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The Leonard Award Address

Presented 1996 July 25, Berlin, Germany

The elemental composition of stony cosmic spherules

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Abstract–Five hundred stony cosmic spherules collected from deep-sea sediments, polar ice, and the stratosphere have been analyzed for major and some minor element composition. Typical spherules are products of atmospheric melting of millimeter sized and smaller meteoroids. The samples are small and modified by atmospheric entry, but they are an important source of information on the composition of asteroids. The spherules in this study were all analyzed in an identical manner, and they provide a sampling of the solar system's asteroids that is both different and less biased than provided by studies of conventional meteorites. Volatile elements such as Na and S are depleted due to atmospheric heating, while siderophiles are depleted by less understood causes. The refractory nonsiderophile elements appear not to have been significantly disturbed during atmospheric melting and provide important clues on the elemental composition of millimeter sized meteoroids colliding with the Earth. Typical spherules have CM-like composition that is distinctively different than ordinary chondrites and most other meteorite types. We assume that C-type asteroids are the primary origin of spherules with this composition. Type S asteroids should also be an important source of the spherules, and the analysis data provide constraints on their composition. A minor fraction of the spherules are melt products of precursor particles that did not have chondritic elemental compositions. The most common of these are particles that are dominated by olivine. The observed compositions of spherules are inconsistent with the possibility that an appreciable fraction of the spherules are simply chondrules remelted during atmospheric entry.

INTRODUCTION

Cosmic spherules are solidified droplets of meteoroids that melt during hypervelocity entry into the atmosphere. They have been collected in significant quantities from a number of special environments such as polar ice and deep-sea sediments where they are both concentrated and separable from terrestrial material (Murray and Renard, 1883; Parkin and Tilles, 1968; Millard and Finkelman, 1970; Parkin *et al.*, 1980; Hodge, 1981; Maurette *et al.*, 1986; Jehanno *et al.*, 1988; Maurette, 1993; Yamakoshi, 1994; Taylor *et al.*, 1996). Falling at a rate of $>1/m^2$ per year, they are by far the most abundant form of extraterrestrial material on the Earth. Entry calculations, isotopic fractionation, and cosmogenic isotopes indicate that the majority of the collected spherules are droplets of 0.1 to 1 mm sized meteoroids that melted during atmospheric entry. This meteoroid size range is of particular importance because it includes the peak of the mass distribution of meteoritic material accreted by the Earth (Grun *et al.*, 1985; Love and Brownlee, 1993). The total mass of 0.1 to 1 mm sized meteoroids that annually enter the atmosphere is roughly 1000× the cumulative mass of bodies in the 10 cm to 1 m range (Kyte and Wasson, 1986). The spherules are an important but underutilized resource of information on meteoroid composition. We have measured the elemental composition of a significant number of spherules to provide new insight into the composition of millimeter sized and smaller meteoroids in the inner solar system. It is expected that nearly all of the spheres >50 μm are asteroidal, and these results provide information on the composition of what may be the most common main belt asteroid types. A portion of the spherule population may be cometary if there is a significant source of cometary particles with low inclination and low eccentricity orbits.

The spherules provide a different and potentially less biased means of investigating asteroid compositions than is provided by conventional meteorites of centimeter and larger size. Conventional meteorites reach the Earth only by selective gravitational perturbations, and once at the Earth, they must be very strong to survive atmospheric entry without fragmentation. In contrast, millimeter sized and smaller particles reach the Earth by Poynting Robertson drag, a process that causes orbital decay of all small particles. Because they are small, they decelerate at higher altitudes where the dynamic ram pressure is small and they do not have to be strong to survive atmospheric entry. As will be discussed later, small particles actually melt before they break. Once molten, all particles have similar shapes and their range of mechanical properties is more constrained than for unmelted particles. Cosmic spherules provide a means of sampling meteoroid types not represented by conventional meteorites. Unlike meteorites, which tend to be rather strong objects, most millimeter sized particles observed as meteors entering the atmosphere are "porous, crumbly objects made of loosely conglomerate, sponge-like material" (Verniani, 1969). The spheres do, however, have a strong selection effect for survival; they must not entirely vaporize due to atmospheric heating. Unlike conventional meteorites, where temperature gradients can restrict vaporization to the surface, small particles are more uniformly heated in their interiors. Particles <50 μm commonly survive without melting (Love and Brownlee, 1991; Flynn, 1988), but larger ones commonly melt and undergo substantial vaporization.

Although biased towards low-entry velocity, cosmic spherules offer a unique way to study large numbers of extraterrestrial particles up to millimeter size. Most of the physical properties of spherule producing meteoroids are severely altered by atmospheric heating, but the elemental ratios of some elements appear to be preserved. It cannot be proven that the element ratios are preserved in any or all cases, but we will present evidence that some element ratios are not changed either by entry heating or by residence on the Earth's surface. In this study, we determined the bulk elemental compositions of spherules ranging in size from 1 μm to 1 mm in diameter to provide information on the nature of the largely unexplored millimeter sized meteoroids that impact the Earth.

SPHERULE TYPES

Extraterrestrial spherules can be classified by composition into three general types: S (stony), I (iron), and FSN (iron-sulfur-nickel). The spherules used in this study were all of the S type, the class that dominates the terrestrial influx of spherules. The type-S spherules have approximately chondritic elemental composition for many elements, and they appear to provide the most direct clues to the composition of their parent bodies. Although all analytical work done here was on S spherules, we will briefly discuss the I and FSN types because of possible relationships they may have to the stony types.

The "iron" spheres are composed of oxides including magnetite, wüstite, and hematite and often they contain either a substantial FeNi metal core (Blanchard *et al.*, 1980) or a small nugget composed of the platinum group elements (Brownlee *et al.*, 1984; Bonte *et al.*, 1987). Iron nickel metal cores and even Pt nuggets are found in some type-S spheres (Bonte *et al.*, 1987), and at least some of the I spheres are probably Fe cores that have been ejected from S spherules. The FSN spheres are composed of iron oxide and FeNi sulfide. They normally are found only in sizes <20 μm in diameter and usually in stratospheric collections, although they have also been reported in polar ice collections (Robin *et al.*, 1988). The rarity of large FSN spheres in surface collections could be due to several processes. The stronger heating of larger spherules could vaporize S from sulfide droplets resulting in formation of type-I spherules. It is also possible that other effects such as low surface tension of sulfide might result in fragmentation of large droplets.

