions considered here are free of both melilitic and hibonite, although sp-pxy inclusions are abundant in Murchison (MacPherson et al. 1983) and even more so in Mighei (MacPherson and Davis 1994). We have no spinel-perovskite inclusions, although such inclusions have been reported (Macdougall 1981). Some inclusions in our suite have rims of Fe-bearing phyllosilicate enclosed in an outer rim of aluminous diopside. Most inclusions have many rounded cavities, like those shown in MacPherson et al. (1983) and Macdougall (1981) that are commonly lined with melilitic or pyroxene, but some have few cavities and may be considered compact. Some spherules have uniform distributions of phases whereas others have phases that are concentrated in their cores relative to their edges. Representative photomicrographs (back-scattered electron images) of different types of spherules are shown in Figure 1.

**Spinel-hibonite-perovskite inclusions.** These inclusions would fall into the SHIB category of Ireland (1988). Most of these samples consist of hibonite laths and anhedral perovskite enclosed in spinel. The widths of hibonite laths range from just a few micrometers up to ~25 μm, and their lengths are 10–50 μm. Of the 12 samples in this category, nine are complete or nearly complete spherules and three are irregularly shaped fragments. Four spherules (e.g., Fig. 1a) have a uniform distribution of phases and four have hibonite-rich cores and spinel-rich rims (Fig. 1b). The remaining complete inclusion has an unusual structure, with a massive outer rim of spinel and a porous core of spinel + perovskite separated by a band of hibonite + perovskite. Among the three fragments of sp-hib-pv spherules, one is dominated by coarse hibonite with interstitial perovskite and spinel; one has approximately equal proportions of spinel and hibonite with minor perovskite; and one has sparse, thin hibonite laths and small, round perovskite grains enclosed in spinel. **Spinel-perovskite-pyroxyene inclusions.** With only one exception, these inclusions consist of fine (5–10 μm), anhedral...
FIGURE 1. Back-scattered electron images of spinel-rich inclusions from Murchison. (a) sp-hib-pv inclusion with a uniform texture and silicate rim. (b) sp-hib-pv inclusion with a hibonite-rich interior and spinel-rich mantle. (c) sp-pv-pyx inclusion with massive spinel and small inclusions of pv and pyx. (d) sp-pv-pyx inclusion with lath-shaped spinel that appears to pseudomorph hibonite. (e) sp-pv-mel inclusion with massive spinel and blebbly mel and pv. (f) sp-hib-pv-mel inclusion fragment with coarse hib in the interior and a spinel-rich mantle. (g) zoned sp-hib-pv-mel inclusion fragment, with a mel-rich core and sp-, hib-rich mantle. (h) coarse sp-hib-pv-mel inclusion fragment. al-diop: aluminous diopside; Fe-sil: Fe-bearing silicate; Hib: hibonite; Mel: melilite; Piv: perovskite; Pyx: pyroxene; Sp: spinel.
perovskite, and pyroxene (aluminous diopside) enclosed in porous or massive spinel. An example is shown in Figure 1c. All of these inclusions have rims of Al-diopside as well. One inclusion, M98RXL-5, differs markedly from the others in this group and is shown in Figure 1d. It is quite large (~200 × 150 μm) and consists of lath-shaped spinel with interstitial pyroxene and perovskite. Pore space and perovskite abundances decrease and pyroxene increases from core to rim. The inclusion is enclosed in rim layers of pyroxene and olivine.

**Spin-Perovskite-Melilites.** Six of these eight inclusions are texturally similar to the typical sp-pv-py inclusions, having fine, anhedral perovskite and melilitite enclosed in cavity-riddled spinel (Fig. 1e). One sp-pv-mel inclusion has both fine and coarse (~25 μm) melilitite enclosed in spinel. The remaining sp-pv-mel inclusion is dominated by melilitite and resembles a fragment of a compact Type A inclusion, with coarse, euhedral spinel, and fine perovskite enclosed in melilitite. Type As are melilitite-rich, coarse-grained refractory inclusions that are commonly found in CV3 chondrites and are quite rare in CMs. Only two of the sp-pv-mel inclusions have rims of pyroxene.

