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Mass-dependent fractionation of Mg, Si, and Fe isotopes in five stony cosmic spherules

CONEL M. O'D. ALEXANDER,¹ S. TAYLOR,² JEREMY S. DELANEY,³ PEIXUE MA,⁴ and GREGORY F. HERZOG^{4,*}¹Department of Terrestrial Magnetism, 5241 Broad Branch Road NW, Washington, DC 20005, USA²Cold Regions Research and Engineering Laboratory, 72 Lyme Road, Hanover, NH 03755, USADepartments of ³Geological Sciences and ⁴Chemistry, Rutgers University, Piscataway, NJ 08854, USA

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Abstract—We have measured with an electron microprobe the Mg, Al, Si, Ca, Ti, Mn, and Fe contents of five strongly heated stony cosmic spherules (sCS) from the South Pole water well. We have also measured the isotopic compositions of Si, and when possible of Mg and of Fe in these objects by ion microprobe. Except for iron, the measured elemental compositions are chondritic within a factor of 2. In four samples, the ratio of ⁵⁷Fe/⁵⁶Fe exceeds the terrestrial value by 3.5‰ to 48‰. Mass-dependent fractionation of the isotopes of Si ranges from ~2 to ~8 ‰/AMU in three samples. Mg is clearly fractionated in only one sample, for which $\delta^{25}\text{Mg} = \sim 8$ ‰. The extent of mass-dependent fractionation of the isotopes and, by implication, of evaporative loss generally follows a trend Mg < Si < Fe. The trend is similar to that found in laboratory heating experiments of charges with solar composition. Although the observed isotopic inhomogeneities within some samples call into question the strict validity of the Rayleigh equation for the sCS, its approximate application to our new and to previously published results for Mg suggests that evaporative losses of greater than 40 wt.% occur rarely from sCS, and that the precursor grains of the sCS had a CM-carbonaceous-chondrite-like complement of Mg, Si, Ca, and Al. Low Fe contents relative to CM abundances could reflect an unusual precursor composition, or, more probably, losses by processes that did not fractionate isotopes, i.e., ejection of immiscible FeS and FeNi beads from the melt or rapid, complete separation and decomposition of FeS at the surface. Copyright © 2002 Elsevier Science Ltd

1. INTRODUCTION

Love and Brownlee (1991) estimate that micrometeorites with diameters between 100 μm and 1000 μm lose ~80% of their mass by evaporation as they pass through the atmosphere. Isotopic studies of metallic (I-type) cosmic spherules have confirmed one implication of this conclusion, namely, the systematic enrichment of the heavier isotopes of Cr, Fe, Ni, and O (Davis et al., 1991; Engrand et al., 1998; Herzog et al., 1999), which is a signature pattern for evaporation. Systematic isotopic enrichments of this kind have not been widely reported for stony (S-type) cosmic spherules, sCS. We report elemental (Mg, Al, Si, Ca, Ti, Mn, Fe) and isotopic (Mg, Si, Fe) analyses of five sCS with a view toward assessing the extent of evaporative loss. Where the isotopic data indicate that such losses have occurred, we use those data to try to improve estimates of preentry composition and to constrain the extent of loss by other mechanisms. According to Love and Brownlee (1991), the large diameters (>70 μm) of the particles that we selected for study favor an asteroidal rather than a cometary origin. Even so, we hoped to find a distinctive, perhaps cometary particle among the smaller objects.

Unlike the isotopic data for I-type (iron) cosmic spherules, the isotopic data for S-type (stony) cosmic spherules are fragmentary and show no consistent patterns of enrichment. Davis et al. (1991) report apparent enrichments in ²⁵Mg as large as 6‰ in seven sCS. They note, however, the absence of two associated effects that they would have expected to find: enrichments in the isotopic abundances of the more volatile

element Si, and enrichments in the chemical abundances of refractory elements such as Ca and Al. Misawa et al. (1992), Schnabel et al. (1999), and Esat and Taylor (1987) report no detectable mass-dependent fractionation of Mg in five sCS, nine sCS, and one interplanetary dust particle (IDP), respectively. Among 10 IDPs and 3 sCS analyzed isotopically for Mg, Esat et al. (1979) identify only one particle, a sCS, clearly enriched in ²⁵Mg and ²⁶Mg by mass-dependent fractionation. More positively, Nyquist et al. (1995) observe appreciable mass-dependent fractionation of Fe and Cr in three (deep-sea) sCS and Engrand et al. (1998) present an intriguing and complex pattern of variations in oxygen isotopes in several Antarctic CS.

The scatter of these results may simply reflect the diversity of the population sampled: Petrographic studies indicate that even within their respective groups, both unmelted micrometeorites and sCS have had a variety of thermal histories (Maurette et al., 1991; Brownlee et al., 1997; Engrand et al., 1998; Genge et al., 1996). Some phyllosilicate-rich particles never melted; other particles contain unmelted relict grains; and at the far end of the spectrum, the sCS melted completely. Importantly for this work, the sCS themselves differ from one another. Textures range from porphyritic through barred olivine, to glass. Compositions vary, too, and certain rare sCS are greatly enriched in the refractory elements Ca, Al, and Ti, just as one might expect for objects that lost mass by evaporation (Taylor et al., 2000), or, perhaps, derived from Ca- and Al-rich inclusions.

We took the evidence cited above to mean that that mass-dependent isotopic fractionation could be restricted to certain types of sCS. By focusing on cosmic spherules thought to have been highly heated during atmospheric entry, we sought to see

* Author to whom correspondence should be addressed (herzog@ruitchem.rutgers.edu).

Table 1. Physical properties of stony cosmic spherules.

	Mass (μg)	Shape	Density (g/cm^3)
MM8	22 ± 1	ellipsoid	3.7 ± 0.5
MM9	17 ± 1	spherule	2.4 ± 0.6
MM11	5.0 ± 0.5	shell	
MM15	3.0 ± 0.5	spherule	2.6 ± 0.7
MM14	4.0 ± 0.5	spherule	3.9 ± 1.1

more clearly the overall importance of evaporation, to search for patterns of loss in order to compare them with those established in laboratory studies (e.g., Hashimoto, 1983), and to gain additional insights into the precursor composition.

Throughout this article we will use the term *micrometeorite* generically to mean any recovered extraterrestrial particle less than 1 mm in its longest dimension. We will use the term *cosmic spherule* to refer to a micrometeorite that melted. To conform to common practice, we will refer to micrometeorites that did not melt as *unmelted micrometeorites*.

