

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

STEVEN B. SIMON,^{1,*} LAWRENCE GROSSMAN,^{1,2} IAN D. HUTCHEON,³ DOUGLAS L. PHINNEY,³
PETER K. WEBER,³ AND STEWART J. FALLON³

¹Department of the Geophysical Sciences, University of Chicago, 5734 S. Ellis Avenue, Chicago, Illinois 60637, U.S.A.

²The Enrico Fermi Institute, University of Chicago, 5640 S. Ellis Avenue, Chicago, Illinois 60637, U.S.A.

³Glenn T. Seaborg Institute, Lawrence Livermore National Laboratory, P.O. Box 808, Livermore, California 94551, U.S.A.

ABSTRACT

We report petrography, mineral chemistry, bulk 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-, 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 $F_{\text{Mg}} = 4.3 \pm 2.6\text{‰/amu}$ and another with isotopically light Ca ($F_{\text{Ca}} = -3.4 \pm 2.0\text{‰/amu}$), however, all the inclusions we analyzed have normal isotopic compositions within their 2 σ 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-, 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 (CaAl₁₂O₁₉) 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) consis-

tently have shown that melilite should condense after hibonite and before spinel. Contrary to these predictions, however, spinel-free, hibonite-melilite inclusions have not been reported. Instead, hibonite-, 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 \pm 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.

* E-mail: sbs8@midway.uchicago.edu

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_{Mg} , F_{Si} , $F_{Ca} > 0$), assuming Rayleigh-type fractionation occurred. We might also expect that melilite-free inclusions would be more fractionated than those with melilite. 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).

ANALYTICAL METHODS

Polished sections of 40 refractory spherules and fragments thereof that were separated from the Murchison (CM2) chondrite by standard freeze-thaw techniques (e.g., MacPherson et al. 1980) were studied with a JEOL JSM-5800LV scanning electron microscope at the University of Chicago equipped with an Oxford/Link ISIS-300 energy dispersive X-ray analysis system and classified by mineral assemblage. Wavelength-dispersive analyses of a subset of this suite were obtained with a Cameca SX-50 electron microprobe at the University of Chicago, operated at 15 kV and 25 nA. Pure oxide, synthetic glass, and natural mineral standards were used. Data were reduced with the modified ZAF correction procedure PAP (Pouchou and Pichoir 1984).

Initial isotopic analyses were performed with a modified ims-3f ion microprobe at Lawrence Livermore National Laboratory (LLNL) following conventional procedures (e.g., Goswami et al. 1994; Ireland 1990). The phases of interest in the inclusions were located by optical microscopy and ion imaging; a small field aperture inserted in the sample image plane ensured acceptance of secondary ions only from the single phase of interest. Mass-dependent isotope fractionation for Mg and Ca was determined relative to the respective compositions of appropriate terrestrial minerals. Standards included Burma spinel, Madagascar hibonite, synthetic Åk60 melilite glass, DeKalb diopside, and Miakejima plagioclase. The magnitudes of isotope fractionation, F_{Mg} and F_{Ca} , were calculated as the permil/amu deviation in the respective $^{25}Mg/^{24}Mg$ and $^{44}Ca/^{40}Ca$ ratios relative to values measured in the appropriate terrestrial standards. Positive F_{Mg} and F_{Ca} values reflect compositions enriched in the heavier isotopes relative to terrestrial standards. Excesses in ^{26}Mg , from the decay of ^{26}Al , were determined using a power law mass-fractionation correction; excesses are expressed as $\delta^{26}Mg$ relative to the reference $^{26}Mg/^{24}Mg$ value of 0.13932. Quoted uncertainties are two standard deviations of the mean, and are propagated to include contributions from the reproducibility of standards and the error of individual analyses.

In a second series of analyses, Mg isotope ratios were determined with the LLNL NanoSIMS 50 ion microprobe. An ^{16}O primary beam of 10–30 pA focused to 0.2–0.3 μm diameter was rastered over selected areas of the inclusions ranging in size from $20 \times 20 \mu m$ to $3 \times 3 \mu m$ to generate quantitative isotope ratio images. Positive secondary ions of the three Mg isotopes and $^{27}Al^{+}$ (corresponding to mass 13.5) were measured in multi-detection mode with four different electron multipliers at a mass-resolving power of ~3500–4000. For each area, 20–40 consecutive images were taken and then combined to produce an integrated 256×256 pixel image. The data were processed as quantitative isotopic ratio images using custom software (*L'Image*; L.R. Nittler). Each analysis area was subdivided into regions

of interest (ROIs) corresponding to the different mineral phases contained in the image and the isotopic composition for each ROI calculated by integrating over all the pixels within the ROI. For each inclusion, the Mg isotope compositions were normalized to the composition of spinel grains analyzed previously with the ims-3f. The Al/Mg ratios were determined using sensitivity factors generated by analyses of the terrestrial standards. The reproducibility of $^{25}Mg/^{24}Mg$ and $^{26}Mg/^{24}Mg$ ratios was within several permil. These variations are included in the errors given for F_{Mg} and $\delta^{26}Mg$.

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-pyroxene (pyx); 8 sp-pv-melilite (mel); 6 sp-hib-pv-mel; 2 sp-hib; 2 sp-pyx; 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±melilite inclusions, and these dominate our suite. Few inclusions considered here are free of both melilite and hibonite, although sp-pyx 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 melilite 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-pyroxene inclusions. With only one exception, these inclusions consist of fine (5–10 μm), anhedral