The S-type particles dominate the spherule flux to Earth. The stony spherules usually have approximately chondritic elemental abundances except for large depletions in S and moderately volatile elements such as Na and K. There are several petrographic subclasses of the S class, and we will call them "common," G and V. Approximately 90% of the S spheres are "common" type spheres, and they are composed of olivine and magnetite (or magnesioferrite; Robin *et al.*, 1992) crystals with interstitial glass. These well-crystallized spherules occur with a wide range of grain sizes and textures (Fig. 1), but typically they are composed of micron-sized or smaller grains. The most abundant, and presumably most strongly heated, resemble barred olivine chondrules, while less common and apparently less heated ones have porphyritic textures (Brownlee *et al.*, 1983; Taylor and Brownlee, 1991). The G spherules, as originally described by Blanchard *et al.* (1980), are mainly composed of a dendritic network of magnetite with a small amount of interstitial glass. They are dominated by magnetite but we consider them to be a subclass of stony spherules because they contain a silicate component. This contrasts with the I spherules, which contain no silicate. The G spheres differ from other S spheres because they are dominated by continuous networks of magnetite instead of containing subordinate amounts of isolated magnetite grains or dendritic clusters. The silicate component appears to be glass, but it has not been studied in detail. There does not appear to be a gradation from G to other S types. Approximately 6% of the deep-sea spherules are of the G type but they may be rarer in other collections.

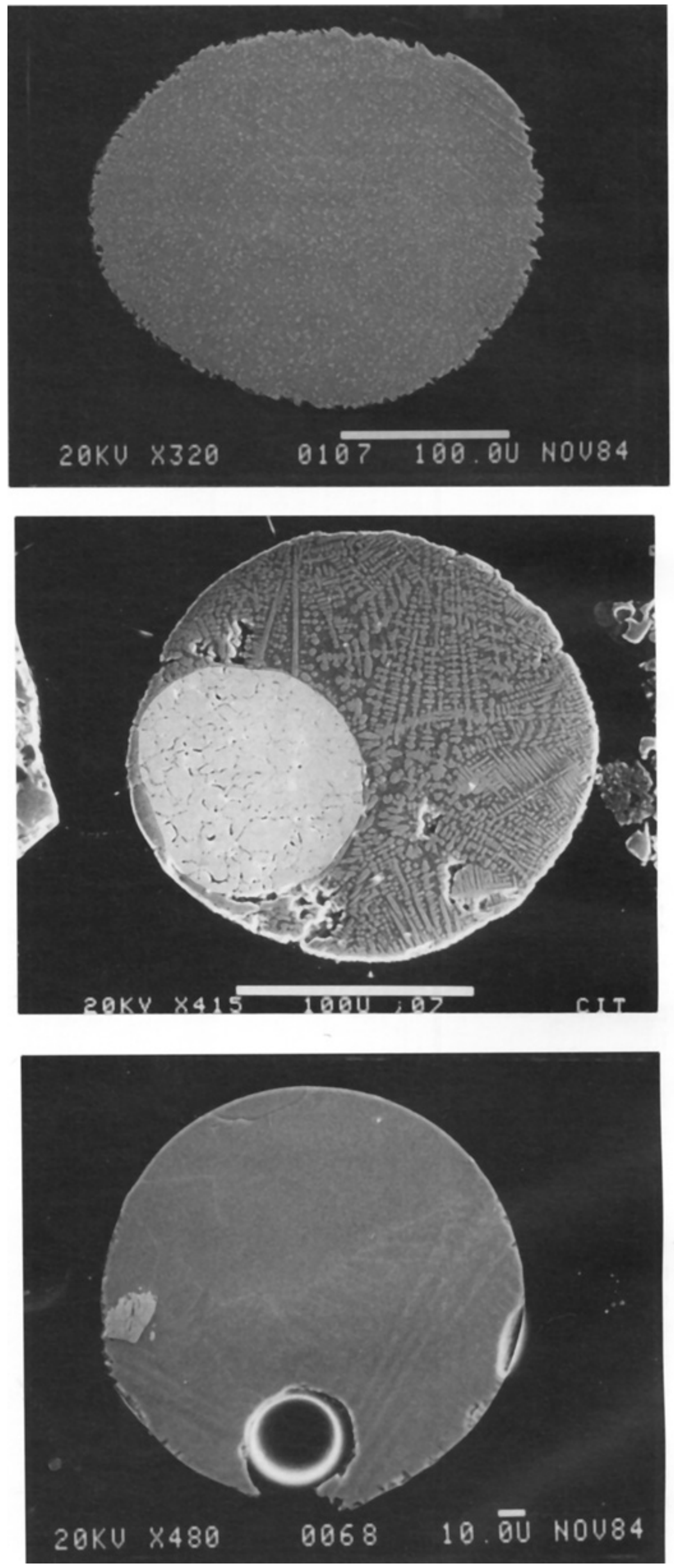

FIG. 1. Secondary electron micrographs of sectioned, polished cosmic spherules: (upper) Typical spherule 300 μm long, (middle) G spherule with metal FeNi core, 200 μm long and (lower) V spherule, 150 μm in diameter. The top portion is glass and the bottom half is crypto-crystalline. The bright feature on the left is a relict chromite grain and the vesicle at the bottom is a natural feature of the spherule.

Another subclass of the stony spherules is the V (vitreous) class originally described by Robin (1988). The V spherules are either completely glassy or cryptocrystalline and do not contain magnetite or olivine in discernible sizes >1 μm. Unlike other S spheres that are opaque due to their content of tiny magnetite crystals, many of the V spheres are transparent or translucent. The V class comprises ~5% of the spherules collected nonmagnetically in Greenland, and they often are Si rich with an approximately pyroxene normative composition (Maurette *et al.*, 1986; Taylor and Brownlee, 1991). Even higher abundances of type-V spherules have been reported in samples collected in the South Pole water well, probably the least-biased and best-preserved source of cosmic spherules (Taylor *et al.*, 1996). They are much rarer in deep-sea sediment samples probably due to either magnetic bias during collection or dissolution in sea water. Although no intermediate class spherules between common S and V were analyzed in this study, we would consider a sphere to be a V type if >50% if its volume were glass and it did not have a porphyritic texture. A special class of V spherule that has only been recognized in stratospheric collections and in sizes <30 μm has a peculiar composition that is consistent with partial volatilization of Fe and Si from a chondritic composition starting material as suggested by vaporization experiments. Relative to chondritic proportions, they are enriched in Ca, Al, Ti, and Mg and are depleted in Fe. They have been called CAT (Brownlee *et al.*, 1982) and CAS (Kordesh *et al.*, 1983) spheres and one was shown to have a strong isotopic fractionation in Mg that is consistent with significant Rayleigh distillation (Esat *et al.*, 1979). The elemental composition of the spherules is qualitatively similar to the evaporative residue produced by laboratory heating of chondritic materials (Hashimoto *et al.*, 1979; Hashimoto, 1983). Unpublished work by M. Zolensky (pers. comm.) showed that one CAT sphere was composed of glass and corundum. Some of these spheres could be lunar ejecta as suggested by D. Gault and D. McKay (pers. comm.).

