BULK CHEMICAL AND ISOTOPIC COMPOSITIONS OF SPINEL-, HIBONITE-RICH SPHERULES: CLUES TO THEIR ORIGIN.

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Introduction: Melilite-free, spinel-, hibonite-bearing spherules, a major type of refractory inclusion in CM2 chondrites, consist of phases that are predicted by thermodynamic calculations to condense from a cooling gas of solar composition but are not predicted to coexist with each other. Throughout updates and additions to the data base over the years, calculations [e.g. 1-3] consistently show that melilite should condense after hibonite and before spinel, and that hibonite should react completely with the gas to form spinel. Despite this, hibonite-, spinel-bearing inclusions that are melilite-free or very melilite-poor are much more abundant in CM chondrites than hibonite-melilite or melilite-spinel inclusions. The origin of the melilite-free inclusions has puzzled researchers for years. One way to reconcile the observed assemblages with the condensation calculations is if melilite originally present was lost due to evaporation of Ca, Si and Mg during heating of the precursors [4]. The loss of SiO_2 and CaO from an Al_2O_3-rich CMAS liquid would stabilize spinel and prevent extensive Mg evaporation. If evaporation occurred while the inclusions were partially molten, then they should be measurably enriched in the heavier isotopes of the affected elements (i.e., F_{Mg}, F_{Ca} >0). Previous studies of Ca [5] and Mg [6] isotopes in hibonite-spinel inclusions showed $-10<F_{Mg}<7$ and $-4<F_{Ca}<5$, providing a hint that Ca and Mg evaporation did take place, but failing to reveal any correlation between Mg and Ca isotopic compositions, or between isotopic and chemical compositions. We have undertaken a petrologic and ion probe study of spinel-bearing inclusions from Murchison to see if they are isotopically fractionated and if there are any correlations of isotopic composition with mineral assemblage. Petrographic classifications and textural descriptions were given in a previous report [7]. Here we focus on the bulk chemical and isotopic compositions of the inclusions.

Methods: Polished sections of 40 refractory spherules and fragments thereof, separated from the Murchison (CM2) chondrite by standard freeze-thaw techniques, were studied by SEM and classified by mineral assemblage [7]. Subsets of this suite were analyzed by electron probe and by ion probe. Bulk compositions of 18 inclusions were determined by modal recombination. For this work we mainly selected rim-to-rim sections of inclusions or homogeneous fragments, avoiding heterogeneous fragments of samples. The inclusions are small enough (<~100 µm across) that we can assume that the sections sample them representatively.

Results: The average major-element composition of each inclusion type is given in Table 1. Spinel is the dominant phase in these inclusions, followed by hibonite, and the hibonite-bearing inclusions have the highest TiO_2 and CaO contents. The composition of each inclusion is plotted in Fig. 1. Being very rich in spinel, they are enriched in Al_2O_3 and MgO and depleted in CaO and SiO_2 relative to equilibrium condensate assemblages. The CaO/Al_2O_3 ratios of the Murchison inclusions range from 0.0046 to 0.21, much lower than the solar value of 0.792. The bulk compositions plot well off trajectories of bulk equilibrium condensate compositions, such as the one for a solar gas with $P^{tot}=10^{-3}$ bar shown in Fig. 1. The compositions do not appear to have been displaced from the condensate trajectory by addition of spinel to condensate assemblages; mathematical subtraction of spinel to obtain the solar CaO/Al_2O_3 ratio [8], for example, in many cases yields unrealistic compositions that have negative MgO contents and/or >30 wt% TiO_2. Five inclusions have compositions that, on a plot of CaO *vs.* Al_2O_3, appear to project to sub-solar CaO/Al_2O_3 ratios along the condensate trajectory with the removal of spinel. This might reflect addition of spinel to inclusions formed prior to complete condensation of Ca, but even for these inclusions, correction to the lower CaO/Al_2O_3 ratios also results in negative MgO contents.

To see how much melilite must be added to the

Table 1. Compositions of Murchison spherules, by petrographic type. Sp: spinel; Hib: hibonite; Pv: perovskite; Mel: melilite; Pyx: pyroxene. Uncertainties are based on the ranges of values observed. Where greater than one, the numbers of inclusions averaged are given in parentheses.