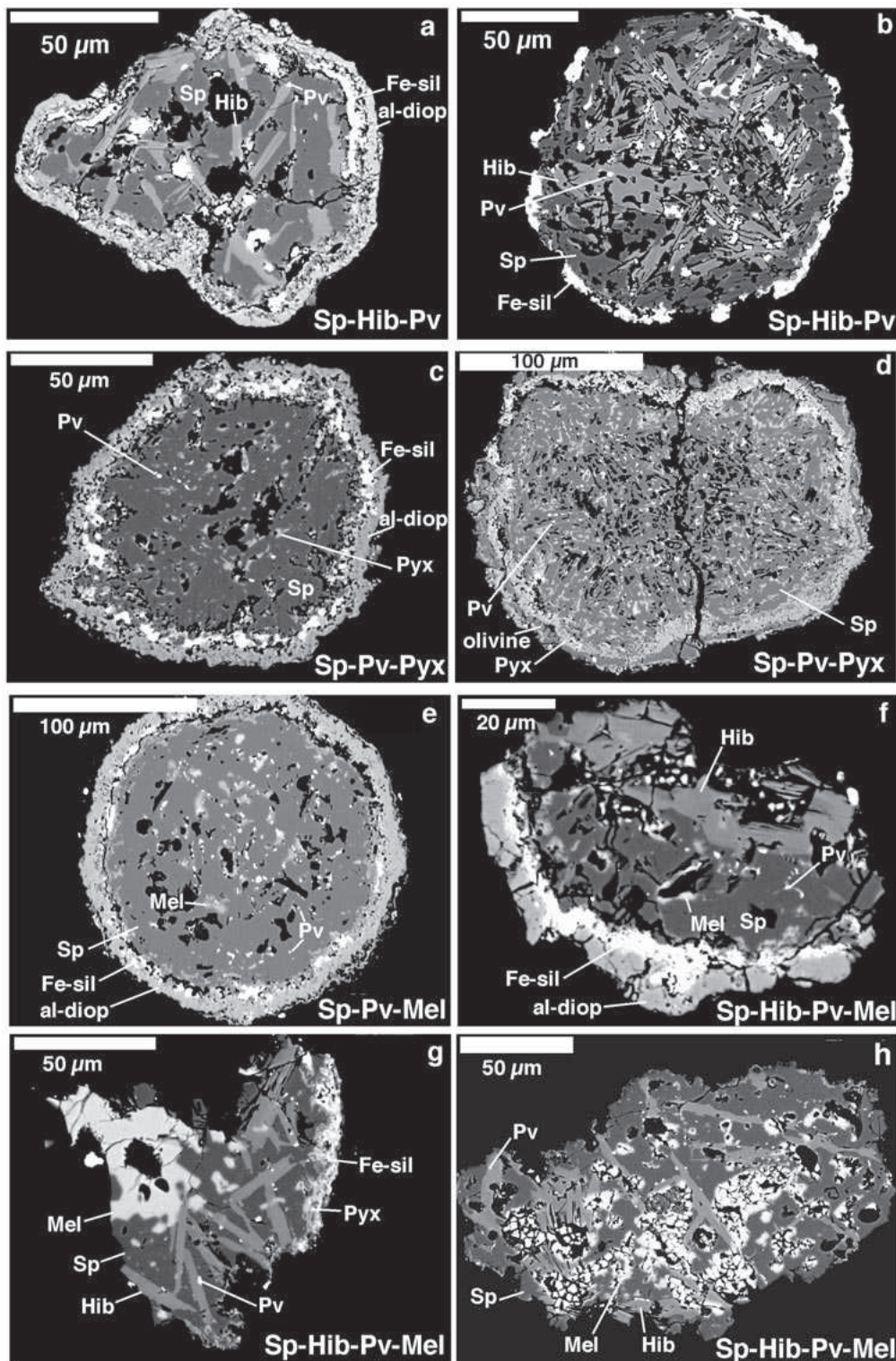


FIGURE 1. Back-scattered electron images of spinel-rich inclusions from Murchison. (a) sp-hib-pv inclusion with a uniform texture and silicate rim. (b) sp-hib-pv inclusion with a hibonite-rich interior and spinel-rich mantle. (c) sp-pv-pyx inclusion with massive spinel and small inclusions of pv and pyx. (d) sp-pv-pyx inclusion with lath-shaped spinel that appears to pseudomorph hibonite. (e) sp-pv-mel inclusion with massive spinel and blebby 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; Pv: 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 ($\sim 200 \times 150 \mu\text{m}$) 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.

Spinel-perovskite-melilite inclusions. Six of these eight inclusions are texturally similar to the typical sp-pv-pyx inclusions, having fine, anhedral perovskite and melilite enclosed in cavity-riddled spinel (Fig. 1e). One sp-pv-mel inclusion has both fine and coarse ($\sim 25 \mu\text{m}$) melilite enclosed in spinel. The remaining sp-pv-mel inclusion is dominated by melilite and resembles a fragment of a compact Type A inclusion, with coarse, euhedral spinel, and fine perovskite enclosed in melilite. Type As are melilite-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.

Spinel-hibonite-perovskite-melilite 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 melilite and perovskite. One spherule fragment, M92H2-5 (Fig. 1g), is zoned, with a spinel-hibonite-perovskite mantle enclosing a melilite-spinel core. Another, M98L4 (Fig. 1h) is unusual in having relatively abundant and coarse melilite 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, spherical object $100 \mu\text{m}$ across. The outer $\sim 25 \mu\text{m}$ consist of spinel with interstitial melilite and perovskite. The interior is dominated by hibonite with finer, anhedral melilite, perovskite, and spinel. The melilite in this inclusion is in contact with either hibonite or cavities. Inclusion MUM-1 is an unusual (for a CM chondrite), melilite-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, melilite, anorthite, and diopside.

Spinel-hibonite 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. Both samples are structurally zoned, with interiors consisting of fluffy aggregates of hibonite laths, $5\text{--}10 \mu\text{m}$ long, partially enclosed by an outer zone of relatively massive spinel. At the spinel-hibonite contact, spinel has a lathlike morphology similar to that of the hibonite.

Spinel-pyroxene inclusions. These two samples consist of porous spinel with small ($<10 \mu\text{m}$), anhedral inclusions of pyroxene, in a texture similar to that of typical sp-pv-pyx spherules (Fig. 1c). Both of the sp-pyx spherules are rimmed by pyroxene.

Spinel-melilite-anorthite inclusion. One unrimmed spherule consists almost completely of spinel, with sparse, small ($<10 \mu\text{m}$) inclusions of anhedral melilite and anorthite.

Mineral chemistry

In all inclusions considered here, spinel is very close to end-member MgAl_2O_4 in composition, with small Ti, V, Cr, and Fe oxide components. Contents of V_2O_3 and TiO_2 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 TiO_2 or V_2O_3 contents. Except for the sp-hib-pv-mel inclusions (Fig. 2d), the groups shown have bimodal distributions of V_2O_3 contents. In the sp-pv-pyx inclusions, there is a gap from ~ 0.15 to $0.25 \text{ wt}\% \text{ V}_2\text{O}_3$; among sp-hib-pv inclusions (Fig. 2b), spinel from a given inclusion has either $<0.2 \text{ wt}\% \text{ V}_2\text{O}_3$ or $>0.2 \text{ wt}\% \text{ V}_2\text{O}_3$; and, among sp-pv-mel inclusions (Fig. 2c), there is a gap from ~ 0.2 to $0.34 \text{ wt}\% \text{ V}_2\text{O}_3$, and only one inclusion has spinel with V_2O_3 contents between 0.2 and $0.55 \text{ wt}\%$; unlike the other types, several of these inclusions contain spinel with $>0.55 \text{ wt}\% \text{ V}_2\text{O}_3$. Spinel in the two melilite-rich inclusions, MUM-4 and MUM-1 (open triangles in Figs. 2c and 2d, respectively), is the most V_2O_3 -rich among the present samples, but it is not as V-rich as spinel in fluffy Type A inclusions, which typically contains $>1.5 \text{ wt}\% \text{ V}_2\text{O}_3$ (MacPherson and Grossman 1984). Figure 2 also shows that spinel with $>0.5 \text{ wt}\% \text{ TiO}_2$ 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 Ti^{4+} (and Si^{4+}) enters hibonite along with Mg in a coupled substitution for two Al^{3+} cations. We assume that the small amounts of FeO in some of the analyses are due to secondary substitution for Mg, so we plot $\text{Mg} + \text{Fe}$ vs. $\text{Ti} + \text{Si}$ in Figure 3, and the line for which $\text{Ti} + \text{Si} = \text{Mg} + \text{Fe}$ is shown for reference. In these samples the TiO_2 content of hibonite ranges from 1.1 to $9.0 \text{ wt}\%$. There is much overlap between the sp-hib-pv and the sp-hib-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 $\text{Ti} + \text{Si} = \text{Mg} + \text{Fe}$ line, especially those at

TABLE 1. Representative analyses of hibonite in Murchison inclusions (wt%)

	1	2	3	4	5
MgO	1.52	1.90	2.99	3.99	4.22
Al_2O_3	86.55	85.87	82.13	79.60	78.60
SiO_2	0.18	0.25	0.17	0.67	0.27
CaO	8.71	8.56	8.33	8.29	8.42
TiO_2	2.95	3.50	5.73	7.10	8.38
V_2O_3	0.14	0.04	0.29	0.36	0.12
FeO	0.07	0.14	0.04	BDL	BDL
Total	100.12	100.26	99.68	100.01	100.01
Cations per 19 oxygen anions					
Mg	0.254	0.317	0.504	0.674	0.713
Al	11.428	11.327	10.964	10.620	10.506
Si	0.020	0.028	0.020	0.076	0.031
Ca	1.046	1.026	1.011	1.006	1.024
Ti	0.249	0.295	0.488	0.605	0.715
V	0.006	0.002	0.013	0.016	0.006
Fe	0.006	0.013	0.004	0	0
Total cations	13.009	13.008	13.004	12.997	12.995

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 ($0.036 \text{ wt}\% \text{ FeO}$).