Spherules of terrestrial origin are found in most environments on Earth and care must be taken in valid identification of extraterrestrial spheres. Criteria for identifying extraterrestrial spherules are described by Blanchard *et al.* (1980) and Brownlee (1981). In the environments where the samples in this study were collected, the abundance of extraterrestrial spherules exceeds that of any terrestrial contribution by orders of magnitude and the only evident "contamination" comes from obvious anthropogenic spherules. Most of these are common products of welding and abrasive cutting and they are compositionally and morphologically distinct from cosmic spherules. In general practice, cosmic spherules are identified on the basis of composition and mineral content as determined in the SEM or microprobe. The validity of these identifications has been confirmed by a variety of other techniques. Clayton *et al.* (1986) have shown that the O-isotopic composition of the stony spheres is not on the terrestrial fractionation line and is generally consistent with origin from a material with an isotopic composition similar to CM chondrites. This data is inconsistent with a major contribution by CI material. Near saturation levels of the cosmogenic isotopes ^{26}Al, ^{53}Mn and ^{10}Be have been found in stony and iron spherules (Raisbeck *et al.*, 1985, 1986; Nishiizumi, 1983; Nishiizumi *et al.*, 1991). The ratio of ^{26}Al/^{10}Be in the spheres is high, thus indicating significant ^{26}Al production by solar flare particles that were not shielded by more than a few centimeters of material. Nishiizumi *et al.* (1991) conclude that the irradiation times were in the range of 10^5 to 10^7 years in the inner solar system, and that the parental materials could have been either centimeter sized or smaller bodies or near-surface materials of larger bodies. Trace-element composition (Ganapathy *et al.*, 1978) and ^{87}Sr/^{86}Sr ratios provide further evidence of extraterrestrial origin (Papanastassiou *et al.*, 1983).

SAMPLES AND METHODS

Five hundred stony spherules ranging in diameter from 1 μm to 1 mm were analyzed in this study. The spherules were collected from the stratosphere, the ocean floor, and from Antarctica. Four hundred of the spheres were collected from Pacific sediments 1000 km east of Hawaii at a depth of 5300 m with a towed magnetic sled (Brownlee *et al.*, 1979). The samples were recovered from the top 10 cm of sediment and spheres should have a range of ages extending to ~100,000 years estimated from the sediment accumulation rate. The deep-sea spherules were collected magnetically and low-Fe particles must be underrepresented in this collection, but it does not appear that magnetic collection produces a strong bias for the most common particle types. Examination of nonmagnetically collected sea-floor particles and Greenland spherules shows that >90% of them have magnetite contents that are sufficiently high to allow magnetic collection. Figure 2 shows a comparison of the Al and Fe compositions of the deep-sea spheres used in this study with Greenland spherules collected nonmagnetically by Maurette *et al.* (1986, 1987). Small differences are seen in the data, but generally there is good agreement between the two sets of samples. Particularly important is that there are not large numbers of low-Fe particles missed by sea-floor collections. The deep-sea samples were restricted to sizes >100 μm because of the methods used in their recovery. Smaller spherules were obtained from Antarctic and stratospheric collections. The Antarctic spherules were collected by Maurette *et al.* (1989) by melting subsurface blue ice near Cap-Prudhomme. These spherules ranged in size up to 1 mm, but most that we analyzed were in the 50 to 100 μm size range. The 68 particles were collected nonmagnetically and they have terrestrial ages, during which time they were encased in solid ice, that range to approximately a million years. Thirty two of the smallest particles in this study are rare silicate spherules collected with NASA U2 and WB 57 aircraft at altitudes near 20 km (Brownlee *et al.*, 1977; Warren and Zolensky, 1994). The stratospheric spheres in this study range in diameter from 1.5 μm to 18 μm, and they comprise all of the particles <50 μm shown in Fig. 6. These are contemporary spheres, and unlike the other spheres they were never exposed to water and never touched the surface of the Earth. They are a numerically small sample and only give a glimpse of what a more extensive study of small spherules would yield.

The spheres that were >50 μm in diameter were potted in epoxy, and polished sections were prepared for microprobe analysis. The smaller ones were not sectioned and they were analyzed in the SEM. The microprobe analyses were done with the MAC probe at the California Institute of Technology and the JEOL 733 probe at the University of Washington using Bence-Albee corrections. Each particle was analyzed with a single 30 μm spot in the unetched interior of the sphere. This is the largest spot that can be used without causing crystal spectrometer focus errors. The analysis volume varies between light and heavy elements but is ~1000 μm^3. We consider that these analyses provide a good bulk spherule composition based

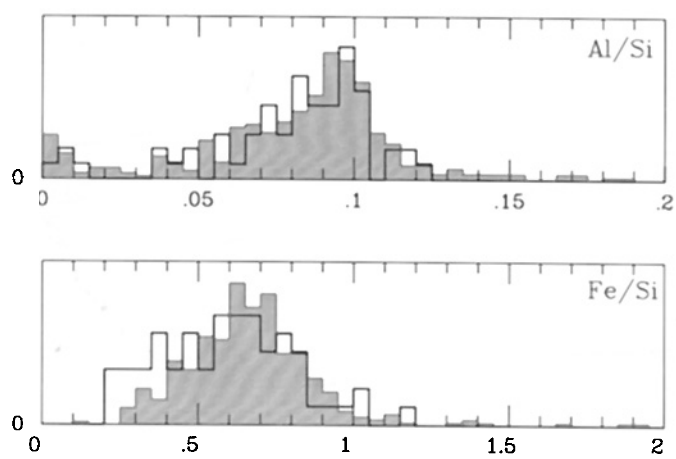

FIG. 2. Comparison of atomic element to Si ratios of stony spherules collected in Greenland with those collected in the deep sea for Al and Fe. The shaded histogram shows abundances of 400 deep-sea spherules, and the bold outlined histogram shows the abundances of 61 spherules from Greenland.

on homogeneity measurements discussed in the error section. Individual spheres show a very wide range of etching, but the unetched cores selected for analysis are very readily observed optically in the probe. The etched periphery is rougher and darker than unetched areas because of removal of interstitial glass. Only spherules with unetched cores and with grain sizes $<10\ \mu m$ were used for this study. Most of the spheres were analyzed for Na, Mg, Al, Si, P, Ca, Ti, Cr, Mn, Fe, and Ni. Sodium and S proved to be below detection limits for the majority of the samples. A set of larger spheres were additionally analyzed for Co.

Seventeen of the smallest particles from Antarctica and all of the stratospheric spherules were analyzed as unsectioned particles in a JEOL 35C scanning electron microscope (SEM) with an energy dispersive x-ray spectrometer (EDX) using a rastered beam that covered most of the particle. Flat polished mineral standards were used, and measured k-values for the particles were input into the Armstrong-Buseck particle correction program (Armstrong and Buseck, 1975) to yield quantitative element ratios.