2. EXPERIMENTAL METHODS

2.1. Sample Selection and Preparation

About one in one hundred cosmic spherules returned from the South Pole water well (SPWW) is unusual in having high Ca, Al, and Ti contents relative to chondritic values and little or no Fe (Taylor et al., 2000). Like a few other types of sCS, these spherules are oblate and white and have barred olivine textures in cross section. Taylor et al. (2000) suggest that they are larger versions of the Ca-, Al-, and Ti-rich spherules (or CAT spherules) found in stratospheric collections. Brownlee et al. (1982) attribute their unusual compositions to severe atmospheric heating. We selected for study four spherules that looked like CAT spherules under the microscope. In choosing the samples, we were aware that some other types of sCS have the same general appearance as CAT spherules and, indeed, one of the four spherules turned out to have normal levels of Ca, Al, and Ti. For comparison purposes, we also included a brown glass cosmic spherule, MM11, which proved to be hollow. All had diameters between 70 μm and 250 μm . We placed the particles in holes drilled in an Al disk, set the particles in epoxy, and polished them for ion microprobe analysis and electron microprobe analysis.

2.2. Electron Microprobe Analyses

We analyzed 10 spots on each spherule at the Rutgers University Microanalysis Facility using the JEOL JXA-8600 microprobe and averaged the results. The electron beam, $\sim 10 \mu\text{m} \times \sim 10 \mu\text{m}$, was continuously rastered to avoid heating the sample. In each case, several analyses were made at locations close to the pits excavated by the beam of the ion microprobe. Instrument calibration was based on standard silicates with data reduction using conventional Bence-Albee procedures (Bence and Albee, 1968).

2.3. Ion Microprobe Analyses

All isotope measurements were carried out with the Carnegie Cameca 6f ion microprobe using a 12.5-kV O^- primary beam in the shaped or flat-bottomed illumination mode, a 10-kV secondary accelerating voltage, a 50-eV energy window, and a 100- μm field aperture. Primary beam currents ranged between 0.3 nA and 5 nA; spot sizes were $\sim 20 \mu\text{m}$ across.

Because of potential interferences at other Fe isotopes, only ^{56}Fe and ^{57}Fe were measured. The principal remaining interference was ^{56}FeH at ^{57}Fe . To resolve the hydride from ^{57}Fe , analyses were performed at a mass resolution of ~ 8000 . The Mg and Si isotopes measurements were conducted at a mass resolution of ~ 3500 to resolve ^{24}MgH from ^{25}Mg

and ^{28}SiH from ^{29}Si . The standard used to measure the instrumental mass fractionation factors for all three elements was a BHVO basaltic glass. Several attempts to fabricate a glass with a composition closer to that of the sCS did not succeed. BHVO glass, however, is a reasonable standard for FeO in silicates (Alexander and Wang, 2001). At present the influence of composition on instrumental fractionation factors for MgO and SiO_2 is not known, but we anticipate it to be small.

3. RESULTS AND DISCUSSION

3.1. Elemental Composition

In Table 1 we present some physical properties of the spherules and in Table 2 their elemental compositions. The hollow glass spherule MM11 has an elemental composition similar to those of other glass spherules (Harvey and Maurette, 1991; Kurat et al., 1994; Taylor et al., 2000) but its higher-than-average Si content and lower-than-average Al content results in a low Al/Si ratio, consistent with enrichment in enstatite. Samples MM9 and MM14 are compositionally similar to Ca-, Al-, and Ti-rich spherules from the SPWW (Taylor et al., 2000). Particle MM15 has a high Al/Ca ratio and a low Si content. One other particle, MM8, evidently had a nonchondritic precursor. In MM8, low Al and Ca contents and a high Mg/Si ratio suggest a forsterite-rich parent (Brownlee et al., 1997). All particles had very low iron contents, as expected from their colors. The measured Fe/Si ratios of the spherules, 0.03 on average, are quite low, only 4% of the CI value and 10% of the values typical of other sCS (Brownlee et al., 1997). The range of compositions that we see and those reported elsewhere suggest that the spherules' parent materials were spatially heterogeneous on a scale of millimeters.

Alexander (2001) has recently presented a kinetic model for calculating the compositional evolution of initially "chondritic" and forsteritic silicate melts undergoing evaporation. His results provide a framework for interpreting how the elemental compositions of the sCS changed. Under the conditions assumed for the calculation (isothermal heating at 1700°C to 2400°C for 1 to 2 s), both Si and Mg evaporate appreciably whereas Al does not. Thus, as evaporation proceeds, the Si/Al and Mg/Al ratios decrease, although at different rates. In Figures 1 and 2 we have plotted the compositional trajectories of hypothetical particles that start with CI and other chondritic compositions. Figure 1 also shows the measured elemental composition of the five spherules. Compositions for three of those spherules (MM9, MM14, and MM15) plot close to the curve for CI-like material undergoing evaporation. We infer that the materials parental to the spherules had generally chondritic preatmospheric compositions except for the low Fe abundance. A more precise characterization of the precursor based on Si/Al and Mg/Al ratios alone is not possible because the compositional trajectories of objects with different initial elemental abundances tend to converge. Inspection of Figure 1 confirms that spherule MM8 did not have a chondritic precursor. The position of MM8 on the plot reflects a low Al content and suggests a forsteritic parent. The position of MM11 is more consistent with an enstatite-rich parent. To obtain more information about how much of the spherules evaporated, we turn to the isotopic data.

Table 2. Elemental composition (wt %) and melting temperature, T_M ($^{\circ}\text{C}$), of cosmic spherules.

	MgO	Al ₂ O ₃	SiO ₂	CaO	TiO ₂	MnO	FeO	Sum	T_M^f
Stony cosmic spherules									
MM8 ^a	51.7 ± 2.2	1.13 ± 0.15	41.6 ± 1.9	1.13 ± 0.16	0.07 ± 0.02	0.08 ± 0.03	1.84 ± 0.16	97.6	1857
MM9 ^a	43.2 ± 0.4	5.70 ± 0.27	44.5 ± 0.3	4.45 ± 0.05	0.23 ± 0.02	—	0.25 ± 0.02	98.4	1725
MM11 ^a	35.4 ± 0.3	1.57 ± 0.03	51.3 ± 0.2	1.33 ± 0.04	0.09 ± 0.02	0.37 ± 0.02	7.69 ± 0.12	97.8	1639
MM14 ^a	45.2 ± 3.3	7.04 ± 1.77	38.9 ± 0.8	5.7 ± 1.6	0.33 ± 0.02	—	0.05 ± 0.03	97.2	1784
MM15 ^{a,g}	41.8 ± 1.7	10.0 ± 0.5	31.7 ± 0.9	2.8 ± 0.6	0.46 ± 0.09	—	0.03 ± 0.03	86.9	
MM15 ^{a,h}	47.0 ± 1.9	11.3 ± 0.6	35.7 ± 1.0	3.1 ± 0.7	0.51 ± 0.11	—	0.04 ± 0.04	≐97.6	1823
Av. deep sea ^b	23.1	2.29	32.5	1.79	0.07	0.23	39.8		
Av. SPWW glass ^c	31.6	3.10	47.9	2.64	0.15	0.38	14.0		
CAT spherules ^c	45.7	6.09	41.6	5.59	0.29	0.13	0.95		
Type B1 CAI ^d	10.2	29.6	29.1	28.8	1.3		0.6		
Carbonaceous chondrites ^e									
CI	16.1	1.6	22.5	1.3	0.25	0.07	23.4		
CM	19.4	2.2	27.6	1.8	0.22	0.10	27.0		
CO	24.0	3.3	33.4	2.7	0.19	0.16	30.2		

^a This work.