**Spin-Perovskite-Melilites-Melilites Inclusions.** This group exhibits the most textural diversity among the petrographic types we have distinguished. Only two spherule fragments have textures that are similar to each other. One is shown in Figure 1f. They are dominated by spinel and hibonite with fine, anhedral inclusions of melilitite and perovskite. One spherule fragment, M92HZ-5 (Fig. 1g), is zoned, with a spinel-hibonite-perovskite mantle enclosing a melilitite-spinel core. Another, M98L4 (Fig. 1h) is unusual in having relatively abundant and coarse melilitite occurring interstitial to hibonite laths and enclosed in spinel. Two sp-hib-pv-mel inclusions included in this study, BB-1 and MUM-1, were first described and shown by MacPherson et al. (1983). The former is an unrimmed, spheroidal object 100 μm across. The outer ~25 μm consist of spinel with interstitial melilitite and perovskite. The interior is dominated by hibonite with finer, anhedral melilitite, perovskite, and spinel. The melilitite in this inclusion is in contact with either hibonite or cavities. Inclusion MUM-1 is an unusual (for a CM chondrite), melilitite-dominated inclusion. A chain of subhedral spinel crystals runs through the inclusion, and most of the hibonite is enclosed in spinel. Along one edge of the inclusion fragment is a rim sequence of, from inside to outside, spinel, melilitite, anorthite, and diopside.

**Spin-Perovskite-Melilites Inclusions.** One of these samples, SH-6, was previously shown and described by MacPherson et al. (1984). The other sample, SH-5, is texturally similar to SH-6.

<table>
<thead>
<tr>
<th>Mineral chemistry</th>
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In all inclusions considered here, spinel is very close to end-member MgAl2O4 in composition, with small Ti, V, Cr, and Fe oxide components. Contents of V2O3 and TiO2 in spinel in the four most abundant inclusion types are summarized in Figure 2. Within each plot, each symbol (e.g., filled triangles) represents data from one inclusion, and the sample numbers are given in the legend. For some inclusions, the analyses tend to form tight clusters on these plots, whereas the spinel in other inclusions exhibits fairly wide ranges of TiO2 or V2O3 contents. Except for the sp-hib-pv-mel inclusions (Fig. 2d), the groups shown have bimodal distributions of V2O3 contents. In the sp-pv-py inclusions, there is a gap from ~0.15 to 0.25 wt% V2O3; among sp-hib-pv inclusions (Fig. 2b), spinel from a given inclusion has either <0.2 wt% V2O3 or >0.2 wt% V2O3; and, among sp-pv-mel inclusions (Fig. 2c), there is a gap from ~0.2 to 0.34 wt% V2O3, and only one inclusion has spinel with V2O3 contents between 0.2 and 0.55 wt%; unlike the other types, several of these inclusions contain spinel with >0.55 wt% V2O3. Spinel in the melilitite-rich inclusions, MUM-4 and MUM-1 (open triangles in Figs. 2c and 2d, respectively), is the most V2O3-rich among the present samples, but it is as V-rich as spinel in fluffy Type A inclusions, which typically contains >1.5 wt% V2O3 (MacPherson and Grossman 1984). Figure 2 also shows that spinel with >0.5 wt% TiO2 is more common in pyroxene-bearing inclusions than in the other inclusion types.

Hibonite compositions are summarized in Figure 3 and representative analyses are given in Table 1. Hibonite exhibits a range of Ti and Mg contents, which are strongly correlated, as Ti4+ (and Si4+) enters hibonite along with Mg in a coupled substitution for two Al3+ cations. We assume that the small amounts of FeO in some of the analyses are due to secondary substitution for Mg, so we plot Mg + Fe vs. Ti + Si in Figure 3, and the line for which Ti + Si = Mg + Fe is shown for reference. In these samples the TiO2 content of hibonite ranges from 1.1 to 9.0 wt%. There is much overlap between the sp-hib-pv and the sp-pv-mel inclusions, with the former exhibiting a slightly wider range of Ti and Mg contents than the latter. The analyses that plot below the Ti + Si = Mg + Fe line, especially those at

| TABLE 1. Representative analyses of hibonite in Murchison inclusions (wt%) |
|-----------------------------|------------------|------------------|------------------|------------------|
| MgO                         | 1.52             | 1.90             | 2.99             | 3.99             |
| Al₂O₃                       | 86.55            | 85.87            | 82.13            | 79.60            |
| SiO₂                        | 0.18             | 0.25             | 0.17             | 0.67             |
| CaO                         | 8.71             | 8.56             | 8.33             | 8.29             |
| TiO₂                        | 2.95             | 3.50             | 5.73             | 7.10             |
| V₂O₃                        | 0.14             | 0.04             | 0.29             | 0.36             |
| FeO                         | 0.07             | 0.14             | 0.04             | BDL              |
| Total                       | 100.12           | 100.26           | 99.68            | 100.01           | 100.01           |

Notes: 1 = from a sp-hib inclusion. 2, 3 = sp-hib-pv. 4, 5 = sp-hib-pv-mel. BDL = below detection limit of electron probe (0.036 wt% FeO).
the high Ti + Si end of the trend, probably reflect the presence of a small Ti³⁺ component, which can substitute for Al directly and therefore is not coupled with Mg.