Errors

For the microprobe data, the relative errors due to counting statistics (standard deviation/mean value) for the major elements (MgO, SiO_2 and FeO) are on the order of 1%. The relative errors of Al_2O_3 and CaO were on the order of 2% for concentrations near their peaks of their abundance histograms. Of the minor elements, TiO_2 and MnO, the relative errors (at median values) are <10%, increasing to 20% for half of the median values. The relative errors of P_2O_5, Cr_2O_3 and NiO increase from 10% to 20% for decreasing abundances. The Na abundance in almost all the particles is below detection limits, which indicates an order of magnitude depletion below chondritic values. The relative errors for Co were ~20%. Repeated analyses on the same samples on different days and with different machines indicated reproducibility generally consistent with counting errors. The main source of error in analysis of the spherules was internal inhomogeneity. Analyses of many individual $30\ \mu m$ spots in fine-grained spheres showed that the standard deviation of the major elements was usually <5% of the measured value, which indicates that a random $30\ \mu m$ spot does provide a good representative analysis of bulk spherule composition. Coarse-grained porphyritic spheres showed the highest level of inhomogeneity with standard deviations of >10% in some cases, but only a few of such spheres were included in this study.

Weathering effects provide a potential source of error in measuring true spherule composition. We feel that our microprobe analyses completely avoid such errors because we selectively analyzed only unweathered spherule cores. Usually, more than half of a spherule cross-section is unweathered, and the demarcation between etched and unetched is easily seen with probe optics. Etched rims have voids where glass is lost and they are much less reflective than unaltered cores. The ability to select pristine centers of the spherules is a very important advantage of this analysis technique. Bulk spherule analyses or even probe analyses of spherule exteriors would include weathered regions and would yield spurious results due to the loss and absorption of elements in the weathered portions of the samples. The deep-sea spherules resided in oceanic sediments for an appreciable amount of time and they show various degrees of chemical alteration (Blanchard *et al.*, 1980; Brownlee, 1981). The Antarctic spheres are affected but only in relatively minor ways (Koeberl and Hagen, 1989). In weathered spherules, dissolution removes the glass phase first from the periphery of the spheres and then progresses inward, thus depleting the elements that reside in the glass (*e.g.*, Si, Al, Ca, and some Fe). The effected glass is totally removed leaving only void spaces that have very sharp contacts with remaining glass, olivine and magnetite (Fig. 3). The etching is readily apparent in sectioned spheres as small and large void spaces. All of the particles which were microprobed showed some evidence of alteration.

To test whether any hidden alteration had occurred in what appear to be unetched cores of deep-sea spheres, Bates (1986) compared the abundances of Ca, Al, and Si in spheres that showed various degrees of etching. He found no correlation between either the Al or Ca abundance in the cores and the fraction of the sphere that was etched. He concluded that chemical weathering had not added or removed Ca or Al from the apparently pristine cores. In his study the "amount" of etching, defined as the ratio of the diameter of the unetched core to the spherule diameter, varied by a factor of ten. We believe that this is very strong evidence that weathering processes are not altering the composition of the cores that show no evidence for pitting or etching as optically viewed in polished section. It is ironic that particles that survive atmospheric entry without melting are chemically altered in polar ice (Presper *et al.*, 1993) and deep-sea environments, while those that are melted during entry appear to be essentially unmodified by weathering in their cores. This is largely due to porosity differences between spheres and unmelted particles. The lack of chemical alteration of the cores is consistent with the observation by Papanastassiou *et al.* (1983) that the $^{87}Sr/^{86}Sr$ ratios in only lightly weathered deep-sea spherules showed no significant exchange with sea water.

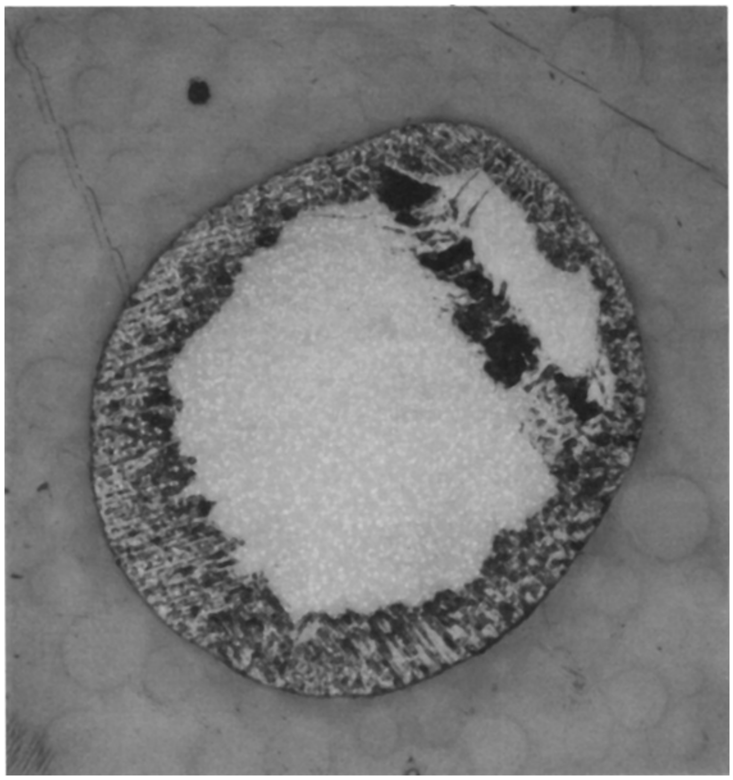

FIG. 3 Optical micrograph of sectioned, polished stony deep-sea spherule showing peripheral etching. The diagonal mark is a polishing artifact.

A limitation of the study presented here is the emphasis on deep-sea spherules. These samples are usually more altered than polar ice spherules, and most of the ones used were magnetically collected. We also tended to concentrate on spherules in the 100 to 400 μm diameter range. Spherules that are smaller, larger, or nonmagnetic are less represented in this study.

RESULTS

Most of the spherules studied have compositions that show general similarity to chondritic proportions, with the major differences being depletions of certain elements. When normalized to Si, the element distributions can be grouped into three main categories: (1) peak near solar values; (2) peak at moderately depleted values, and (3) highly depleted and peak near probe detection limits.

Table 1 compares the median values of the sphere suite (and the mean of each type of sphere) with that of solar and various meteoritic abundances. The medians are a crude and sometimes misleading way to summarize the spherule data. A much more meaningful presentation of the data is given in Figs. 4 through 8 showing a series of histograms plotted for each size category for a particular element. To study the relationship between sphere diameter and abundance for each of these elements, four different size groupings were made. Overall, the data agrees well with other published data for S-type spheres (Blanchard *et al.*, 1980; Yamakoshi, 1984; Bonte *et al.*, 1987; Koeberl and Hagen, 1989; Taylor and Brownlee, 1991; Nishiizumi *et al.*, 1995). Data obtained by neutron activation of whole spheres does show enhanced Al and Ti (Yamakoshi, 1994) over microprobe analysis of unetched spherule cores. It is likely that this difference is due to surface weathering of the spherules. This difference under-

TABLE 1. Cosmic spherules.