^b Brownlee et al. (1997).

^c From the South Pole Water Well; Taylor et al. (2000).

^d Type B1 Ca-Al-rich inclusion (MacPherson et al., 1988).

^e Wasson and Kallemeyn (1988).

^f Calculated for a pressure of one atmosphere after Beattie (1993), who estimates errors of less than 20 $^{\circ}\text{C}$.

^g MM15 has a crystalline quench texture with many voids; the high proportion of void space accounts for the low elemental total.

^h Composition of MM15 adjusted to give same total mass percentage as do the other four cosmic spherules, i.e., 97.6%.

3.2. Isotopic Composition

We report isotopic abundances as conventional δ -values in Table 3. The quantity Φ [%/AMU] (Table 4) provides a measure of the degree of mass-dependent fractionation. Specifically, Φ is the weighted, least-squares slope (Williamson, 1968) of a linear plot, forced through the origin, of $\delta^Y E$ vs. $Y-A$. Here, E denotes Mg or Si; A is the mass of the reference isotope

(^{24}Mg or ^{28}Si); and the index Y runs over the masses of the other stable isotopes. With only two isotopes of Fe measured, we cannot be sure that the fractionation of iron is mass-dependent. We think it likely, however, based on the results for Mg and Si and on published results for Fe in CS (Herzog et al., 1999; Nyquist et al., 1995). For Fe, we assume $\Phi_{\text{Fe}} = \delta^{57}\text{Fe}$.

Iron is clearly fractionated in the four spherules that have enough Fe for isotopic analysis, that is, Φ differs from zero by more than 2σ . Silicon is fractionated in MM11, MM15, and

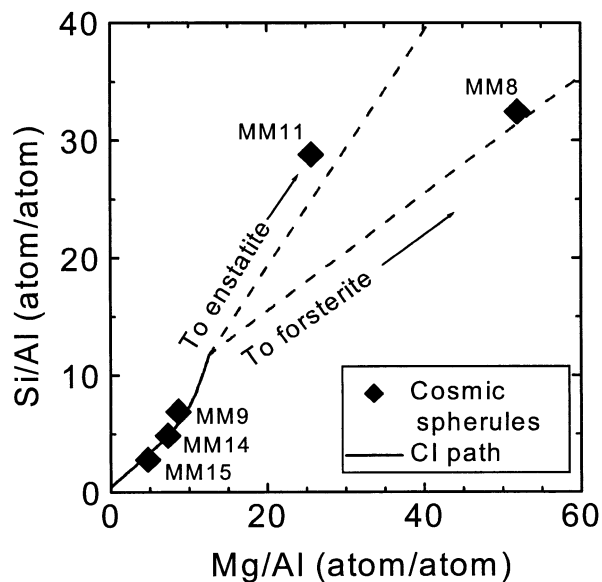


Fig. 1. Mg/Al and Si/Al ratios of five sCS. Three of the spherules plot close to the solid line. That line shows how the composition of CI-like starting material changes as evaporation proceeds. MM8 appears in a region that suggests a forsteritic precursor; MM11 contains relatively little Al and has high Mg/Al and Si/Al ratios, perhaps because its precursor was rich in enstatite.

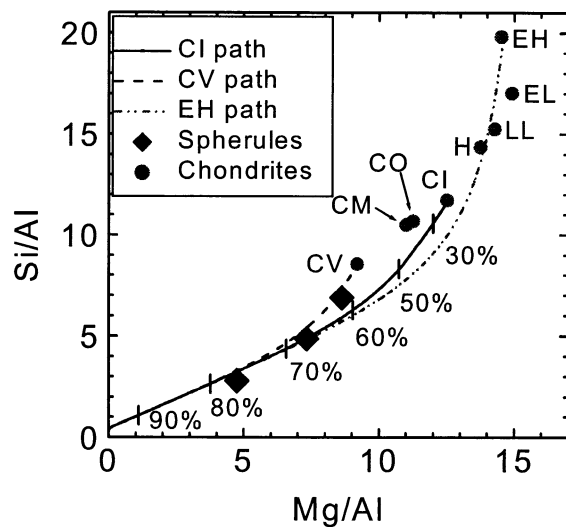


Fig. 2. Mg/Al and Si/Al ratios of three cosmic spherules are shown along with the evaporation trajectories calculated for various chondritic precursor materials. The short lines crossing the CI trajectory mark off different degrees of evaporation. Regardless of starting composition, the trajectories tend to converge after $\sim 30\%$ of the material has evaporated.

Table 3. Isotopic composition of stony cosmic spherules.

Sample	$\delta^{57}\text{Fe}$	$\delta^{29}\text{Si}$	$\delta^{30}\text{Si}$	$\delta^{25}\text{Mg}$	$\delta^{26}\text{Mg}$
MM8	3.5 ± 1.2	-0.3 ± 0.4	-1.4 ± 0.7	-3.0 ± 0.8	-5.8 ± 1.4
MM8		0.2 ± 0.4	0.0 ± 0.7	-3.1 ± 0.8	-6.0 ± 1.4
Avg.	3.5 ± 1.2	-0.1 ± 0.4	-0.7 ± 1.0	-3.1 ± 0.8	-5.9 ± 1.4
MM9	9.8 ± 2.2	0.5 ± 0.6	1.0 ± 0.8	-1.6 ± 0.8	-3.5 ± 1.4
MM9		1.9 ± 0.5	2.5 ± 0.6	-0.9 ± 0.8	-2.6 ± 1.4
MM9		0.4 ± 0.4	0.9 ± 0.6		
Avg.	9.8 ± 2.2	0.9 ± 0.8	1.5 ± 0.9	-1.2 ± 0.8	-3.0 ± 1.4
MM11	4.5 ± 0.4	2.1 ± 0.4	4.4 ± 0.5		
MM15		3.9 ± 0.2	6.0 ± 0.4		
MM14	44 ± 9	8.8 ± 0.4	16.6 ± 0.6	8.0 ± 0.8	16 ± 1
MM14	22 ± 10	7.9 ± 0.4	15.2 ± 0.6	7.1 ± 0.8	14 ± 1
MM14	48 ± 7				
Avg.	38 ± 14	8.4 ± 0.6	15.9 ± 1.0	7.6 ± 0.8	14.7 ± 1.7

$\delta^x\text{Y} = ([^x\text{Y}/^a\text{Y}]_{\text{measured}} / [^x\text{Y}/^a\text{Y}]_{\text{terrestrial}} - 1) \times 1000$; $^a\text{Y} = {}^{56}\text{Fe}, {}^{28}\text{Si}, {}^{24}\text{Mg}$

MM14; and magnesium only in MM14. Negative values of $\delta^{25}\text{Mg}$ and $\delta^{26}\text{Mg}$ in MM8 may indicate some measurement bias for this element. In general, for a given cosmic spherule, we find $\Phi_{\text{Mg}} < \Phi_{\text{Si}} < \Phi_{\text{Fe}}$. Also, for this set of samples, Φ_{Si} and perhaps Φ_{Fe} correlate inversely with mass. The apparent dependence on spherule mass is interesting but has not emerged in previous studies and the observation needs additional corroboration. The degree of isotopic fractionation in MM14 is large relative to that observed in most cosmic spherules and conventional meteorites (Davis et al., 1991; Herzog et al., 1999; Wang et al., 2001; Galy et al., 2000).