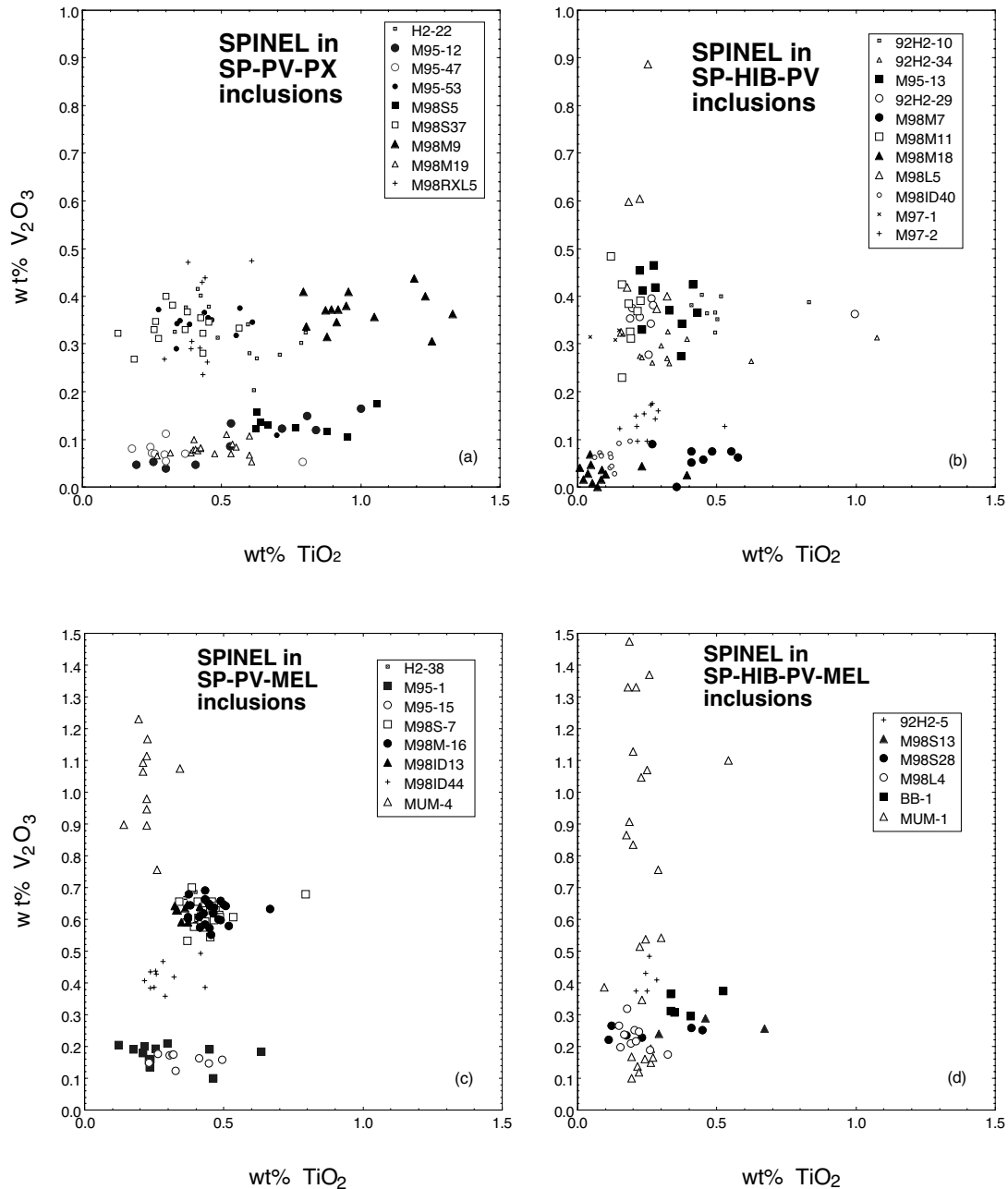


FIGURE 2. V_2O_3 and TiO_2 contents of spinel in the four most abundant types of inclusions considered here. Spinel in hibonite-bearing inclusions tends to have <0.5 wt% TiO_2 , and melilite-bearing inclusions are more likely to contain V_2O_3 -rich spinel than melilite-free ones. Abbreviations as used previously.

the high Ti + Si end of the trend, probably reflect the presence of a small Ti^{3+} component, which can substitute for Al directly and therefore is not coupled with Mg.

The average V_2O_3 and TiO_2 contents of coexisting hibonite and spinel are compared in Figure 4. In a given inclusion, there is a strong positive correlation between the average V_2O_3 content of hibonite and that of spinel (Fig. 4a). In contrast, no such correlation is observed for the TiO_2 contents of these coexisting phases (Fig. 4b). The different systematics probably reflect dif-

ferent 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% TiO_2 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% Na_2O and, with the exception of MUM-4, is more aluminous than Åk_{15} . In MUM-4 the melilite is Åk_{20-30} . There

is no correlation between Na_2O 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 Åk_{20-30} but, unlike that in MUM-4, most spinel in the compact Type As has <0.8 wt% V_2O_3 (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 V_2O_3 , and melilite that is mostly $\text{Åk}_{>25}$ (Simon and Grossman 2006).

Pyroxene in the spherules is Mg-, Ca-rich clinopyroxene with a wide range of Al_2O_3 and TiO_2 contents. Representative

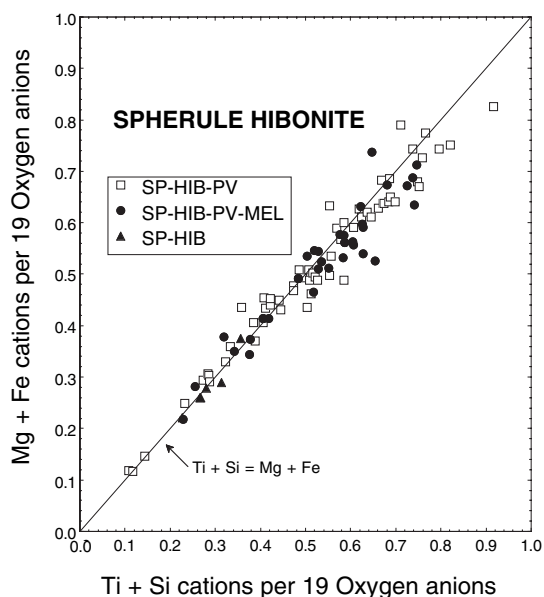


FIGURE 3. Plot of total Mg + Fe cations against total Ti + Si cations per 19 oxygen anions in hibonite from Murchison inclusions. The strong correlation reflects the dominant substitution mechanism, $\text{Mg} + \text{Ti} \leftrightarrow 2\text{Al}$.