Type	Mg	Al	Ca	Ti	Cr	Mn	Fe	Co	Ni
Stratospheric	1.06	0.233	0.16	n.a.*	0.007	0.005	0.633	n.a.†	0.011
Antarctic	1.06	0.091	0.056	0.002	0.006	0.007	0.528	n.a.	0.013
Deep-sea	1.06	0.083	0.059	0.002	0.008	0.006	1.024	0.003	0.019
All	1.06	0.094	0.065	n.a.	0.007	0.006	0.937	n.a.	0.018
Stratospheric micrometeorites (unmelted)‡									
Smooth(CS)‡	0.82	0.082	0.021	n.a.	0.016	0.007	0.742	n.a.	0.052
Porous(CP)‡	1.02	0.070	0.047	n.a.	0.017	0.013	0.705	n.a.	0.044
Coarse‡	1.20	0.075	0.13	n.a.	0.013	n.a.	0.585	n.a.	0.033
Bulk IDP§	0.98	0.075	0.051	n.a.	0.018	0.011	1.080	n.a.	0.055
Bulk chondrites									
CI#	1.07	0.085	0.061	0.002	0.014	0.010	0.900	0.002	0.049
CM$	1.05	0.095	0.069	0.003	0.013	0.007	0.819	0.002	0.045
H	0.96	0.070	0.052	0.002	0.012	0.007	0.818	0.002	0.045
L	0.93	0.069	0.050	0.002	0.011	0.007	0.584	0.002	0.031

The means are influenced by sampling biases, particularly for Fe where a few spheres with very high Fe can appreciably shift the mean. The peaks in the individual element distributions can vary appreciably from the means and it is possible that they better represent the bulk composition of the parental materials than the means in this table. Iron is the element most effected by the sample collection biases of this study.

* n.a. = Not analyzed or not determined; this is usually because the element is normally below detection limit for the analysis method and samples used.

† Cobalt was only analyzed in 61 spheres. These were done on a special microprobe run where conditions were optimized for Co analysis. The data for all of the other elements was obtained from all of the 500 spherules analyses and in only a few cases were measurements below detection limits.

‡ Mg, Al, Ca, and Fe from Schramm *et al.* (1989). More accurate analyses are reported here for Cr, Mn and Ni.

§ Bulk IDP is a calculated value that includes IDPs dominated by FeNi sulfides. See Schramm and Brownlee (1989).

\# CI chondrite average from Anders and Grevesse (1989).

$ CM, H, and L chondrite averages from Wasson and Kallemeyn (1988).

scores the importance of analysis of unaltered cores *vs.* whole spherule analysis.

The spherule data set can be compared to elemental composition data of small unmelted stratospheric IDPs compiled by Schramm *et al.* (1989), Jessberger *et al.* (1992) and Arndt *et al.* (1996).

Undepleted Elements

Magnesium–The Mg/Si atomic ratios of the spheres are strongly peaked with a mean value of 1.06, and 85% of the particles have ratios between 0.7 and 1.3 (Fig. 4). The mean value is close to the CI value of 1.07, but the peak of the distribution is a better match with CM. The peak is distinctly higher than the mean value for H and L chondrites. There is a slight increase in the mean Mg content with spherule size (Figs. 5 and 6). The symmetry of the Mg/Si distribution is strong evidence that selective volatilization of Si did not occur. In vaporization experiments, Si is more volatile than Mg (Hashimoto, 1983), and if any significant fraction of the spherules had experienced selective loss of Si, there should be a tail on the Mg/Si distribution leading to higher values.

Aluminum–The Al/Si distribution is peaked near CI values (Figs. 4 and 7), but it is offset in the high direction and the distribution is dramatically broader than the Mg/Si curve. The peak is in good agreement with the CM mean and CI matrix. It is much higher than ordinary chondrites and much lower than CV. The distribution is bimodal with a small peak at zero. The major peak and mean are much higher than for bulk L and H chondrites. The smallest spheres have large dispersion in values and appear to have a higher mean Al/Si ratio. Although this could just be a sampling effect, the distribution of Al compositions of the small spherules is offset to higher values than unmelted IDPs of similar size.

Calcium–The Ca/Si histograms are shown in Figs. 4 and 8. The distributions are broad and there is systematic depletion relative to the CI mean for the smallest spheres, but for large spheres the distribution becomes more peaked and the fraction of spheres which are Ca-depleted diminishes. Unlike Al, there is no peak at zero for the entire size range. There is a remarkable difference between the composition of the larger spheres and what is seen for the 10 μm stratospheric IDPs. The stronger Ca depletion in the IDPs either implies that they are not derived from the same parental materials as large spheres or that sample averaging in the larger particles has mixed Ca-depleted components with those with very high Ca. To bring these data sets into agreement would require the existence of a population of very high-Ca IDPs. Although IDPs with high Ca/Al do exist, they appear to be too rare to balance with the Ca depleted histograms for the 10 μm IDPs.

Moderately Depleted Elements

Manganese–This is the most strongly peaked element other than Mg, although its peak is depleted relative to bulk CI by >25%. The distribution peak agrees very well with CM, thus implying a similarity with CM composition material unless the shift is due to volatilization. The symmetry of the peak (Fig. 9) argues against a shift due to volatilization. Selective volatilization in particles with higher entry velocity would skew the distribution, thus producing tailing in the direction of lower Mn. There is no major variation of Mn with size.

Iron–Although the mean Fe/Si for the deep-sea spherules is in fact greater than CI (Table 1), most of the spherules are depleted relative to CI by ~25% as shown in Fig. 6. The peak in the distribution is close to the bulk Fe/Si ratio of L chondrites. There are many effects that can influence the Fe/Si in S-type spherule collections. Some Fe may be lost with S during atmospheric heating. Iron content effects density and magnetic properties and this results in sampling biases. There is a group of unusual stony spheres that are extremely Fe rich (17 that plot out of the range of Fig. 10). When this component is added to the Fe-depleted population, the mean Fe/Si ratio is increased up to a high and possibly misleading value. These high-Fe spheres are probably overrepresented in the deep-sea spherule collections because of the magnetic method of collection. The 25% Fe depletion seen for most of the particles may underestimate the actual Fe depletion because the deep-sea spheres were collected magnetically, and it is likely that a low-Fe component is missing in the deep-sea spherule collection. There is an observed cutoff of particles in the deep-sea spherule collection with Fe/Si <~0.25. The low-Fe stony spheres in the Antarctica, and stratospheric collections are very rare in the deep sea. Though examination of nonmagnetic collections did not reveal the presence of a large number of deep-sea spherules with Fe/Si ratios less than the cutoff, it may well be that these particles do not survive long in the deep sea since glass is predisposed to sea water etching. Even without these biases, it is still not clear that the Fe abundance in the spheres provides reliable information on the composition of parent