The average V₂O₃ and TiO₂ contents of coexisting hibonite and spinel are compared in Figure 4. In a given inclusion, there is a strong positive correlation between the average V₂O₃ content of hibonite and that of spinel (Fig. 4a). In contrast, no such correlation is observed for the TiO₂ contents of these coexisting phases (Fig. 4b). The different systematics probably reflect different partitioning behavior, as discussed below. The sample that has V-rich hibonite and plots off the trend in Figure 4a is a fragment of an otherwise typical sp-hib-pv inclusion. The sample with Ti-rich spinel, plotting at ~0.98 wt% TiO₂ in Figure 4b, is the unusual, fluffy sp-hib inclusion SH-6.

Melilite compositions are plotted in Figure 5, which shows that all melilite in the inclusions analyzed for this study has ≤0.05 wt% Na₂O and, with the exception of MUM-4, is more aluminous than Åk 15. In MUM-4 the melilite is Åk₃₆-₃₈.
is no correlation between Na₂O and åkermanite contents. The Al-rich melilite compositions of the melilite-rich inclusions are like those of the fluffy Type A inclusions found in CV3 chondrites (MacPherson and Grossman 1984) but the textures of the Murchison inclusions are more compact. Like that in MUM-4, most melilite in compact Type A inclusions is Åk₂₀–₃₀ but, unlike that in MUM-4, most spinel in the compact Type As has <0.8 wt% V₂O₃ (Simon et al. 1999). To complete the comparison, in Type B coarse-grained inclusions, also found in CV3 chondrites, spinel typically has 0.15–0.6 wt% V (Connolly et al. 2003), or 0.2–0.9 wt% V as V₂O₃, and melilite that is mostly Åk₂₅ (Simon and Grossman 2006).

Pyroxene in the spherules is Mg-, Ca-rich clinopyroxene with a wide range of Al₂O₃ and TiO₂ contents. Representative analyses are given in Table 2. Unlike the Ti-rich pyroxene in coarse-grained inclusions, termed “fassaite” by Dowty and Clark (1973), the pyroxene in the spherules is very poor in Sc₂O₃ and V₂O₃. For example, most Sc₂O₃ contents are below the detection limit of the electron microprobe and all are <0.06 wt%. These values are lower than the Sc₂O₃ contents of most of the fassaite in compact Type A (Simon et al. 1999) and Type B (Simon et al. 1991) inclusions in CV3 chondrites, which reach ~2 and ~1 wt%, respectively. Pyroxene V₂O₃ contents are more like those of coarse-grained inclusions and are mostly between 0.1 and 0.5 wt%. Contents of Al₂O₃ in spherule pyroxenes are plotted against TiO₂(Tot) (all Ti reported as TiO₂) contents in Figure 6, which shows that almost all pyroxene in the rims of inclusions has <2 wt% TiO₂(Tot) and is Al-poor compared to that in the interiors. Most pyroxene in the interiors of spherules is Al-rich, has >5 wt% TiO₂(Tot) and Ti³⁺/Ti(Tot) from 0.16–0.65 (mostly between 0.2 and 0.4), calculated according to the methods of Beckett (1986). This contrast indicates that, even though most of the pyroxene in the interiors of inclusions fills interstices, it is not simply rim material that penetrated into the inclusions.

In one spinel-perovskite-pyroxene inclusion we found a small (~3 μm), rounded, Ca-free oxide grain. It is enclosed in spinel and contains about 17 wt% MgO, 19% Al₂O₃, and 64% TiO₂, corresponding to a formula approaching Mg₂Al₂Ti₄O₁₃. Spherule bulk chemical compositions

From the phase volume proportions and their densities, weight proportions of the phases in a subset of spherules were determined and, along with average phase compositions, were used to calculate inclusion bulk compositions. Neither phases in rim layers nor secondary alteration products were included in the modes. For this work we selected rim-to-rim sections of spherules or fragments that appear to be from homogeneous inclusions. For concentrically zoned spherules, compositions of cores and mantles were calculated separately, then combined according to their weight proportions. We avoided inclusion fragments with heterogeneous distributions of phases, but otherwise the inclusions are small enough (~100 μm across) that we can assume that the sections sample them representatively. Average composi-
The inclusions are all dominated by spinel and thus, are rich in Al\textsubscript{2}O\textsubscript{3} (all have >50 wt\%) and MgO (all >15 wt\%). The spinel-hibonite-perovskite inclusions can be quite perovskite-rich and as a result this group has the highest average TiO\textsubscript{2} as well as the lowest SiO\textsubscript{2} contents. The CaO/Al\textsubscript{2}O\textsubscript{3} ratios of the inclusions range from 0.0045 to 0.21, much lower than the solar value of 0.79.