3.3. Evaporative Losses

Wang et al. (2001) have studied the evaporation of well-mixed melts of solar composition. Their results indicate that the degree of isotopic fractionation depends on the fraction of material lost at any stage but not on the temperature or the composition. With appropriate parameters, the Rayleigh law relates the fraction, f , of an element, E , retained to the degree of isotopic enrichment, $\delta^Y E$, of an isotope of mass Y :

$$\Phi = \frac{\delta^Y E}{Y - A} = \frac{f\left(\frac{1}{\alpha} - 1\right) - 1}{Y - A} \times 1000 \quad (1)$$

We have calculated the fractions of Fe, Si, and Mg that the cosmic spherules retained (Table 4) from this equation and from empirical fractionation factors, α , for Mg, Si, and Fe determined by Wang et al. (1994, 2001). From the fractions retained, in turn, we have reconstructed the original compositions and masses of the samples (Table 5) by assuming (1) no loss of Al, Ca, or Ti; and (2) that Fe, Si, and Mg evaporate in

concert with 1.0, 2.0, and 1.0 atoms of oxygen, respectively. In this way we arrive at the following losses (wt.%) assignable to evaporation: MM8, 1%; MM9, 5%; MM11, 17%; MM15, >16%; and MM14, 50%. It is important to note that mechanisms other than evaporation may have removed iron; we discuss below losses of immiscible phases.

Even if an object lost 75% of its mass, the net decrease in diameter probably did not exceed 40%. The mass losses attributed to evaporation, 0.05 to 0.5 of the original mass, are lower than those estimated by Love and Brownlee (1991), 0.7 to 0.9 for particles of similar size.

3.4. Possible Precursors

The immediate precursors of the sCS were themselves almost certainly small objects in space (Nishiizumi et al., 1995). It would, accordingly, make sense to search for likely sources of micrometeorites among the dust bands of the solar system, perhaps in those associated with Eos, Themis, or Koronis as suggested by Kortenkamp and Dermott (1998). Unfortunately, at present we lack elemental data for the asteroids that have the precision needed for a comparison with our data for sCS. Out of necessity, then, we skip back to the previous stage in the evolution of the particles, when they were still in their parent bodies. For some types of asteroids, at least, we have good elemental data from analyses of meteorites with which to compare the results for sCS.

We would not expect each of the tiny sCS studied to have sampled the precursor in a representative way. For this reason, in assessing possible precursors for our strongly heated sCS, we have averaged the five preatmospheric compositions. The av-

Table 4. Degree of mass dependent fractionation, Φ , and fractional retention, f , of Fe, Si, and Mg of stony cosmic spherules.

	Fe		Si		Mg	
	Φ	f	Φ	f	Φ	f
MM8	3.5 ± 1.2	0.67 ± 0.09	-0.2 ± 3.1	$\equiv 1$	-3.0 ± 0.5	$\equiv 1$
MM9	9.8 ± 2.2	0.33 ± 0.08	0.8 ± 0.4	0.91 ± 0.04	-1.4 ± 0.5	$\equiv 1$
MM11	4.5 ± 0.4	0.60 ± 0.03	2.2 ± 0.2	0.77 ± 0.02		$\equiv 1$
MM15			3.4 ± 0.1	0.66 ± 0.01		$\equiv 1$
MM14	38 ± 14	0.02 ± 0.02	8.1 ± 0.4	0.38 ± 0.02	7.5 ± 0.6	0.61 ± 0.02

Table 5. Compositions (wt %) of stony cosmic spherules reconstructed so as to compensate for the effects of evaporation.

Sample	MgO	Al ₂ O ₃	SiO ₂	CaO	TiO ₂	FeO
MM8	52.4	1.15	42.2	1.2	0.08	3.0
MM9	41.9	5.53	47.4	4.3	0.22	0.62
MM11	29.9	1.33	56.3	1.1	0.08	11.3
MM15	40.6	9.75	46.5	2.7	0.44	
MM14	38.1	3.60	52.4	2.9	0.17	2.8
Avg.	40.6	4.3	49.0	2.4	0.2	4.4

eraging process seems likely to give a better sample of the parent body or bodies, which we believe to have been heterogeneous on a scale of mm or more. Corrections for evaporative loss bring the average measured elemental ratios of Mg/Si, Ca/Si, and Al/Si, but not of Fe/Si into fairly good agreement with H, CI, and CM values (Fig. 3). Eberhardt (1998), Mumma et al. (1993), and Jessberger and Kissel (1991) have reviewed the elemental composition of cometary dust. After normalization to CI chondrites, elemental ratios in comets are as follows: Mg/Si, 0.51; Al/Si, 0.43; Ca/Si, 0.56; and Fe/Si, 0.33. None of the evaporation-corrected ratios of the sCS matches those of achondrites or of the comet Halley (Eberhardt, 1998; Jessberger and Kissel, 1991). A twofold change in Si content, however, would reconcile the average Mg/Si, Al/Si, and Ca/Si ratios of comets and of sCS. Such an adjustment seems large but Jessberger et al. (1999) stress that the composition inferred for Halley silicates has considerable uncertainty. MacPherson et al. (1988) present average elemental compositions for calcium- and aluminum-rich inclusions (CAI) in CM and CV chondrites. We compare the average composition of our sCS with that of average type B1 CAIs (MacPherson et al., 1988) in Figure 3. The agreement is poor and still worse for other types of CAIs, which have even more Ca, Ti, and Al and less Mg and Si.

In this context, it is of interest to return to sphere *a* described by Esat et al. (1979) and mentioned in the introduction. According to Love and Brownlee (1991), the diameter of this sphere, only 10 μm , places it squarely in the range predominantly though not solely populated by cometary particles. Sphere *a* has the most highly fractionated Mg of any stony micrometeorite analyzed to date, $\Phi_{\text{Mg}} = 11.3\%$. Compositionally, it is rich in Mg, Al, and Ca and relatively poor in Fe and Si just as one might anticipate for a high-velocity object

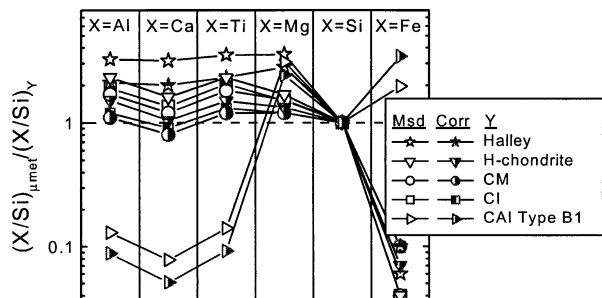


Fig. 3. Major element ratios of melted sCS normalized to the composition of CI-, of CM-, and of H-chondrite meteorites and to that of Halley-like material before (Msd) and after (Corr) corrections for evaporative loss.