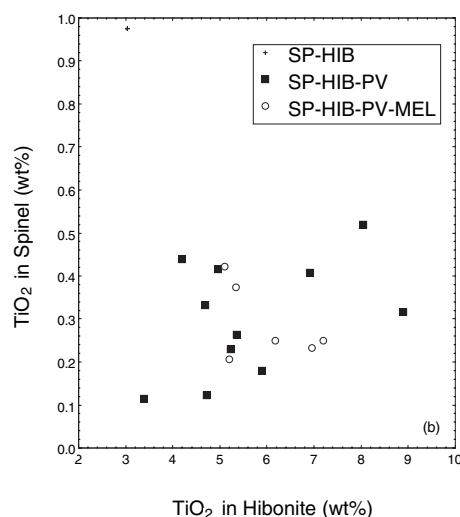
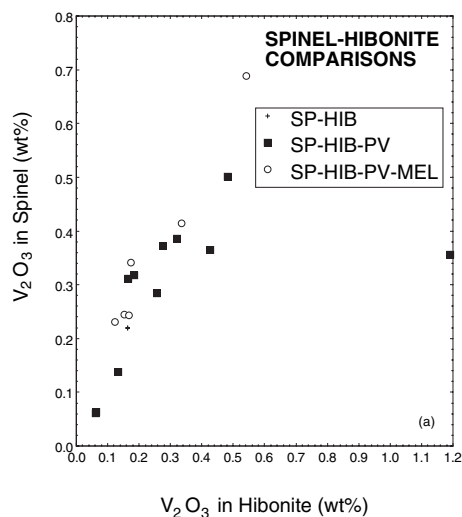


FIGURE 4. Plots of (a) average V_2O_3 in spinel vs. average V_2O_3 in coexisting hibonite, and (b) average TiO_2 in spinel vs. average TiO_2 in coexisting hibonite. Each point represents one inclusion.

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 Sc_2O_3 and V_2O_3 . For example, most Sc_2O_3 contents are below the detection limit of the electron microprobe and all are <0.06 wt%. These values are lower than the Sc_2O_3 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 V_2O_3 contents are more like those of coarse-grained inclusions and are mostly between 0.1 and 0.5 wt%. Contents of Al_2O_3 in spherule pyroxenes are plotted against $\text{TiO}_2(\text{Tot})$ (all Ti reported as TiO_2) contents in Figure 6, which shows that almost all pyroxene in the rims of inclusions has <2 wt% $\text{TiO}_2(\text{Tot})$ and is Al-poor compared to that in the interiors. Most pyroxene in the interiors of spherules is Al-rich, has >5 wt% $\text{TiO}_2(\text{Tot})$ and $\text{Ti}^{3+}/\text{Ti}(\text{Tot})$ 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% Al_2O_3 , and 64% TiO_2 , corresponding to a formula approaching $\text{Mg}_2\text{Al}_2\text{Ti}_4\text{O}_{13}$.

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-

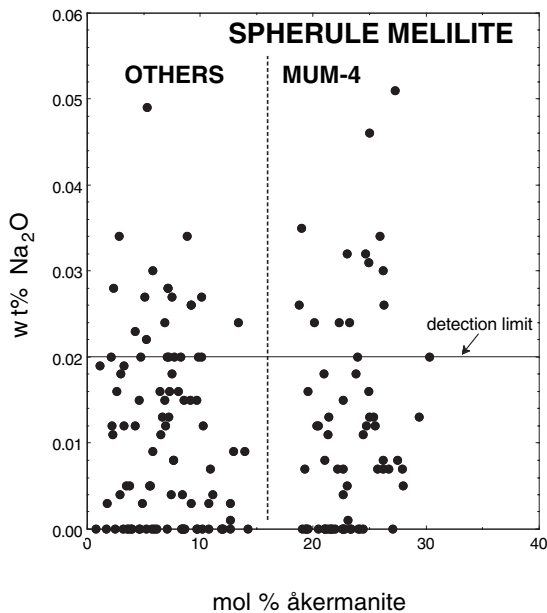


FIGURE 5. Melilite compositions in Murchison inclusions. All melilite is gehlenite-rich (low in the åkermanite end-member) and low in Na_2O .

tions of each group are listed in Table 3. The inclusions are all dominated by spinel and thus, are rich in Al_2O_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_2 as well as the lowest SiO_2 contents. The $\text{CaO}/\text{Al}_2\text{O}_3$ 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 $P(\text{Tot}) = 10^{-3}$ bar shown in Figure 7, a plot of MgO vs. Al_2O_3 contents. Compositions of phases and their end-member components are also plotted. Compositions of inclusions 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 $\text{CaO}/\text{Al}_2\text{O}_3$ 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_2 .

We also tried a calculation in which a sufficient amount of gehlenite was added to each spherule composition to increase its $\text{CaO}/\text{Al}_2\text{O}_3$ 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

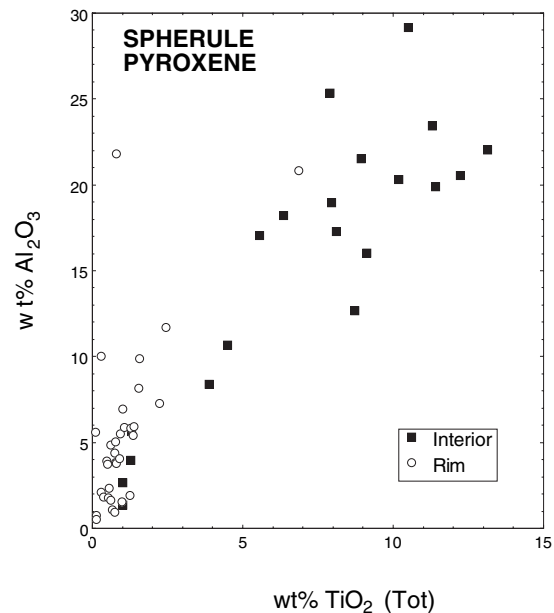


FIGURE 6. Al_2O_3 and $\text{TiO}_2(\text{Tot})$ contents in pyroxene in Murchison inclusions. Pyroxene in the interiors of inclusions tends to be richer in these oxides than pyroxene in the rims of inclusions.

TABLE 2. Analyses of pyroxene in Murchison inclusions (wt%)

	1	2	3*	4*	5*
MgO	18.46	15.89	9.96	12.87	10.68
Al_2O_3	0.53	6.92	18.23	11.94	17.85
SiO_2	55.40	50.58	39.39	42.44	36.82
CaO	25.71	25.84	24.90	24.92	23.69
$\text{TiO}_2(\text{Tot})$	0.13	1.02	6.36	8.04	11.09
V_2O_5	BDL	0.06	0.15	0.28	0.42
FeO	0.10	0.25	0.56	BDL	0.04
TiO_2	–	–	3.92	5.36	8.47
Ti_2O_3	–	–	2.16	2.34	1.98
Total	100.33	100.56	99.27	100.15	99.95
Cations per 6 oxygen anions					
Si	1.988	1.821	1.456	1.553	1.338
$^{\text{VI}}\text{Al}$	0.012	0.179	0.544	0.447	0.662
$^{\text{IV}}\text{Al}$	0.011	0.115	0.251	0.068	0.103
Mg	0.987	0.853	0.551	0.703	0.581
Ca	0.989	0.997	1.000	1.000	1.000
Ti^{4+}	0.004	0.028	0.110	0.149	0.242
Ti^{3+}	–	–	0.067	0.072	0.062
V	0	0.002	0.004	0.008	0.011
Fe	0.003	0.007	0.017	0	0.001
Total oct.	1.994	2.002	2.000	2.000	2.000

Notes: 1, 2 = rim pyroxene. 3–5 = interior pyroxene. BDL = below limit of detection of electron probe (0.027 wt% V_2O_5 or 0.036 wt% FeO). $\text{TiO}_2(\text{Tot})$ = all Ti assumed to be Ti^{4+} , or TiO_2 .