The spherule bulk compositions plot well off trajectories of bulk equilibrium condensate compositions, such as the one calculated for a solar gas at P(Tot) = 10^{-3} bar shown in Figure 7, a plot of MgO vs. Al\textsubscript{2}O\textsubscript{3} contents. Compositions of phases and their end-member components are also plotted. Compositions of phases that are dominated by two phases, such as sp-pv-pyx inclusions that have only minor perovskite, fall along mixing lines between their major phases. The inclusion compositions do not appear to have been displaced from those of condensates by addition of spinel to condensate assemblages. Mathematical subtraction of spinel from the compositions to yield the solar CaO/Al\textsubscript{2}O\textsubscript{3} ratio, using the method of Grossman et al. (2000), in many cases yields unrealistic compositions that have negative MgO contents and/or >30 wt\% TiO\textsubscript{2}.

We also tried a calculation in which a sufficient amount of gehlenite was added to each spherule composition to increase its CaO/Al\textsubscript{2}O\textsubscript{3} ratio to the solar value. As Figure 7 shows, these “corrected” compositions plot on or close to the condensate trajectory. The scatter in the data is greatly reduced, and the compositions plot much closer to the condensate trajectory, compared to the raw data, on all oxide-oxide plots even though melilite is not present in all of the inclusions. Large proportions of melilite, ~4 g mel per gram of inclusion, are needed. As a result, after renormalization, the melilite-corrected compositions of the spherules are similar to compositions of compact

Type A (very melilite-rich) inclusions that have been corrected to the solar CaO/Al\textsubscript{2}O\textsubscript{3} ratio by melilite subtraction, which for these inclusions is analogous to addition of spinel (Grossman et al. 2000). Corrected Type A compositions are also shown in Figure 7. They have slightly lower Al\textsubscript{2}O\textsubscript{3} and CaO and higher MgO contents than the corrected spherule compositions.

<table>
<thead>
<tr>
<th>1</th>
<th>2</th>
<th>3*</th>
<th>4*</th>
<th>5*</th>
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<tbody>
<tr>
<td>MgO</td>
<td>18.46</td>
<td>15.89</td>
<td>9.96</td>
<td>12.87</td>
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<tr>
<td>Al\textsubscript{2}O\textsubscript{3}</td>
<td>0.53</td>
<td>6.92</td>
<td>18.23</td>
<td>11.94</td>
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<tr>
<td>SiO\textsubscript{2}</td>
<td>55.40</td>
<td>50.58</td>
<td>39.39</td>
<td>42.44</td>
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<tr>
<td>CaO</td>
<td>25.71</td>
<td>25.71</td>
<td>24.90</td>
<td>24.92</td>
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<tr>
<td>TiO\textsubscript{2}(Tot)</td>
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<tr>
<td>TiO\textsubscript{3}</td>
<td>BDL</td>
<td>0.06</td>
<td>0.15</td>
<td>0.28</td>
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<tr>
<td>FeO</td>
<td>0.10</td>
<td>0.25</td>
<td>0.56</td>
<td>BDL</td>
</tr>
<tr>
<td>TiO\textsubscript{2}</td>
<td>–</td>
<td>–</td>
<td>3.92</td>
<td>5.36</td>
</tr>
<tr>
<td>TiO\textsubscript{3}</td>
<td>–</td>
<td>–</td>
<td>2.16</td>
<td>2.34</td>
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<td>100.38</td>
<td>100.56</td>
<td>99.27</td>
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</table>

**Notes:** 1, 2 = rim pyroxene. 3–5 = interior pyroxene. BDL = below limit of detection of electron probe (0.027 wt\% V\textsubscript{2}O\textsubscript{3} or 0.36 wt\% FeO). TiO\textsubscript{2}(Tot) = all Ti assumed to be Ti\textsuperscript{4+}, or TiO\textsubscript{2}.