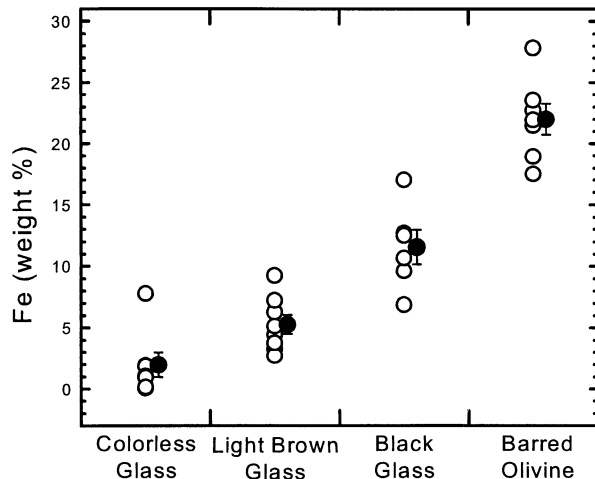


Fig. 4. The colors of glassy cosmic spherules from the SPWW (Taylor et al., 2000) become lighter as Fe content decreases. The Colorless Glass group includes two spherules rich in Ca, Al, and Ti (CAT spherules). Filled circles show group averages with standard deviations of the mean.

that underwent extensive evaporation. In sum, sphere *a* has the attributes expected for a cometary particle. Interestingly, its composition is almost identical to that of MM14, a much larger particle, which by virtue of its size, probably did not come from a comet according to Love and Brownlee (1991). Although we realize that no firm conclusion can rest on so limited a comparison, we note the possible implication that cometary and asteroidal silicates are both CM-like. Alternatively, sphere *a* may be what Love and Brownlee (1991) term a spray or ablation droplet from an asteroid (see below).

3.5. Depletion of Iron

The iron in sCS occurs in the silicate minerals, in the interstitial glass, and as magnetite grains disseminated in interstitial glass. Magnetite concentrations vary appreciably within individual spherules. The distribution of Fe/Si ratios in SPWW sCS is bimodal with peaks at ~ 30 and 80% of the CI value (Taylor et al., 2000). Systematic variations of iron content with spherule type broaden the peaks. Depletions of iron of $\sim 25\%$ relative to chondritic values characterize silicate spherules with barred olivine or porphyritic textures (Brownlee et al., 1997). Glass spherules show larger depletions that correlate with color (Fig. 4) and CAT-like spherules have the largest iron depletions of all (Taylor et al., 2000). With respect to iron content, the cosmic spherules analyzed here most closely resemble the CAT spheres (Table 2). As noted above, the spherules studied contain only $\sim 10\%$ as much Fe as typical sCS. Even after corrections for evaporation, the cosmic spherules contain 5 to 7 times less iron than CI-, CM-, or H- chondrites. Conceivably, the precursors of the cosmic spherules were depleted in iron. It seems more likely, however, that the precursors began with CI- or CM-like complements of iron, and then lost them, both by evaporation *and* by physical segregation and ejection of iron-rich phases. Below we explore further some of the evidence for

segregation and ejection and the mechanisms by which they occur.

Brownlee et al. (1997) and Genge and Grady (1998) have argued that Fe depletion begins with the formation of immiscible Fe-rich phases within the molten spherule. A CI-like parent would contain nearly 5.9 wt.% S, 1 wt.% Ni (which we assign to sulfides although it may also be present in phyllosilicates), and 18.2 wt.% Fe. From stoichiometry and consistent with the petrography of CI chondrites, it follows that roughly half of the Fe (9.3 wt.%) may occur as troilite and other sulfides. Such sulfides, which melt or decompose at relatively low temperatures, segregate themselves from the molten cosmic spherules (Fig. 5a) just as they do in chondrules. The FeS or FeNiS phases generally form nonspherical blebs. These phases appear quite fluid: They are found between olivine laths in barred olivine spherules and are seen to "wet" the outside of a spherule (Fig. 5a). In contrast, the FeNi beads tend to be spherical and smaller. They, like the sulfide blebs, often work their way to the edge of the spherule but unlike them, once there, maintain their spherical shapes (Fig. 5b). As suggested above, CI-like parent material would have enough sulfur to carry away only about half the iron; for a CM-like parent, the corresponding limit is 22% and for an H-like parent, 7%. We cannot be certain that the parental materials had either a CI- or a CM composition, but we know from other work that scoriaeous micrometeorites with low S contents (<0.25%) have not lost much of their iron (see Table 4, Kurat et al., 1994). Thus, we infer that the parental material did not have enough sulfur to carry away more than ~25% of the iron and that the loss of metallic Fe-Ni or some other iron-rich phase such as magnetite, must also play a role in the depletion of Fe.

The solar furnace experiments described by King (1982, 1983) provide direct evidence that beads of metallic iron form during the rapid heating of Murchison and Allende to temperatures above 2400°C. Loss of this metallic iron may occur by physical removal or by evaporation of the beads. Interestingly, King (1982) reports that rapid heating of Murchison and Allende sometimes forms hollow spheres, similar to our MM11.

We do not know the mechanisms that reduce the iron. Brownlee et al. (1997) plausibly propose carbon as a reducing agent. Type CI, CM, and CR chondrites and ureilites (but not meteorites of other types) contain enough C for the reaction $C + 2FeO \rightarrow 2Fe + CO_2$ to convert to metal all the Fe^{2+} not bound to S. Further, as some spherules retain Fe, not all Fe need be reduced. A difficulty for this mechanism is the ready availability of atmospheric oxygen, but it may not diffuse rapidly enough to the interior of the particles to compete with the micrometeoritic oxygen for the carbon. Reduction might also take place spontaneously, without a conventional reducing agent such as carbon. Jakes et al. (1992) summarize observations supporting spontaneous, high-temperature reduction in silicate melts at super liquidus temperatures. They note that these liquids may have been in an unusual state (superheated) with the implication that normal expectations concerning the relative stabilities of reduced and oxidized phases may not apply. Koeberl (1994) observes that tektites, which, like sCS underwent rapid heating, contain iron in a more reduced state [i.e., more Fe and Fe(II)], than did their likely precursor. He concludes that the impact process that produced the tektites was reducing and that the details need explaining.