* $\text{Ti}^{3+}/\text{Ti}^{4+}$ 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).

Type A (very melilite-rich) inclusions that have been corrected to the solar $\text{CaO}/\text{Al}_2\text{O}_3$ 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_2O_3 and CaO and higher MgO contents than the corrected spherule compositions.

TABLE 3. Average compositions (and ranges) of spinel-rich inclusions from Murchison

	Sp-Hib-Pv (7)	Sp-Hib-Pv-Mel (3)	Sp-Pv-Mel (3)	Sp-Pv-Px (8)	Sp-Mel-An	Sp-Px
MgO	20.83 (15.37–25.47)	16.51 (15.72–18.06)	26.48 (25.86–27.32)	26.01 (23.95–27.92)	28.36	27.47
Al ₂ O ₃	64.51 (54.17–72.09)	66.00 (64.56–67.38)	67.18 (66.58–68.33)	62.72 (53.67–69.94)	70.24	67.33
SiO ₂	0.49 (0.17–1.62)	3.71 (2.03–5.19)	1.04 (0.62–1.54)	4.77 (0.52–12.41)	0.57	2.50
CaO	6.41 (2.82–11.38)	9.99 (7.89–11.92)	3.18 (2.05–3.85)	3.87 (0.68–7.32)	0.32	1.68
TiO ₂	7.76 (3.52–15.93)	3.79 (2.58–4.65)	2.12 (1.67–2.51)	2.61 (0.95–5.21)	0.52	1.03

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

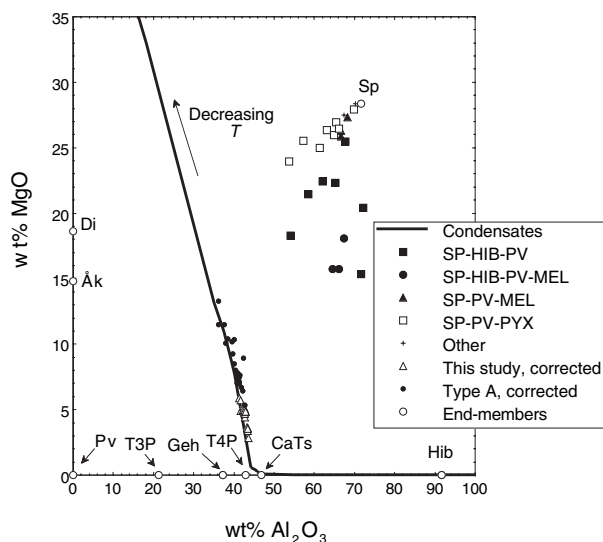


FIGURE 7. Plot of MgO vs. Al₂O₃ for spherule bulk compositions and compact Type A and spherule compositions “corrected” to the solar CaO/Al₂O₃ ratio of 0.792 (Anders and Grevesse 1989), compared to a trajectory of bulk compositions of condensates from a solar gas at $P(\text{Tot}) = 10^{-3}$ bar. Åk: åkermanite; CaTs: Ca-Tschermak’s molecule (CaAl₂SiO₆); Geh: gehlenite; T3P: Ti³⁺-bearing pyroxene component (CaTiAlSiO₆); T4P: Ti⁴⁺-bearing pyroxene component (CaTiAl₂O₆). Other abbreviations as used previously.

Spherule bulk isotopic compositions

Isotopic compositions of a small suite of inclusions were determined by ion-microprobe analysis. The inclusions are small enough that we assume that the analyses are representative of the bulk compositions. Results are summarized in Table 4 and Figure 8. Data for samples with both F_{Mg} and F_{Ca} available are plotted in Figure 8a. Where only F_{Mg} is available, the data are plotted in Figure 8b. In most cases, our 2σ uncertainties are <50% of the uncertainty of 5‰/amu obtained for F_{Mg} and for F_{Ca} by Ireland (1988, 1990). Within each inclusion, coexisting phases have uniform F_{Mg} and F_{Ca} values. If the spherules underwent evaporation while partially molten in the solar nebula, the isotopic compositions of Mg and Ca should be strongly fractionated in favor of the heavy isotopes. This is not observed in our results for either Mg or Ca. Except for one inclusion, BB-1, which is weakly to moderately fractionated ($F_{\text{Mg}} = 4.3 \pm 2.6$ ‰/amu), only small mass-fractionation effects are seen, with F_{Mg} within error of 0 for the other nine inclusions analyzed. MacPherson and Davis (1994), in their study of refractory inclusions from Mighei, also found low F_{Mg} values for spinel-rich objects. We found F_{Ca} to be within error of 0 for four of five inclusions analyzed. The sample with F_{Ca} that is not within analytical uncertainty of 0‰/amu is M92H2-34; its $F_{\text{Ca}} = -3.4 \pm 2.0$ ‰/amu, so its Ca isotopic composition is light.

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

	Type*	$F_{\text{Mg}} \pm 2\sigma$	$F^{(44}\text{Ca}/^{40}\text{Ca}) \pm 2\sigma$
M92H2-5	SHPvM	0.4±1.4	-0.7±2.2
M98L4	SHPvM	-0.8±1.2	0.5±2.4
BB-1	SHPvM	4.3±2.6	not measured
MUM-1	SHPvM	-1.1±2.0	not measured
M92H2-34	SHPv	1.2±1.2	-3.4±2.0
M92H2-10	SHPv	-0.6±1.4	1.4±2.4
M98M11	SHPv	3.2±5.2	-0.8±2.8
M98M18	SHPv	1.8±3.2	not measured
M98M9	SPvPx	-1.2±4.1	not measured
M92H2-37	SPx	0.8±2.2	not measured

* SHPvM: = spinel-hibonite-perovskite-melilite. SHPv = spinel-hibonite-perovskite. SPvPx = spinel-perovskite-pyroxene. SPx = spinel-pyroxene.

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 7.3×10^5 year, when they formed. In a sample that initially contained live ²⁶Al, $\delta^{26}\text{Mg}$ 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-mel 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/²⁷Al 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-mel inclusion (M92H2-5, shown in Fig. 1g) has a very low initial ratio, $<3.6 \times 10^{-6}$. 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 melilite-bearing, coarse-grained inclusions from CV chondrites (MacPherson et al. 1995; Simon et al. 2001). It is therefore unusual to find a melilite-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, as shown in Figure 2, also 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-