* Ti\textsuperscript{3+}/Ti\textsuperscript{4+} ratio calculated by assuming stoichiometry and normalizing to four cations, including one Ca cation, per six oxygen anions, according to the method of Beckett (1986).
### Table 3. Average compositions (and ranges) of spinel-rich inclusions from Murchison

<table>
<thead>
<tr>
<th></th>
<th>Sp-Hib-Pv (7)</th>
<th>Sp-Hib-Pv-Mel (3)</th>
<th>Sp-Pv-Mel (3)</th>
<th>Sp-Pv-Px (8)</th>
<th>Sp-Mel-An</th>
<th>Sp-Px</th>
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<tr>
<td>MgO</td>
<td>20.83 (15.37–25.47)</td>
<td>16.51 (15.72–18.06)</td>
<td>26.48 (25.86–27.32)</td>
<td>26.01 (23.95–27.92)</td>
<td>28.36</td>
<td>27.47</td>
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<tr>
<td>Al₂O₃</td>
<td>64.51 (54.17–72.09)</td>
<td>66.00 (65.36–67.38)</td>
<td>67.18 (66.58–68.33)</td>
<td>62.72 (53.67–69.94)</td>
<td>70.24</td>
<td>67.33</td>
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<tr>
<td>SiO₂</td>
<td>0.49 (0.17–1.62)</td>
<td>3.71 (2.03–5.19)</td>
<td>1.04 (0.62–1.54)</td>
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<tr>
<td>CaO</td>
<td>6.41 (2.82–11.38)</td>
<td>9.99 (7.89–11.92)</td>
<td>3.18 (2.05–3.85)</td>
<td>3.87 (0.68–7.32)</td>
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<tr>
<td>TiO₂</td>
<td>7.76 (3.52–15.93)</td>
<td>3.79 (2.58–4.65)</td>
<td>2.12 (1.67–2.51)</td>
<td>2.61 (1.95–2.51)</td>
<td>0.52</td>
<td>1.03</td>
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</table>

Note: Where greater than one, the numbers of inclusions averaged are given in parentheses in the column headings.

### Table 4. Weighted means of Mg and Ca isotopic analyses of four refractory inclusion types from Murchison (‰/amu)

<table>
<thead>
<tr>
<th>Type</th>
<th>F_Mg ± 2σ</th>
<th>F_Ca²⁶/Ca²⁴ ± 2σ</th>
</tr>
</thead>
<tbody>
<tr>
<td>M92H2-5</td>
<td>SHPvM</td>
<td>0.4±1.4</td>
</tr>
<tr>
<td>M98L4</td>
<td>SHPvM</td>
<td>–0.8±1.2</td>
</tr>
<tr>
<td>BB-1</td>
<td>SHPvM</td>
<td>4.3±2.6</td>
</tr>
<tr>
<td>MUM-1</td>
<td>SHPvM</td>
<td>–1±2.0</td>
</tr>
<tr>
<td>M92H2-34</td>
<td>SHPvM</td>
<td>1.2±1.2</td>
</tr>
<tr>
<td>M92H2-10</td>
<td>SHPv</td>
<td>–0.6±1.4</td>
</tr>
<tr>
<td>M98M11</td>
<td>SHPv</td>
<td>3.2±5.2</td>
</tr>
<tr>
<td>M98M18</td>
<td>SHPv</td>
<td>1.8±3.2</td>
</tr>
<tr>
<td>M98M9</td>
<td>SPx</td>
<td>–1±4.1</td>
</tr>
<tr>
<td>M92H2-37</td>
<td>SPx</td>
<td>0.8±2.2</td>
</tr>
</tbody>
</table>


In addition, we investigated Mg-Al systematics in six inclusions. Refractory inclusions commonly contained live 26Al, a short-lived radionuclide that decays to 26Mg with a half-life of 7.3 × 10⁷ years, when they formed. In a sample that initially contained live 26Al, δ²⁶Mg will now be positively correlated with Al/Mg. Our results are given in Table 5 and illustrated in Figure 9. We found that three sp-hib-pv-pyx inclusions (M98L4, MUM-1 and BB-1) and two sp-hib-pv inclusions (M98M11, M92H2-34) have measurable excesses of 26Mg that correlate with Al/Mg, yielding initial 26Al/²⁶Al ratios within error of 5 × 10⁻⁵, as illustrated in Figure 9. This is a common initial ratio among refractory inclusions (MacPherson et al. 1995). In contrast, one sp-hib-pv-pyrox inclusion (M92H2-5, shown in Fig. 1g) has a very low initial ratio, <3.6 × 10⁻⁴. Except for MUM-1, these inclusions could be classified as SHIBs according to the scheme of Ireland (1988), and this type of inclusion commonly contains radiogenic ²⁶Mg (Ireland 1988; 1990), as do most melilit-bearing, coarse-grained inclusions from CV chondrites (MacPherson et al. 1995; Simon et al. 2001). It is therefore unusual to find a melilit-bearing inclusion (M92H2-5) that did not contain live ²⁶Al when it formed.