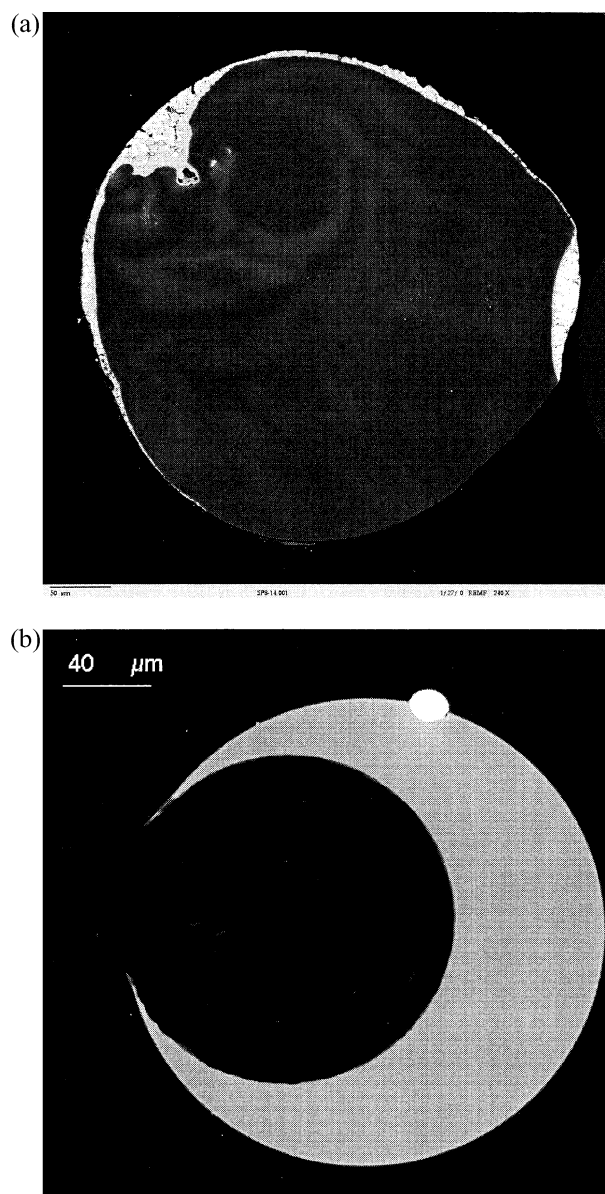


Fig. 5. Immiscible phases rich in Fe and Ni behave in different ways in micrometeorite melts. (a) In sCS SP8-14 (see also Taylor et al., 2000), sulfides have migrated to the surface and spread out over it. (b) In sCS 50-153, metallic iron-nickel has formed a small spherical bead (brightest object) that has maintained its shape.

Genge and Grady (1998) argue that the rarity of metallic Fe in sCS calls for efficient ejection of molten Fe droplets. We agree with their conclusion for spherules that suffered large losses of Fe, but note that in spherules with smaller losses of Fe, some freshly formed metal could have reoxidized and disappeared by dissolving in silicates. Evidence for the in-flight oxidation of some iron comes from the mineralogy of cosmic spherules. In I-type spherules, atmospheric oxidation of Fe virtually always produces wüstite and magnetite (Brownlee, 1985; Kosakevitch and Disnar, 1997), in part, perhaps, because deceleration sends high-density liquid metal forward to meet onrushing oxygen (Yada et al., 1996). In an unmelted, stony micrometeorite, a thin layer of magnetite may coat the surface

and line interior vesicles (Kurat et al., 1994; Klöck et al., 1992; Thomas et al., 1992). Kurat et al. (1994) believe that this magnetite condensed from meteoric Fe(g) and O₂(g) already in the atmosphere. Robin et al. (1992), on the other hand, attribute the magnetite to the oxidation of Fe native (and perhaps freshly reduced) to the incoming spherules. We prefer the latter view.

Magnetite rims on scoriated micrometeorites may point to another mechanism for iron loss. In recent experiments, Toppani and Libourel (2001) subjected grains from the Murchison and the Orgueil carbonaceous chondrites to pulsed heating. At temperatures of 1000°C to 1500°C and in the presence of oxygen, the experimental charges formed thin magnetite rims without bulk fractionation of any major element except sulfur. Toppani and Libourel propose that the magnetite crystallized from an iron-rich partial melt that rimmed the heated grains. Physical ablation of surficial magnetite formed in this way would deplete iron. It would be interesting to analyze the isotopic composition of the magnetite.

For completeness we consider another possible explanation for the apparent iron depletion in the precursor material: limitations on the use of the Rayleigh formalism. In using the Rayleigh equation, we have adopted a fractionation factor for Fe that refers to wüstite (Wang et al., 1994) for lack of experimental results for silicate melts. A smaller fractionation factor for Fe (larger effective mass during evaporation) would increase the calculated losses of Fe for a given value of Φ . Although we doubt that the error in α_{Fe} is large enough to bring the initial concentration of Fe to the level of CI chondrites, we see a need for an experimental measurement. Second, the Rayleigh equation holds only when rapid mixing of the melt ensures uniformity during evaporation. When mixing is slow, use of the equation underestimates evaporative loss. Our measurements of $\delta^{57}\text{Fe}$ in MM14 suggest, albeit with large uncertainties, that $\delta^{57}\text{Fe}$ may vary within MM14 and hence that MM14 did not attain homogeneity. Engrand et al. (1998) have reported variations in $\delta^{18}\text{O}$ of up to 24‰ within one silicate spherule and smaller variations in others. Barring extremely bad luck in sampling, however, it seems unlikely that a full treatment of this effect would introduce 10-fold change in the average calculated loss of Fe due to evaporation.

Finally, we consider total mass balance. By starting with 100 g of material with the average, preevaporative composition of the sCS given in Table 5, and adding 44 g of FeO, we can recover the CM Fe/Si ratio. With the addition of 44 g of FeO, we obtain the following composition (mass %) for the average precursor of the sCS: MgO, 28.2; Al₂O₃, 3.0; SiO₂, 34.0; CaO, 1.7; TiO₂, 0.14; FeO, 33.6. The percentages of MgO and SiO₂ exceed CM values. In CM chondrites, however, the mass percentages of the oxides listed sum to only 75% due to the presence of other elements. Those elements include H, C, Na, P, K, and Mn, which may well have volatilized if present in the precursors of the spherules. If we restore to our 100 g of preevaporative material ~25 of unspecified volatile substances, then we arrive at the following composition: MgO, 23.9; Al₂O₃, 2.5; SiO₂, 28.8; CaO, 1.4; TiO₂, 0.12; FeO, 28.5, which matches the average CM composition fairly well. In sum, the cosmic spherules analyzed could have been produced from 100 μg of CM material that lost: (a) ~20 μg of unspecified volatiles, either by evaporation or ejection; (b) 20 μg of Fe by evaporation or ejection; and (c) 1.5 μg of MgO and 7.0 μg of

SiO₂, by evaporation. Here, we assume $f_{\text{Mg}} = 0.92$ and $F_{\text{Si}} = 0.74$. More important than the details of the calculations above, however, is the implied size of the total mass loss, whether by ejection or evaporation. That total loss is ~50% of the original mass, a result that may be compared with the 80% losses due to evaporation alone estimated for metallic cosmic spherules and from the calculations of Love and Brownlee (1991).