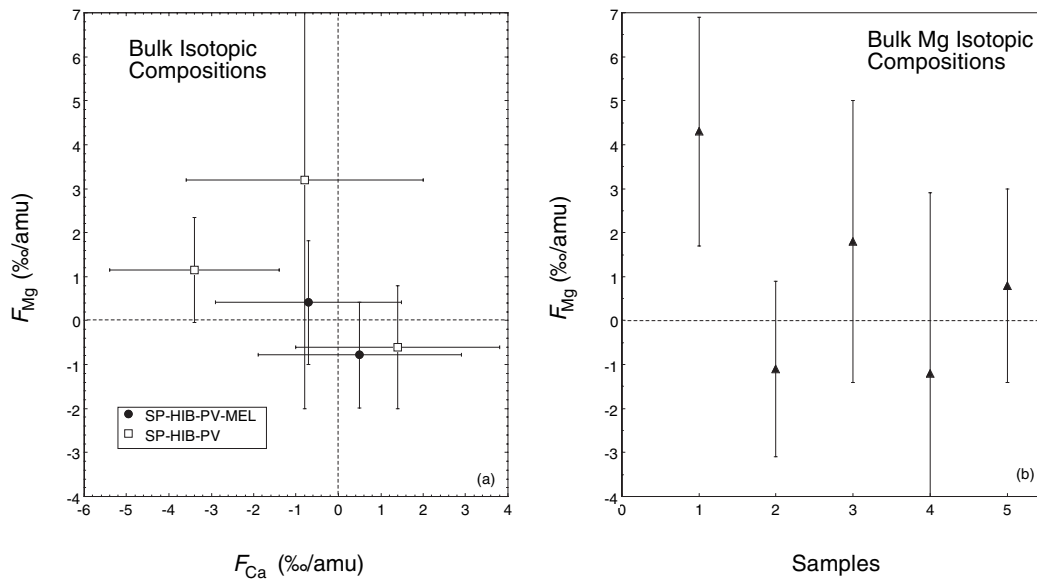


FIGURE 8. Isotopic compositions of refractory inclusions, determined by ion-microprobe analysis. There is no enrichment of the heavy isotopes of Mg or Ca in these samples. Dashed lines representing 0‰ are shown for reference. (a) F_{Mg} vs. F_{Ca} . (b) F_{Mg} for the following samples: 1 = BB-1; 2 = MUM-1; 3 = M98M18; 4 = M98M9; 5 = M92H2-37.

mel inclusions have spinel with higher V_2O_3 contents than spinel in any of the sp-pv-pyx inclusions we analyzed. In addition, the correlation of V_2O_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_2O_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_2O_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 systematics 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

TABLE 5. Ion probe measurements of $\delta^{26}\text{Mg}$ in refractory inclusions from Murchison

Sample	Type	Phase	$^{27}\text{Al}/^{24}\text{Mg}$	$\delta^{26}\text{Mg}$ (‰)
M92H2-34	SHPv	Hib	27 ± 3	12.5 ± 5.3
M92H2-34		Hib	18 ± 3	2 ± 3.6
M92H2-34		Hib	14 ± 2	9 ± 4.8
M92H2-34		Hib	16 ± 2	8.8 ± 4.8
M92H2-34		Hib	15 ± 2	6.8 ± 4.4
M92H2-34		Hib	17 ± 2	3.5 ± 3.6
M92H2-34		Hib	27 ± 3	12.5 ± 5.3
M92H2-34		Hib	18 ± 3	2 ± 3.6
M92H2-34		Sp	2.5	1.5 ± 2.5
M92H2-34	Sp	2.5	1.0 ± 2.5	
M98M11	SHPv	Hib	25.7 ± 3.0	19.1 ± 3.9
M98M11		Hib	24.7 ± 3	15.7 ± 3.5
M98M11		Hib	26.7 ± 4	16.1 ± 2.8
M98M11		Hib	8.0 ± 1	2.1 ± 3.0
M98M11		Hib	13.0 ± 2	8.8 ± 3.0
M98M11		Hib	18.0 ± 3	7.7 ± 3.0
M98M11		Hib	21.0 ± 2	1.7 ± 3.3
M98M11		Hib	23.9 ± 2	11.9 ± 3.4
M98M11		Sp	2.5	0.5 ± 2.5
M98M11		Sp	2.5	1.6 ± 2.5
M98M11		Sp	2.5	0.8 ± 2.5
M98L4	SHPvM	Sp	2.5	0.5 ± 1.5
M98L4		Hib	29.5	6.8 ± 2.6
MUM-1	SHPvM	Sp	2.5	-0.5 ± 1.8
MUM-1		Mel	14 ± 1	2.0 ± 1.8
MUM-1		Hib	44 ± 3	13.6 ± 2.2
MUM-1	SHPvM	Hib	54 ± 4	19.4 ± 3.0
BB-1		Sp	2.5	0.3 ± 1.8
BB-1		Hib	14 ± 1	0.8 ± 2.6
BB-1	SHPvM	Hib	24 ± 2	5.8 ± 2.8
M92H2-5		Mel	17.8	2.5 ± 3.9
M92H2-5		Sp	2.5	-1.5 ± 1.6
M92H2-5	Hib	104.1	-0.4 ± 3.4	

Notes: Abbreviations as used previously. Data for BB-1 are from Tanaka et al. (1980).

(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

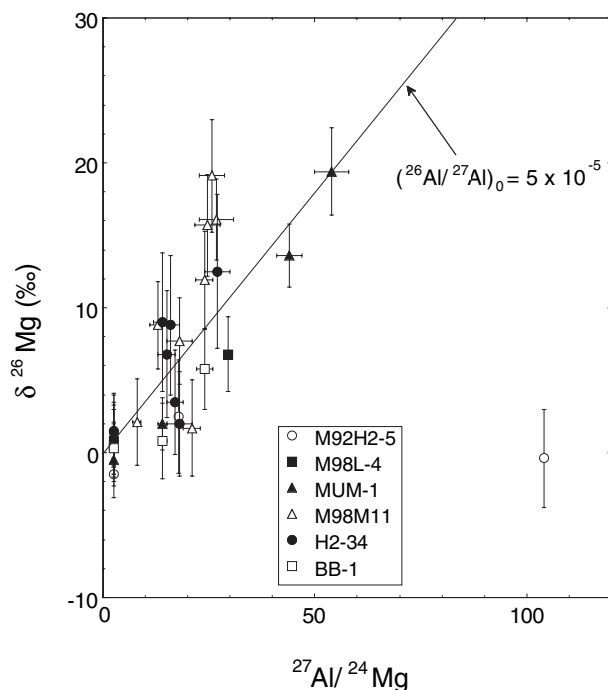


FIGURE 9. Plot showing that there is excess ^{26}Mg correlated with Al/Mg in five of six samples analyzed. The line for an initial $^{26}\text{Al}/^{27}\text{Al}$ ratio of 5×10^{-5} is shown for reference.

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_{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 SiO_2 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/ Al_2O_3 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 F_{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 be-

fore 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- Al_2O_3 - SiO_2) 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, $\sim 20\%$. 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 $\sim 4.0 \times 10^{-6}$ and 2.0×10^{-4} bar at total hydrogen pressures of 1.4×10^{-6} and 1.4×10^{-3} bar, respectively. At these total hydrogen pressures, the ambient pressures of Mg in a solar gas are only 5.5×10^{-11} and 5.5×10^{-8} 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^{-6} 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 melilite,” 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 ($\sim 20\%$) to delay melilite formation relative to spinel (Beckett and Stolper 1994). This mechanism will not work because all Al must be condensed into hibonite before either melilite or spinel becomes stable, and hibonite is needed to react with the gas to make melilite and spinel. Furthermore, the present samples and fine-grained, hibonite-, spinel-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 melilite before spinel.

It has also been suggested (Petaev et al. 2005) that a combination of (1) condensation at low pressure ($< \sim 2.5 \times 10^{-4}$ 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.

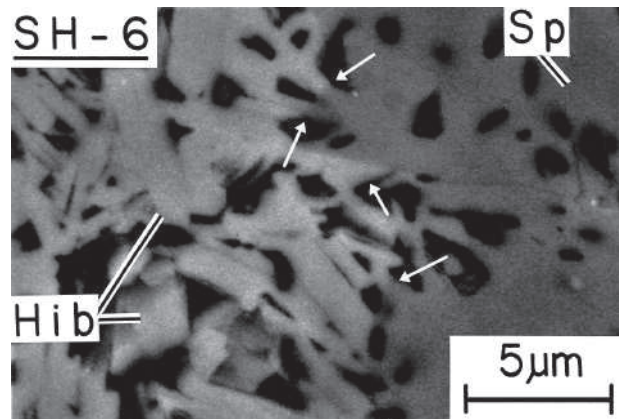


FIGURE 10. Back-scattered electron image of a hibonite-bearing inclusion with clear textural evidence of direct replacement of hibonite by spinel. Examples of crystal laths that are part spinel and part hibonite are indicated by arrows. Abbreviations as used previously. Black regions are epoxy. After MacPherson et al. (1984).