**Discussion**

Significance of petrographic groupings

Some of the inclusions contain very small amounts of one or more of the phases used to classify them. If they were all assembled from the same suite of precursor grains, and if the various petrographic types of inclusions that we distinguished merely reflect nonrepresentative sampling in the laboratory rather than genetic differences, there should be few systematic mineral-chemical differences related to the petrographic groupings. The spinel in one type of inclusion would be no different from that in any other type, and the plots in Figure 2 would all look very similar to each other. Although there is some overlap in compositions among spinel from different types of inclusions, there are differences between types. For example, spinel in most of the sp-pv-pyx inclusions, unlike that in other types, has wide ranges of TiO₂ contents. Several sp-pv-
mel inclusions have spinel with higher V$_2$O$_3$ contents than spinel in any of the sp-pv-pyx inclusions we analyzed. In addition, the correlation of V$_2$O$_3$ contents in coexisting hibonite and spinel (Fig. 4a), and the homogeneity of isotopic compositions of coexisting phases suggest that, within each spherule, the phases are related to each other and do not represent random assemblages of grains that have been sampled with various degrees of accuracy.

Generation of observed mineral assemblages and the “missing melilite”

Many of the inclusions upon which this study is based have features, such as interlocking spinel and hibonite grains, and hibonite laths that interfered with each other during growth, which suggest that they crystallized from molten droplets. In addition, the correlated V and uncorrelated Ti contents of coexisting spinel and hibonite (Fig. 4) are also consistent with igneous histories for the samples. Experiments have shown that V$_2$O$_3$ is compatible in spinel during crystallization from a melt, especially at low oxygen fugacities (Connolly and Burnett 2003). Thus, if V is also compatible in hibonite, it is reasonable that V contents in hibonite and spinel would be correlated with each other and, therefore, with bulk V$_2$O$_3$ contents of the host spherules. On the other hand, TiO$_2$ is strongly incompatible in spinel (Connolly and Burnett 2003). The partitioning behavior of TiO$_2$ in hibonite ranges from weakly incompatible to strongly compatible, and the crystal/liquid partition coefficient decreases with increasing bulk TiO$_2$ content (Beckett and Stolper 1994). This behavior leads to weak relationships between hibonite and bulk TiO$_2$ contents and between spinel and hibonite TiO$_2$ contents. The contrasting systems observed for V and Ti in coexisting spinel and hibonite are thus consistent with their different partitioning behavior with respect to these phases, showing that the spinel and hibonite within most inclusions is genetically related to each other. It is therefore not surprising that the anomalous sample in the Ti plot (Fig. 4b) is SH-6, which is likely a gas-solid condensate that was never molten (MacPherson et al. 1984). The sample with V-rich hibonite, which plots off the V trend in Figure 4a, probably is a condensate also or contains relict hibonite.

At the temperatures required to keep these objects even
partially molten, which are >2200 K for their present bulk compositions, Mg, Si, and even Ca should volatilize in a reducing gas. Our analyses, however, yield values of \( F_{\text{Mg}} \) that are lower than those typical of Type B CAIs (Grossman et al. 2000), implying smaller mass losses than in the case of those inclusions. Evaporative loss of SiO2 and CaO, however, could have led to stabilization of spinel, causing crystallization of spinel and consequent retention of Mg in the spherules, even as heating and evaporation continued.

In addition, our calculations show that to correct the spherule bulk compositions to the solar CaO/Al2O3 ratio requires adding so much melilite that they approach the compositions of Type A inclusions, which MacPherson et al. (1983) suggested as a possible precursor condensate assemblage. To derive the compositions of the spherules that we studied through evaporation from such equilibrium condensates would require losses of 75–95% of the Ca originally present, which would lead to \( \delta_{\text{Ca}} \) values on the order of 17–35‰/amu, assuming Rayleigh distillation. Such fractionations of Ca isotopic compositions are neither observed here nor seen in any previous studies.

A reviewer pointed out that a way to evaporate without isotopic fractionation is to do so from the solid state. For the present samples, this would seem to require that the Ca was predominantly hosted in a phase that became unstable upon heating, leading to its preferential evaporation, due either to the higher vapor pressure of Ca over a less stable phase or a higher kinetic coefficient of evaporation of Ca for that phase, or both. To form Ca-poor inclusions from the residues would require that Ca evaporated faster than it reacted with the condensed phases to form a more stable assemblage and that, even if a Ca-enriched vapor formed, it was removed from contact with the residue before it could recondense. Although this sequence of events cannot be ruled out, it seems very unlikely, because temperatures high enough to cause evaporation of Ca are generally high enough to allow reaction between condensed phases.