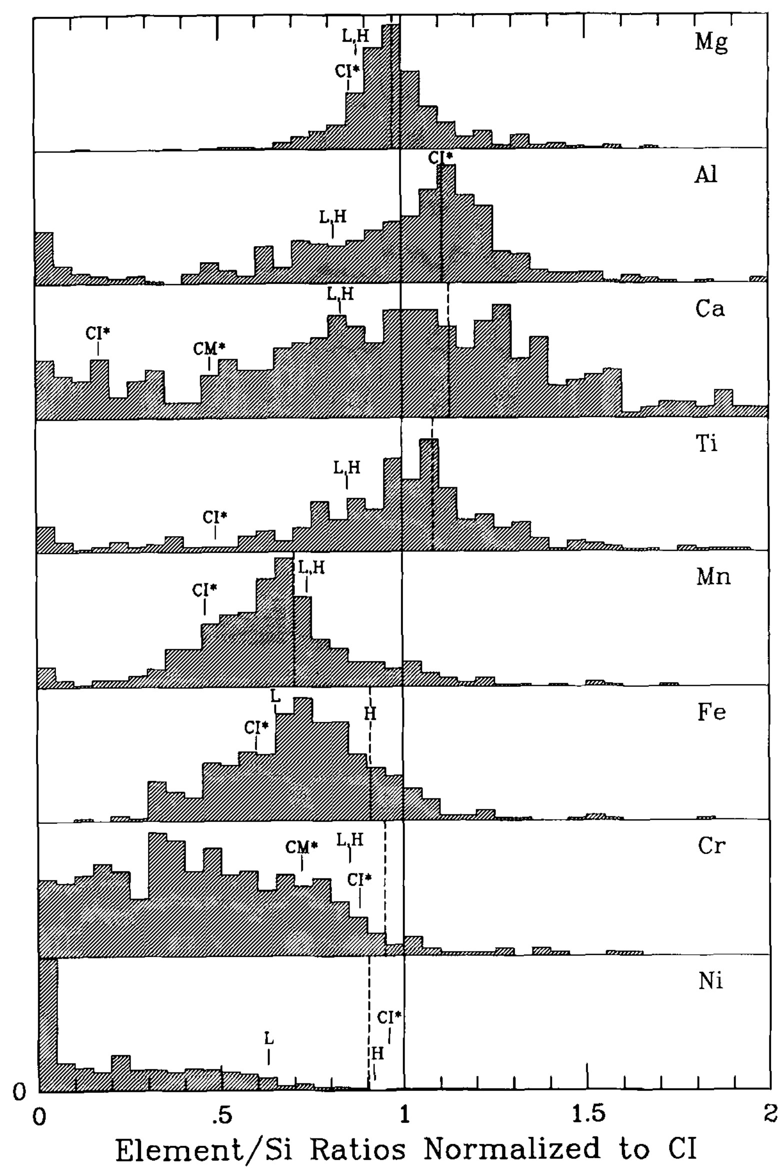

FIG. 4. Element to Si ratios normalized to CI (Anders and Grevesse, 1989) for all stony cosmic spherules 100 μm and greater in size. Dashed line indicates mean CM chondrite composition (Wasson and Kallemeyn, 1988), CI* and CM* indicate mean CI and CM matrix compositions (McSween and Richardson, 1977), and H and L indicate mean H chondrite and L chondrite compositions (Wasson and Kallemeyn, 1988). All of the histograms from Fig. 4 to Fig. 18 are based on the analysis of 500 spherules. The vertical scale of each histogram has been adjusted to allow optimum comparison between data sets. On every histogram, the minimum step size can be seen and this defines the vertical scale of one particle.

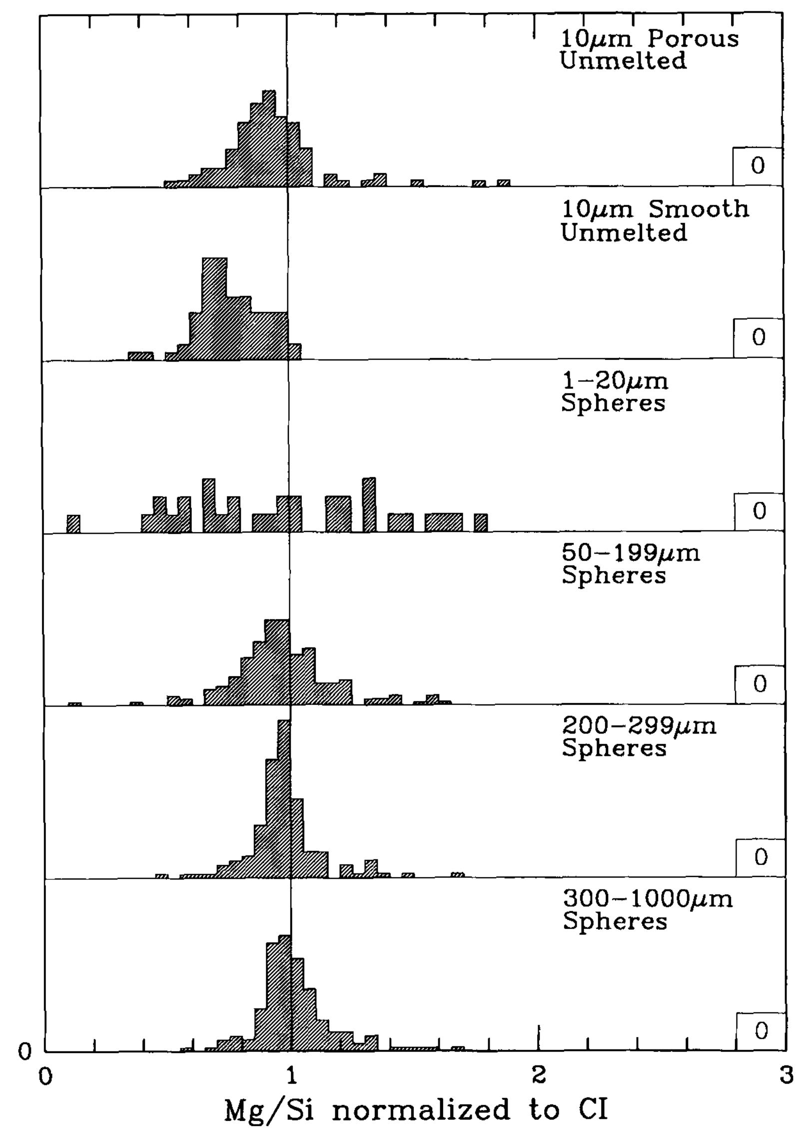

FIG. 5. Ratio distributions of Mg/Si (atom) (normalized to CI) for stony cosmic spherules grouped by size and for the two major classes of chondritic stratospheric micrometeorites, "smooth" and "porous." The number inside of the box indicates the number of spheres that plot outside of range.