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-

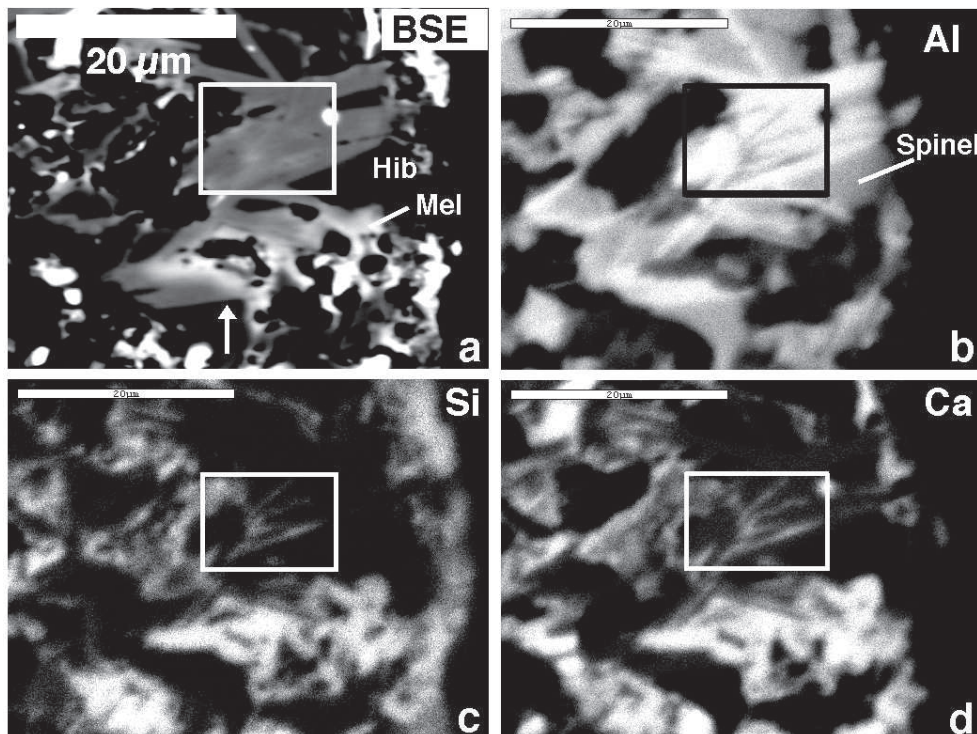


FIGURE 11. (a) Back-scattered electron image, and (b–d) elemental X-ray maps, as indicated, for an area within an sp-hib-pv-mel inclusion from LEW85311, with textural evidence for formation of melilite from hibonite. Arrow indicates a hibonite grain with melilite adjacent to a cavity, and thin bands of melilite can be seen inside the area outlined by the box.

tively). 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 SiO₂-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 suppres-

sion 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 (Al₁₁O₁₆)⁺ (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

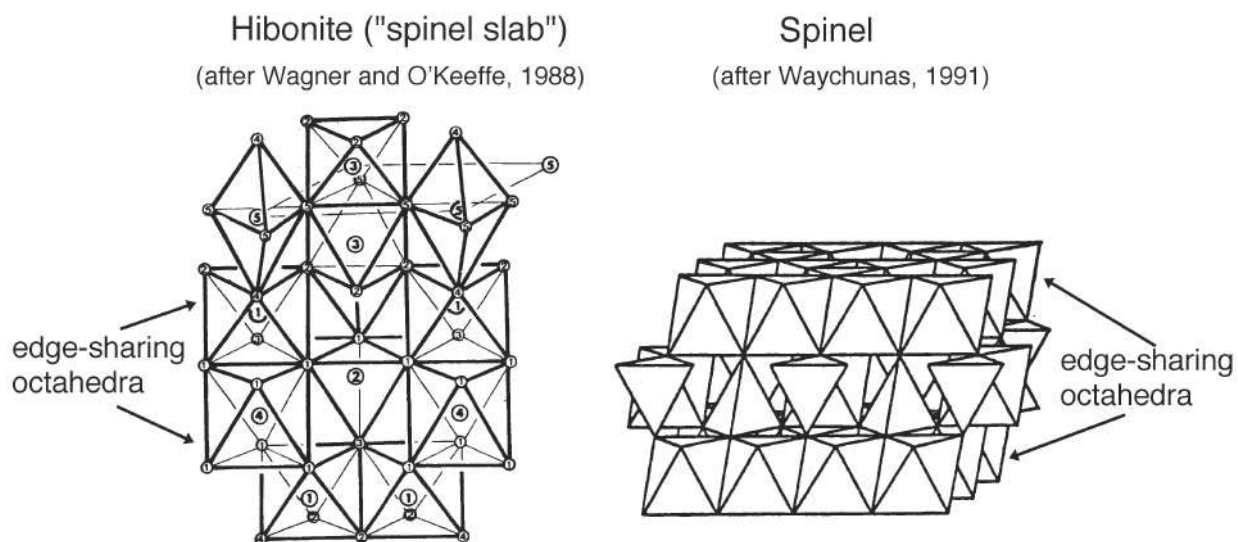


FIGURE 12. Sketch of the "spinel slab" portion of the hibonite structure (left). Large circles represent Al cations; small circles, oxygen anions. The structure is dominated by edge-sharing, Al-containing octahedra, as found in the spinel structure (right).

carbonaceous chondrites, and the melilite-poor inclusions were incorporated into the CMs.

ACKNOWLEDGMENTS

The first author thanks Jim Papike for giving him his start in professional research and for his unwavering support ever since. Helpful reviews by G. Huss and H. Connolly, Jr. led to improvements in the text. This work was supported by NASA through grants NAG-11588 and NNG05GG00G (L.G.) and NNH04AB471 (I.D.H.), and funding is gratefully acknowledged. Part of this work was performed under the auspices of the U.S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under contract no. W-7405-Eng-48.