Another way non-Rayleigh evaporation could have occurred is if relatively high partial pressures of the evaporating elements existed in the ambient gas, retarding their escape and reducing isotopic mass-fractionations in the residue as a result of isotopic exchange. Because the isotopic compositions are uniform from grain to grain within each spherule, such isotopic exchange with the ambient gas would have had to occur while the inclusions were above their solidus. In fact, for all grains within a given spherule to exchange with the same liquid composition, temperatures would have had to be high enough for at least several tens of percent liquid to be present, which is ~2273 K for these compositions. Grossman and Fedkin (2003) modeled evaporation of a CMAS (CaO-MgO-Al2O3-SiO2) liquid into ambient gas in a closed system of solar composition, and found that Mg isotopic exchange occurred when the MgO content of the liquid was close enough to its equilibrium value that the vapor pressure was no more than a factor of ten higher than the ambient pressure. They also calculated the vapor pressure of Mg over a metastable CMAS liquid containing 15 wt% MgO in a system of solar composition over a wide range of hydrogen pressures and temperatures. This value is close to the average MgO content of the spherules, ~20%. Extrapolation of these data implies that the vapor pressures of Mg necessary to stabilize 15 wt% MgO in a CMAS liquid at 2273 K are ~4.0 × 10^-4 and 2.0 × 10^-3 bar at total hydrogen pressures of 1.4 × 10^-3 and 1.4 × 10^-1 bar, respectively. At these total hydrogen pressures, the ambient pressures of Mg in a solar gas are only 5.5 × 10^-4 and 5.5 × 10^-3 bar, respectively, orders of magnitude below the respective values required for incipient back-reaction. Alternatively, if the ambient pressure of Mg is augmented by enrichment of dust relative to gas, the minimum dust enrichments required for incipient back-reaction are >7000 and >350 at total hydrogen pressures of 1.4 × 10^-4 and 1.4 × 10^-3 bar, respectively. Such conditions are unlikely for dynamic reasons (Cassen 2001). Given that most of the inclusions were once molten, the lack of evidence for evaporation is puzzling.

If evaporation did not occur, however, there must be another explanation for the “missing melilitite,” and several have been offered by various workers. Most are problematic. One suggestion that is unsatisfactory is that condensation of a highly aluminous phase removed enough Al (~20%) to delay melilitite formation relative to spinel (Beckett and Stolper 1994). This mechanism will not work because all Al must be condensed into hibonite before either melilitite or spinel becomes stable, and hibonite is needed to react with the gas to make melilitite and spinel. Furthermore, the present samples and fine-grained, hibonite-bearing inclusions have very low Ca/Al ratios relative to a solar gas, which would not be expected for formation from an Al-depleted source. The only way to delay gehlenite condensation relative to spinel would be to remove Ca from the gas in a refractory phase without removing Mg. Removal of early, Al-rich condensates would not lead to condensation of melilitite before spinel.

It has also been suggested (Petaev et al. 2005) that a combination of (1) condensation at low pressure (<2.5 × 10^-4 bar)
under conditions that are far from equilibrium, with rapid cooling of the gas; and (2) incomplete condensation of all minerals that should condense before spinel, including melilite, would lead to condensation of spinel before melilite. There is no direct evidence for this process, and there is no apparent reason why spinel should condense completely when all phases preceding it did not. Petaev et al. (2005) suggest that if the Al-diopside found enclosing spinel-rich nodules in fine-grained CAIs (Krot et al. 2004) is a condensate, it would require that hibonite stop condensing before it consumed all the gaseous Al and that some Al remained in the gas even after the formation of aluminates, melilite, and spinel. For this to occur is very far from the predictions of models of equilibrium condensation (e.g., Yoneda and Grossman 1995), which show that hibonite condensation alone should consume >95% of the Al in the gas, and that melilite formation should use up the rest.

Rare spinel-hibonite inclusions have been found in Murchison that appear to record formation of spinel directly from hibonite. An example is shown in Figure 10. This sample, SH-6, is a fluffy aggregate of hibonite plates with a rind of spinel. It was first described by MacPherson et al. (1984), who presented very strong arguments that this object is a condensate. As pointed out by MacPherson et al. (1984), the interior of this inclusion, visible in the left half of Figure 10, is monomineralic, with euhedral hibonite crystals and a high volume of void space, features that are not consistent with crystallization from a melt, but are consistent with vapor-solid condensation. In addition, some of the spinel grains have a lathlike morphology like that of hibonite. This morphology is very unusual for spinel, and was almost certainly inherited from precursor grains of hibonite. As noted by MacPherson et al. (1984), at the hibonite-spinel contact, there are laths that consist of hibonite at one end and spinel at the other.