3.6. Pattern of Evaporative Loss

The overall pattern of isotopic fractionations, $\Phi_{\text{Mg}} < \Phi_{\text{Si}} < \Phi_{\text{Fe}}$, matches expectations based on laboratory experiments for silicate systems of solar composition undergoing evaporation at high temperature. Hashimoto (1983) and Wang et al. (2001) heated material with solar elemental abundances of Mg, Si, Ca, Al, and Fe to temperatures between 1700°C and 2000°C for up to 2.2 h. Iron evaporated first, followed by Si, and then Mg. Losses of Al and Ca were minor. By combining their observations (see Fig. 8 in Wang et al., 2001) with reported values for Φ_{Mg} , we can infer the fraction of sCS with significant evaporative losses. Specifically, a small number of cosmic spherules with appreciable values of Φ_{Mg} has been found to date—only 2 out of 33 if we exclude those analyzed by Davis et al. (1991). Both of these spherules, however, were CAT spherules which make up only 1% of the SPWW collection. We predict, therefore, that only a small fraction, probably less than 1% of micrometeorites, will be fractionated in Mg. On the other hand, in our suite of samples and those studied by Nyquist et al. (1995), heating typically gave rise to measurable fractionation of Fe, Si, and, probably, O. Based on these observations, we believe that additional analyses of Si and perhaps of Fe isotopes in glass spherules with a range of Fe contents and in more CAT spherules should be helpful in refining estimates of the original, preatmospheric compositions.

3.7. Conditions of Evaporation

Hashimoto (1983) and Wang et al. (2001) have studied the evaporation of melts made from charges of solar composition. We can scale their results to estimate the degree of evaporation expected for sCS. For fixed initial composition and temperature, the time required to achieve a given evaporative mass loss should be proportional to the radius of the particle because evaporation rate scales with surface area and mass with volume. Wang et al. and Hashimoto made experimental charges that were initially ~2000 \times μm in radius. At 1800°C, the charges prepared by Hashimoto lost 57% of their mass in 60 min, 72% in 120 min, and 89% in 220 min. The particles that we analyzed had (final) radii of ~100 μm . From the scaling relation we conclude that a 100 μm radius particle at 1800°C would take ~3 min to lose 57% of its mass, 6 min to lose 72%, and 11 min to lose 89%.

Figure 6 shows what happens to the isotopic composition of a CI-like particle with a radius of 100 μm undergoing Rayleigh fractionation for 1 to 2 s at various temperatures. One to two seconds is the typical duration of heating near the maximum temperature in the calculations of Love and Brownlee (1991). The curves were calculated using a model (Alexander, 2001) that was fitted to the results from the experiments of Hashimoto (1983) and of Wang et al. (2001) at 1700°C to 2000°C. Al-

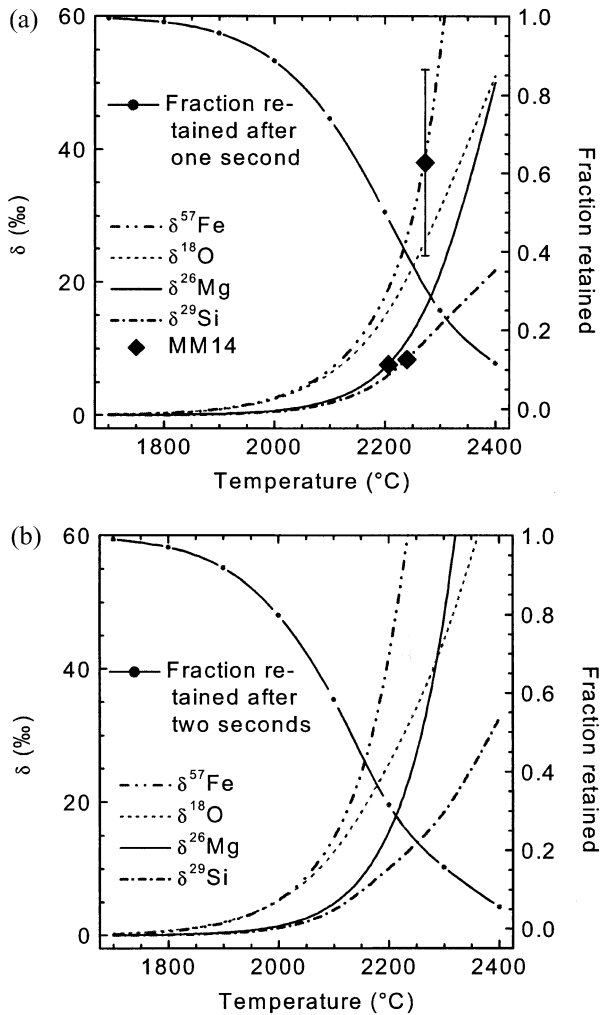


Fig. 6. (a) Model predictions of the degree of isotopic fractionation expected in ^{57}Fe , ^{29}Si , ^{26}Mg , and ^{18}O (left axis) and total mass loss (right axis), assuming free evaporation (i.e., no recondensation) for 1 s at various temperatures. The calculations are based on the model of Alexander (2001). The isotopic fractionation factors are based on the work of Wang et al. (2001). The isotopic data for cosmic spherule MM14 (closed diamonds) are consistent with an evaporation temperature of $2240 \pm 35^\circ\text{C}$. The internal consistency of the data set suggests that the model of Alexander (2001) correctly calculates relative volatilities of the evaporating species. The temperature assumed for these calculations is, however, considerably higher than a model of micrometeorite entry predicts (Love and Brownlee; 1991; see text). (b) Same as (a) but for an evaporation time of 2 s.

though the calculations of Alexander (2001) do not integrate overall possible entry angles, we believe that a full treatment of this effect would not change our conclusions significantly. The Fe, Mg, and Si isotopic compositions of cosmic spherule MM14, which had a CI-like initial composition, are all consistent with a peak temperature of $\sim 2300^\circ\text{C}$ or $\sim 2200^\circ\text{C}$ assuming that heating lasted 1 s or 2 s, respectively.

As noted above, in the model of Love and Brownlee (1991), asteroidal particles typically sustain peak temperatures for 1 or 2 s. Those temperatures, however, never exceed 1900°C . In fact, for particles with diameters comparable to those of the CS we have studied, $\sim 200 \mu\text{m}$, the temperatures rarely exceed

1500°C in their model, and a combination of factors effectively sets a temperature cap near 1700°C for particles of any size. Even at these lower temperatures, Love and Brownlee (1991) estimate that 70 to 90% of the particle mass may evaporate.

Thus we have arrived at inconsistent entry conditions for MM14. Specifically, the peak temperature estimates of 2200 – 2300°C inferred from the model of Alexander (2001) assuming peak heating for 1 to 2 s are much higher than the maximum temperatures cited by Love and Brownlee (1991). The discrepancy arises because the laboratory evaporation experiments on which the model of Alexander (2001) is based indicate much slower evaporation rates than Love and Brownlee (1991) assumed (see above estimates of evaporation times at 1800°C , which is close to the liquidus temperature for MM14). Further our isotopic data for sCS indicate lower degrees of mass loss than Love and Brownlee (1991) predict. We note also that most cosmic spherules have probably lost much less mass by evaporation than has MM14.