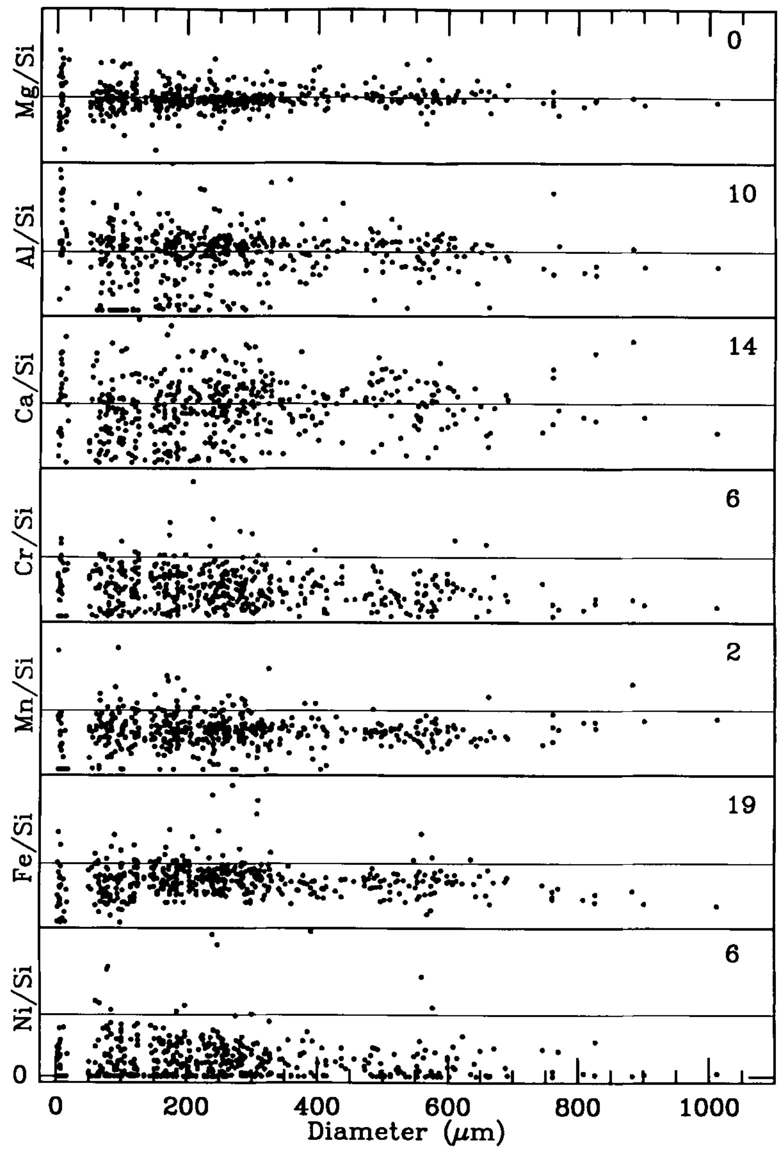

FIG. 6. Atomic element to Si ratios, normalized to CI, *vs.* size for 500 stony cosmic spherules. This plot shows compositional variations, or lack thereof, with size over a factor of a billion in particle mass. The horizontal line in each range marks CI and the total range for each element ratio is 0 to 1.4.

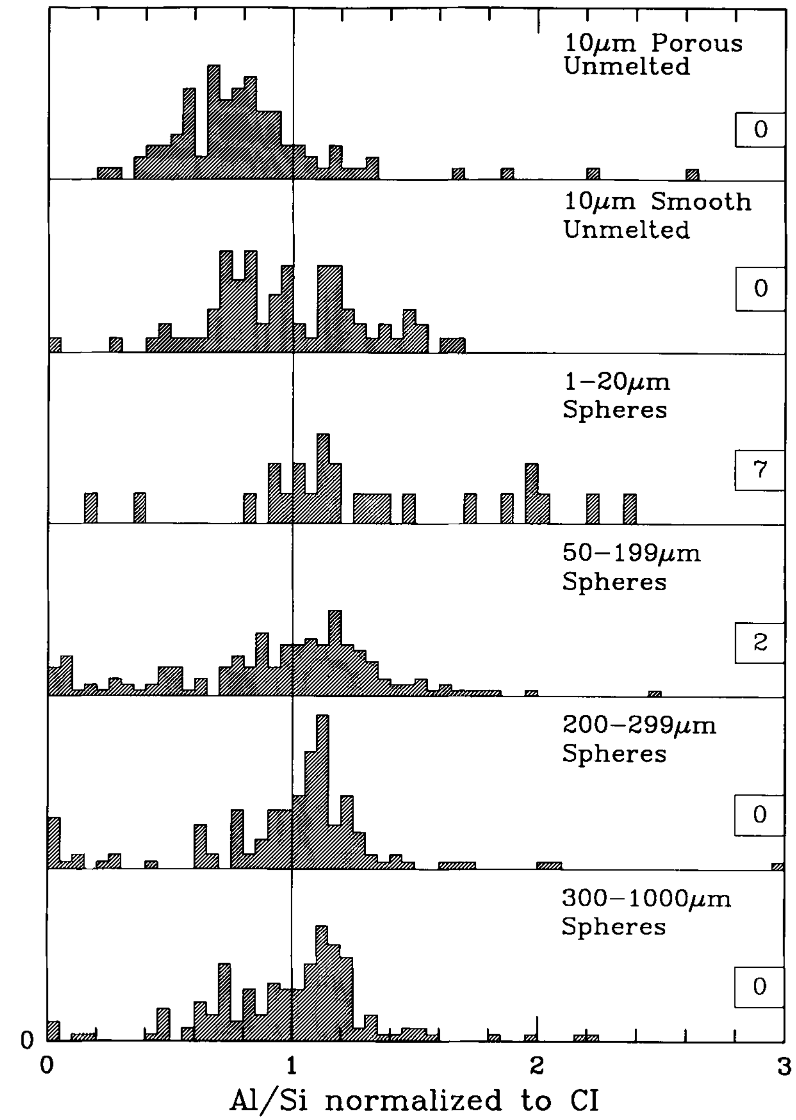

FIG. 7. Ratio distributions of Al/Si (atom) (normalized to CI) for stony cosmic spherules grouped by size and for the two major classes of chondritic stratospheric micrometeorites, "smooth" and "porous." The number inside of the box indicates the number of spheres that plot outside of range.