Several of these are indicated by arrows in Figure 10. Formation of spinel from hibonite appears to have gone to completion in Murchison inclusion M98RXL-5 (Fig. 1d), which consists of spinel laths and interstitial clinopyroxene. It looks like a fluffy hibonite aggregate, but contains no hibonite at all.

There are no known samples that are melilite analogs of M98RXL-5, i.e., dominated by melilite pseudomorphs after hibonite. Simon et al. (2005b), however, have recently described two inclusions from an Antarctic CM2, LEW85311, that exhibit partial replacement of hibonite by melilite. An example is shown in Figure 11, which consists of a back-scattered electron image (Fig. 11a), and Al, Si, and Ca X-ray maps (Figs. 11b–11d, respec-
Note the hibonite grain, indicated by an arrow in Figure 11a, that has been converted to melilite along its upper edge (as seen in this view), where the grain is in contact with a cavity. Nearby, hibonite contains thin, Si-, Ca-bearing bands that occur along cleavage traces and grain boundaries. These can be seen in the X-ray maps within the outlined area. Analyses of these blades and of other, diffuse SiO$_2$-bearing areas within hibonite fall on mixing lines between hibonite and melilite, consistent with finely intergrown mixtures of the two phases. Melilite can follow hibonite in the crystallization sequences of some liquids, but that normally leads to sharp grain boundaries. What we see in this sample, with diffuse hibonite-melilite contacts and melilite occurring adjacent to void space and along cleavage traces, appears consistent with infiltration of the nebular vapor into the inclusion and reaction between hibonite and gas, forming melilite. This inclusion could be a condensate that became rounded by abrasion with other particles. Although there are some inclusions, such as the one in Figure 11, that appear to record incipient conversion of hibonite to melilite, the extent of this reaction appears to have been much more limited than that of the spinel-forming reaction among the refractory inclusions in CM2 chondrites.

The textures of the inclusions shown in Figures 10 and 11 are consistent with equilibrium calculations that show that neither spinel nor melilite simply condense from the nebular vapor onto hibonite; both spinel and melilite form by reaction between solid hibonite and the surrounding gas, after Al is completely condensed, a requirement for either melilite or spinel to be stable (Yoneda and Grossman 1995). Lower temperatures are required for pyroxene formation than for melilite or spinel formation, and it is much more likely that the Al-diopside found in the fine-grained inclusions, like the spinel in the inclusion shown in Figure 10, formed by reaction between Al-poor gas and Al-rich solids, than it is that a significant amount of Al remained in the gas after formation of hibonite, spinel, and melilite (Petaev et al. 2005).

The problems with the above models leave kinetic suppression of melilite condensation relative to spinel, first suggested by Bar-Matthews et al. (1982), as the most likely explanation for the general lack of melilite in hibonite-bearing, spinel-rich inclusions. Why might formation of spinel from hibonite have been favored over melilite formation? Comparison of the crystal structures provides a possible explanation. As noted by Beckett and Stolper (1994), there are similarities between the hibonite structure and that of spinel that could promote formation of spinel rather than melilite. The hibonite structure has Al-oxide layers and Ca-bearing layers. The former, called “spinel slabs” (Wagner and O’Keeffe 1988) or “spinel blocks” (Burns and Burns 1984), have sheets of Al-centered, edge-sharing octahedra, as does spinel. These structures are illustrated in Figure 12. The composition of the “spinel slab” within the hibonite structure is \((\text{Al}_2\text{O}_3)\) (Wagner and O’Keeffe 1988), and Beckett and Stolper (1994) suggested that spinel would readily nucleate on such a substrate. In contrast, the Ca-bearing layers in hibonite are not analogous to any part of the melilite structure. Calcium is 12-coordinated in hibonite and is 8-coordinated in melilite. It should therefore be much easier for spinel—rather than melilite—to form from hibonite. Therefore we favor, as did MacPherson and Davis (1994), kinetic inhibition of melilite formation, relative to spinel formation, as the best explanation for the origin and high abundance of spinel-, hibonite-rich, melilite-poor inclusions, relative to melilite-rich ones, in the CM2 chondrites. Some condensate assemblages were at least partially melted, forming spherules. There were, of course, some regions of the nebula where local cooling rates or other physico-chemical conditions were different, such that melilite did form in proportions relative to spinel that are much closer to the predictions of equilibrium condensation calculations, giving rise to the Types A and B refractory inclusions. Some Type A inclusions appear to be gas-solid condensates (MacPherson and Grossman 1984; Simon et al. 1999), where the Type B inclusions crystallized from partial melts of solid precursors (Stolper and Paque 1986). The melilite-rich inclusions were incorporated into the CV and CO condensates.
carbonaceous chondrites, and the mellilitie-poor inclusions were incorporated into the CMs.

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