REFERENCES CITED

- Anders, E. and Grevesse, N. (1989) Abundances of the elements: Meteoritic and solar. *Geochimica et Cosmochimica Acta*, 53, 197–214.
- Bar-Matthews, M., Hutcheon, I.D., MacPherson, G.J., and Grossman, L. (1982) A corundum-rich inclusion in the Murchison carbonaceous chondrite. *Geochimica et Cosmochimica Acta*, 46, 31–41.
- Beckett, J.R. (1986) The origin of calcium-, aluminum-rich inclusions from carbonaceous chondrites: an experimental study. Ph.D. dissertation, University of Chicago, Illinois.
- Beckett, J.R. and Stolper, E. (1994) The stability of hibonite, melilite and other aluminous phases in silicate melts: Implications for the origin of hibonite-bearing inclusions from carbonaceous chondrites. *Meteoritics*, 29, 41–65.
- Burns, R.G. and Burns, V.M. (1984) Crystal chemistry of meteoritic hibonites. *Proceedings of the 15th Lunar and Planetary Science Conference*, *Journal of Geophysical Research*, 89, supplement, C313–C321.
- Cassen, P. (2001) Nebular thermal evolution and the properties of primitive planetary materials. *Meteoritics and Planetary Science*, 36, 671–700.
- Connolly, H.C., Jr. and Burnett, D.S. (2003) On type B CAI formation: Experimental constraints on f_{O_2} variations in spinel and minor element partitioning and re-equilibration effects. *Geochimica et Cosmochimica Acta*, 67, 4429–4434.
- Connolly, H.C., Jr., Burnett, D.S., and McKeegan, K.D. (2003) The petrogenesis of type B1 Ca-Al-rich inclusions: The spinel perspective. *Meteoritics and Planetary Science*, 38, 197–224.
- Dowty, E. and Clark, J.R. (1973) Crystal structure refinement and optical properties of a Ti^{3+} fassaite from the Allende meteorite. *American Mineralogist*, 58, 230–242.
- Ebel, D.S. and Grossman, L. (2000) Condensation in dust-enriched systems. *Geochimica et Cosmochimica Acta*, 64, 339–366.
- Goswami, J.N., Srinivasan, G., and Ulyanov, A.A. (1994) Ion microprobe studies of Efremovka CAIs: I. Magnesium isotope composition. *Geochimica et Cosmochimica Acta*, 58, 431–447.
- Grossman, L. (1972) Condensation in the primitive solar nebula. *Geochimica et Cosmochimica Acta*, 36, 597–619.
- Grossman, L. and Fedkin, A.V. (2003) CaO-MgO-Al₂O₃-SiO₂ liquids: Chemical and isotopic effects of Mg and Si evaporation in a closed system of solar composition. *Geochimica et Cosmochimica Acta*, 67, 4205–4221.
- Grossman, L., Ebel, D.S., Simon, S.B., Davis, A.M., Richter, F.M., and Parsad, N.M. (2000) Major element chemical and isotopic compositions of refractory inclusions in C3 chondrites: The separate roles of condensation and evaporation. *Geochimica et Cosmochimica Acta*, 64, 2879–2894.
- Ireland, T.R. (1988) Correlated morphological, chemical, and isotopic characteristics of hibonites from the Murchison carbonaceous chondrite. *Geochimica et Cosmochimica Acta*, 52, 2827–2839.
- — — (1990) Presolar isotopic and chemical signatures in hibonite-bearing refractory inclusions from the Murchison carbonaceous chondrite. *Geochimica et Cosmochimica Acta*, 54, 3219–3237.
- Krot, A.N., MacPherson, G.J., Ulyanov, A.A., and Petaev, M.I. (2004) Fine-grained, spinel-rich inclusions from the reduced CV chondrites Efremovka and Leoville: I. Mineralogy, petrology, and bulk chemistry. *Meteoritics and Planetary Science*, 39, 1517–1553.
- Macdougall, J.D. (1981) Refractory spherules in the Murchison meteorite: Are they chondrules? *Geophysical Research Letters*, 8, 966–969.
- MacPherson, G.J. and Davis, A.M. (1994) Refractory inclusions in the prototypical CM chondrite, Mighei. *Geochimica et Cosmochimica Acta*, 58, 5599–5625.
- MacPherson, G.J. and Grossman, L. (1984) “Fluffy” type A Ca-, Al-rich inclusions in the Allende meteorite. *Geochimica et Cosmochimica Acta*, 48, 29–46.
- MacPherson, G.J., Bar-Matthews, M., Tanaka, T., Olsen, E., and Grossman, L. (1980) Refractory inclusions in Murchison: recovery and mineralogical description (abstract). *Lunar and Planetary Science XI*, 660–662. Lunar and Planetary Institute, Houston.
- — — (1983) Refractory inclusions in the Murchison meteorite. *Geochimica et Cosmochimica Acta*, 47, 823–839.
- MacPherson, G.J., Grossman, L., Hashimoto, A., Bar-Matthews, M., and Tanaka, T. (1984) Petrographic studies of refractory inclusions from the Murchison meteorite. *Proceedings of the 15th Lunar and Planetary Science Conference*, *Journal of Geophysical Research*, 89, supplement, C299–C312.
- MacPherson, G.J., Davis, A.M., and Zinner, E.K. (1995) The distribution of aluminum-26 in the early solar system—A reappraisal. *Meteoritics*, 30, 365–386.
- Petaev, M.I., Krot, A.N., and Wood, J.A. (2005) Nebular condensation under incomplete equilibrium: Implications for the fine-grained spinel-rich CAIs (abstract). *Lunar and Planetary Science XXXVI*, no. 1238 (CD-ROM). Lunar and Planetary Institute, Houston.
- Pouchou, J.L. and Pichoir, F. (1984) A new model for quantitative X-ray microanalysis. Part I: Application to the analysis of homogeneous samples. *La Recherche Aérospatiale*, 1984–3, 13–38.
- Simon, S.B. and Grossman, L. (2004) Spinel-rich spherules from Murchison: A review and some questions (abstract). *Workshop on Chondrites and the Protoplanetary Disk*, 185–186. Lunar and Planetary Institute, Houston.
- — — (2006) A comparative study of melilite and fassaite in Types B1 and B2 refractory inclusions. *Geochimica et Cosmochimica Acta*, 70, 780–798.
- Simon, S.B., Grossman, L., and Davis, A.M. (1991) Fassaite composition trends during crystallization of Allende Type B refractory inclusion melts. *Geochimica et Cosmochimica Acta*, 55, 2635–2655.
- Simon, S.B., Davis, A.M., and Grossman, L. (1999) Origin of compact type A refractory inclusions from CV3 carbonaceous chondrites. *Geochimica et Cosmochimica Acta*, 63, 1233–1248.
- Simon, S.B., Davis, A.M., and Grossman, L. (2001) Formation of orange hibonite, as inferred from some Allende inclusions. *Meteoritics and Planetary Science*, 36, 331–350.
- Simon, S.B., Grossman, L., Hutcheon, I.D., and Phinney, D.L. (2005a) Bulk chemical and isotopic compositions of spinel-, hibonite-rich spherules: Clues to their origin (abstract). *Lunar and Planetary Science XXXVI*, no. 2211 (CD-ROM). Lunar and Planetary Institute, Houston.
- Simon, S.B., Keaton, C.G., and Grossman, L. (2005b) Refractory inclusions from the CM2 chondrite LEW85311 (abstract). *Meteoritics and Planetary Science*, 40, A141.
- Stolper, E. and Paque, J.M. (1986) Crystallization sequences of Ca-Al-rich inclusions from Allende: The effects of cooling rate and maximum temperature. *Geochimica et Cosmochimica Acta*, 50, 1785–1806.
- Tanaka, T., Davis, A.M., Hutcheon, I.D., Bar-Matthews, M., Olsen, E., MacPherson, G.J., and Grossman, L. (1980) Refractory inclusions in Murchison: Chemistry and Mg isotopic composition (abstract). *Lunar and Planetary Science XI*, 1122–1124. Lunar and Planetary Institute, Houston.
- Wagner, T.R. and O’Keeffe, M. (1988) Bond lengths and valences in aluminates with the magnetoplumbate and β -alumina structures. *Journal of Solid State Chemistry*, 73, 211–216.
- Waychunas, G.A. (1991) Crystal chemistry of oxides and oxyhydroxides. In D.H. Lindsley, Ed., *Oxide minerals: petrologic and magnetic significance*, 25, p. 11–68. *Reviews in Mineralogy*, Mineralogical Society of America, Chantilly, Virginia.
- Yoneda, S. and Grossman, L. (1995) Condensation of CaO-MgO-Al₂O₃-SiO₂ liquids from cosmic gases. *Geochimica et Cosmochimica Acta*, 59, 3413–3444.

MANUSCRIPT RECEIVED OCTOBER 26, 2005

MANUSCRIPT ACCEPTED APRIL 10, 2006

MANUSCRIPT HANDLED BY C. SHEARER