	Sp-Hib-Pv (6)	Sp-Hib-Pv-Mel (3)	Sp-Pv-Mel (3)	Sp-Pv-Pyx (4)	Sp-Mel-An	Sp-Pyx
MgO	20.56 ±5.05	16.51±1.17	26.48±0.73	25.22±1.26	28.36	27.47
Al_2O_3	64.91±8.96	66.01±1.41	67.18±0.88	59.58±6.20	70.24	67.33
SiO_2	0.31±0.27	3.71±1.58	1.04±0.46	7.28±4.71	0.57	2.49
CaO	6.29±4.28	9.99±2.02	3.18±0.90	5.23±2.36	0.32	1.68
TiO_2	7.93±6.20	3.79±1.03	2.12±0.42	2.69±1.21	0.52	1.03

spherule compositions to obtain condensate compositions, we added a gehlenite component to each composition sufficient to increase its CaO/Al_2O_3 ratio to the solar value. This yields compositions (open triangles) that plot on or close to the condensate trajectory shown in Fig. 1. 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, ~4g mel per gram of inclusion, are needed. As a result, the "melilite-corrected" compositions are similar to compositions of compact Type A (melilite-rich) inclusions that have been corrected to the solar CaO/Al_2O_3 ratio by addition of spinel [8], but with slightly higher Al_2O_3 and CaO and lower MgO contents than the CTAs (Fig. 1).
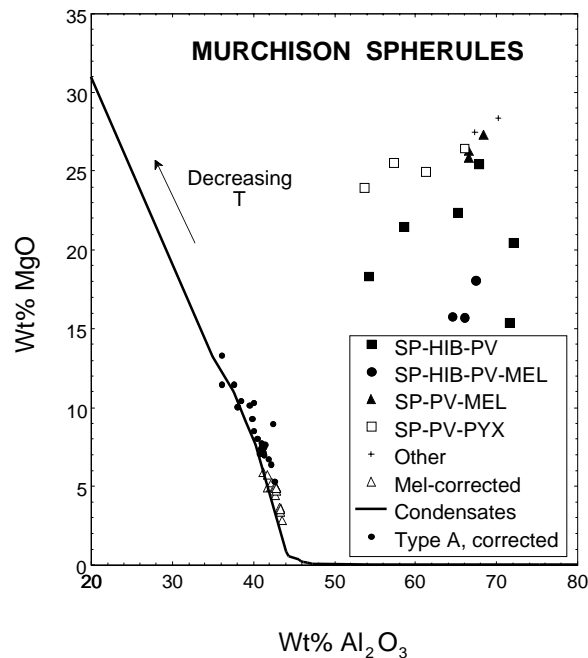
Fig. 1. Bulk compositions of spherules compared to a trajectory of equilibrium condensate compositions for a solar gas at $P^{tot}=10^{-3}$ bar.

Isotopic data. We have thus far obtained Mg-isotopic data for four inclusions and, for three of those, Ca data as well. The weighted means of the analyses are given in Table 2. Only small mass-fractionation effects are seen, with F_{Mg} within error of 0 for three of the four inclusions and F_{Ca} within error of 0 for two of three inclusions analyzed. Within each inclusion coexisting phases have indistinguishable F_{Mg} and F_{Ca} values.

Table 2. Weighted means of Mg and Ca isotopic analyses for two Sp-Hib-Pv-Mel and two Sp-Hib-Pv inclusions (‰/amu).

	Type	$F_{Mg} \pm 2\sigma$	$F(^{40}Ca/^{44}Ca) \pm 2\sigma$
M92H2-5	SHPvM	0.4±1.1	-0.7±2.0
M98L4	SHPvM	-0.8±1.0	0.5±2.1
M92H2-34	SHPv	1.2±0.8	-3.4±1.6
M92H2-10	SHPv	-0.6±1.0	not measured

Also, we found that M92H2-34 and M98L4 have measurable excesses of ^{26}Mg correlated with Al/Mg, yielding initial $^{26}Al/^{27}Al$ ratios of $(5.3\pm1.1)\times10^{-5}$ and $(3.2\pm1.4)\times10^{-5}$, respectively. In contrast, M92H2-5 has an initial ratio of $<3.6\times10^{-6}$. All three inclusions could be classified as SHIBs [6], which commonly contain radiogenic ^{26}Mg [5, 6].

Discussion: The two best explanations for the derivation of the observed bulk compositions, which have been suggested previously [4] for similar inclusions, are: a) equilibrium condensation followed by partial melting and evaporation; and b) non-equilibrium condensation, possibly involving enhanced formation of spinel relative to melilite. Our preliminary Mg and Ca isotopic data are inconsistent with significant mass loss by evaporation in a reducing (classical) solar nebula. Similar results were found by [5]. The F_{Mg} value of H2-34 is slightly positive but lower than those typical of Type B CAIs [8], implying a smaller evaporative mass loss. To obtain its bulk chemical composition from one on the equilibrium condensate trajectory by evaporative loss of melilite would require loss of ~80% of the original mass, yielding a strongly mass-fractionated Ca isotopic composition, F_{Ca} ~ 20‰/amu, which is contrary to observation.

The presence of radiogenic ^{26}Mg shows that the Mg isotopic systematics in at least two of the inclusions probably have not been disturbed. It is unusual, however, to find a melilite-bearing inclusion, such as M92H2-5, that did not contain live ^{26}Al when it formed. Most melilite-bearing, coarse-grained inclusions from CVs have initial $^{26}Al/^{27}Al$ ratios of ~5×10^{-5} [9] as do two other melilite-bearing inclusions from Murchison [10, 11].

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