In Table 2, we present liquidus temperatures calculated for the particles based on the work of Beattie (1993). If the assumption of phase equilibrium holds (see below), then the values shown are lower limits for the peak temperatures that the spherules experienced during entry heating. Three of the five particles have liquidus temperatures that significantly exceed the 1700°C peak temperature cap estimated by Love and Brownlee (1991) for asteroidal particles. To achieve the higher temperatures indicated by their degrees of mass loss, particularly for MM14, entry velocities higher than the 12 km/s typical of falls (Brown et al., 1994, 1996) may be necessary. Alternatively, the cosmic spherules could have formed as ablation droplets, i.e., droplets stripped from the surface of a large, fast-moving object. A larger parent maintains a higher velocity and may sustain a very hot surface for a longer time. We do not favor the ablation droplet hypothesis for two reasons. First, the melt would have to remain at the surface without being blown away. Second, fusion crusts on meteorites do not show the isotopic signature characteristic of extreme evaporative loss (Clayton et al., 1986), although one might argue that the fusion crust that remains formed late in the trajectory, well after the parent object reached its peak temperature. Don Brownlee (personal communication 2001) points out that the high calculated melting temperatures of Table 2 could be misleading if the spherule melts supercooled. A volatile-rich CI-like precursor would have begun melting at much lower temperatures. Although the progressive loss of volatiles such as Na or H_2O would then have raised the melting temperature, the residual liquid may simply not have crystallized.

3.8. Evaporative Losses from I-type and from stony cosmic \times spherules Compared

I-type (metal-rich) cosmic spherules have large, mass-dependent enrichments in the heavy isotopes of O, Cr, Fe, and Ni (Herzog et al., 1999; Engrand et al., 1998). Application of the Rayleigh equation to the isotopic data for metallic CS indicates mass losses of 80 to 85% for all these elements. Our data for what are probably the most strongly heated sCS indicate much less evaporation of iron. If the stony and the I-type spherules had similar entry velocities and sizes, why should such a difference exist? First, we note that I-type particles, by virtue of

their higher densities, would have stopped lower in the atmosphere and experienced higher peak temperatures for longer times than did stony CS with the same initial diameter and velocity. In the temperature range of interest, the vacuum volatility (vaporization rate normalized with respect to concentration) for metallic iron is higher than for iron in oxidized form (Hashimoto, 1983; Wang et al., 1994). Thus, I-type CS should experience greater evaporative losses of Fe than stony CS of comparable size.

The particular behavior of the various forms of iron in stony CS is also relevant in this context. Iron sulfide does not appear in our sCS. We suggested above that on melting, any sulfide present would have melted, coated the surface of the incoming object, and then either decomposed or been swept away. Metallic iron is also absent from our samples. Even if freshly made during atmospheric heating, metallic iron would have had to cling to the surface of the molten silicate for long enough to evaporate. For most of this metallic iron, we suggest that ejection takes place first. Iron in magnetite or hematite evidently evaporates from I-type CS, although more slowly than does metallic Fe. Again, our sCS have very little magnetite, either because it was promptly stripped from the surface or because not much ever formed. As a possible source of Fe for evaporation, we are left with oxidized iron in the silicate melt. Our isotopic data for silicon show that some evaporation from the silicate does take place. Here, following Toppani and Libourel (2001), we suggest that for thermodynamic reasons some iron initially bound in silicates migrated to other phases—magnetite or metal—and at this point evaporation of metallic iron again would have had to compete with other loss mechanisms. In short, we believe that sCS, unlike I-type CS, could not keep iron-rich phases at their surfaces for long enough for evaporation to compete effectively with ejection.

4. CONCLUSIONS

Certain rare stony cosmic spherules from the South Pole Water Well, ~1% of the collection, have the elemental and the isotopic composition expected for objects that have undergone some mass loss by evaporation. Initially, we identified these objects visually, on the basis of their texture and their color (white). We reasoned that a light color would mean a low Fe content and that a low Fe content would result from evaporation. Compositional analyses confirm the low iron contents inferred from the color. Isotopic analyses reveal enrichments in the heavier isotopes of Fe and of Si often, and of Mg occasionally. In general, the enrichments increase in the order $Mg < Si < Fe$. A similar pattern of volatility holds for silicate melts heated to high temperatures in the laboratory. We take this similarity as evidence for significant evaporative losses from the precursors of these cosmic spherules. Heating in the atmosphere probably caused the evaporative losses (Greshake et al., 1998). We rule out heating in space because known meteoritic materials provide no suitable analogs. Chondrules, for example, show little isotopic fractionation (Alexander et al., 1998; Alexander et al., 2000; Alexander and Wang, 2001); and calcium–aluminum-rich inclusions, though isotopically fractionated (Fahey et al., 1987), have the wrong elemental composition (see Table 2).

With some reservations, we have used the Rayleigh equation

and our isotopic data to estimate an average preatmospheric composition of the sCS studied. In agreement with many others, we conclude that the initial composition was chondritic, probably CI- or CM-like, but prefer the latter based on results for oxygen isotopes (Engrand et al., 1998). The largest evaporative mass loss estimated for any one of the cosmic spherules analyzed (MM14) was ~50%, which is equivalent to a 20% decrease in diameter. If we have correctly identified the most heated class of sCS, and, indeed of all micrometeorites, then it follows that most other stony micrometeorites will not have lost significant masses of Al, Mg, Si, or Ca by evaporation, a conclusion testable by further measurements. Loss of iron, in contrast, appears to be common and to result from both the separation of immiscible phases and from evaporation. The assumption of a CI- or CM-like progenitor leads to the conclusion that evaporation of Fe caused less loss of Fe than did the reduction of FeO, perhaps by C, followed by loss of metallic iron and other immiscible phases. Even so, additional measurements of iron isotopic abundances may provide useful clues to the thermal histories of other groups of stony micrometeorites.

The question remains open of whether the sCS studied were cometary or, indeed extrasolar particles (Messenger, 2000). If heating lasted only a few seconds, then the degree of isotopic fractionation that we have observed implies peak temperatures above 2000°C and hence high incoming particle velocities and/or entry angles. Both cometary and extrasolar particles cross the Earth's orbit with relatively high velocities and no doubt melted on passing through the atmosphere (Flynn, 1989; Messenger, 2000). If our particles were not asteroidal, then the pervasiveness of inferred CM-like compositions for sCS could mean that two classes of silicate progenitors, cometary and asteroidal, were much the same in space.

As Zolensky et al. (2000) note, a particle's exposure to cosmic-ray irradiation may also provide clues to origins. While melting and evaporative loss have probably compromised the integrity of the noble gas record in extrasolar objects, we speculate that the isotopes of the rare earths may record a low-energy neutron irradiation as described by Ott and Bege-mann (2000).

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