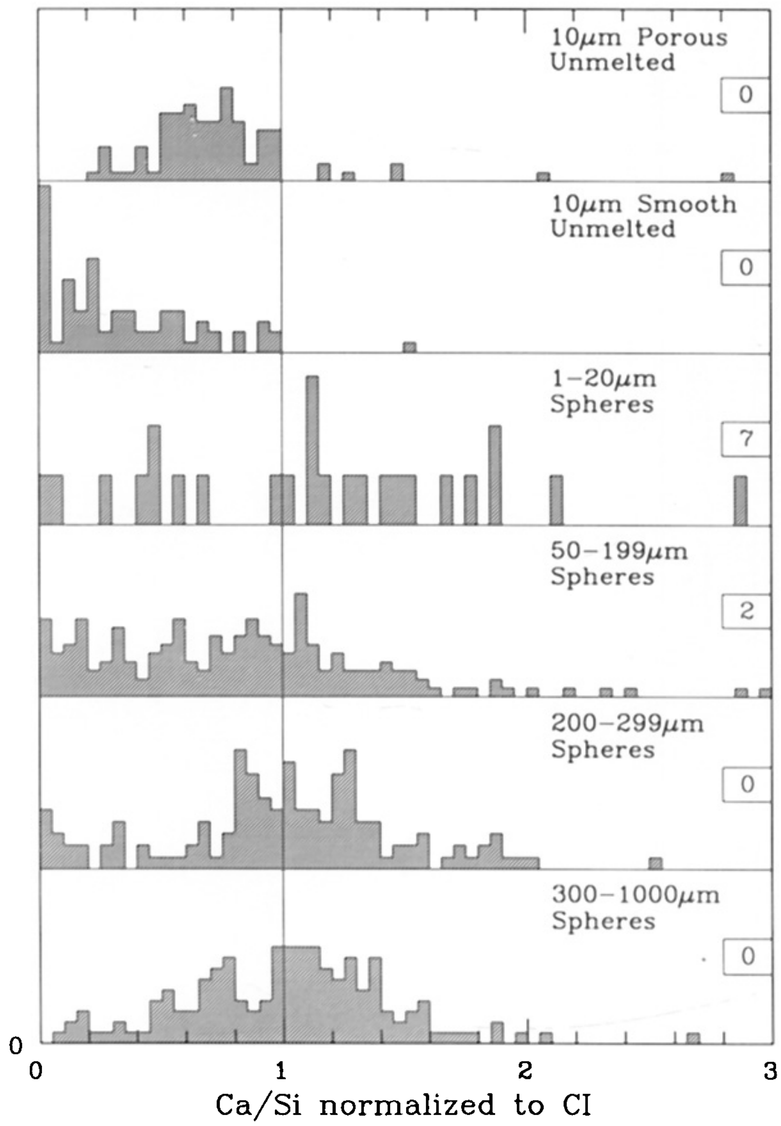

FIG. 8. Ratio distributions of Ca/Si (atom) (normalized to CI) for stony cosmic spherules grouped by size and for the two major classes of chondritic stratospheric micrometeorites, "smooth" and "porous." The number inside of the box indicates the number of spheres that plot outside of range.

bodies because of possible loss of Fe and other siderophiles by either selective volatilization of metal or by the ejection of immiscible beads of metal or sulfide during atmospheric entry. In some cases, spherules may retain metal beads that are not in the plane of the analysis section.

Strongly Depleted Elements

Chromium–This element is depleted relative to CI for all sizes of cosmic spherules, but there is an increasing depletion with size (Fig. 11). The Cr abundances are correlated with Ni, which suggests that they were depleted by the same mechanism.

Nickel–This element is strongly depleted (Fig. 12). There is a broad distribution of Ni/Si values, but the distribution peaks at detection limits. The lowest Ni particles are texturally identical to ones with near solar Ni/Si ratios, and there does not appear to be distinct subgroups, just particles with various levels of Ni depletion. The Ni abundance shows fairly good correlation with Cr (Fig. 13).

Cobalt–Cobalt was measured in only one set of microprobe analyses that included 61 large (>350 μm) deep-sea spheres and 6 large Antarctic spheres. Although the majority of the spheres are depleted in Co/Si relative to CI, there are a few spheres that are highly enriched in Co and plot off the scale of the histogram shown in Fig. 14. These spheres are also enriched in Fe.

Sulfur and Sodium–Even though these elements are abundant in chondrites, they were not quantitatively analyzed for in the spherules because they were depleted by more than an order of magnitude, and in nearly all cases were below detection limits of the microprobe.

DISCUSSION

Depletions

The prominent deviations from chondritic elemental composition are depletion of volatiles and siderophiles. Neither of the depletions of these element groups is seen in the averages of <20 μm unmelted micrometeorites collected in the stratosphere (Schramm *et al.*, 1989). It is likely that the volatile and siderophile depletions in the spherules occurred during atmospheric entry and are not original properties of the meteoroids. Qualitatively similar depletions are seen in >50 μm unmelted micrometeorites from Antarctic ice deposits (Presper *et al.*, 1993). The depletions in the unmelted Antarctic particles may be due to terrestrial weathering processes. The large depletions of Na, S and also Rb (Papanastassiou *et al.*, 1983) are almost surely due to volatilization during atmospheric entry. If the spherule predecessors were so highly depleted in these elements, they would be unique among undifferentiated meteoritic materials. The depletion of Fe, Ni, and Cr in most of the 500 stony cosmic spherules, and Co in most of the 67 spheres for which it was analyzed, indicates the loss of siderophiles. If the precursor materials were composed of coarse-grained assemblages of metal and silicates, then some of the siderophile "loss" could be the result of separation of metal and silicate phases during ejection from a parent body or collisional evolution in the interplanetary medium. The reasonably good correlation of Cr and Ni (Fig. 13) argues against this because it is highly unlikely that most of the Cr could be included in siderophile-rich phases. There is Cr-bearing metal in CM chondrites, but even there, most of the Cr is contained in silicates and chromite as it is in other chondrite classes. Also, the refractory lithophile elements in the spherules indicate an affinity with highly oxidized chondrite groups that do not contain significant amounts of metal. Some stony spheres have metal cores, and in these cases there is a very high fractionation of siderophiles into the metal phase. Typical spheres do not have metal cores that intersect the polished sections. In some cases, the core could be above or below the section plane but the relative scarcity of detected cores is evidence that most stony spherules do not have cores. The common siderophile depletion is evidence that these spheres may have had cores and that they were lost due to internal separation of immiscible liquids or by vaporization of the comparatively high vapor pressure liquid metal. Although Cr can show either siderophilic or lithophilic behavior, correlation with siderophiles indicate that Cr and possibly P (Bates, 1986) acted as siderophiles while the removal was taking place. A strongly reducing environment must

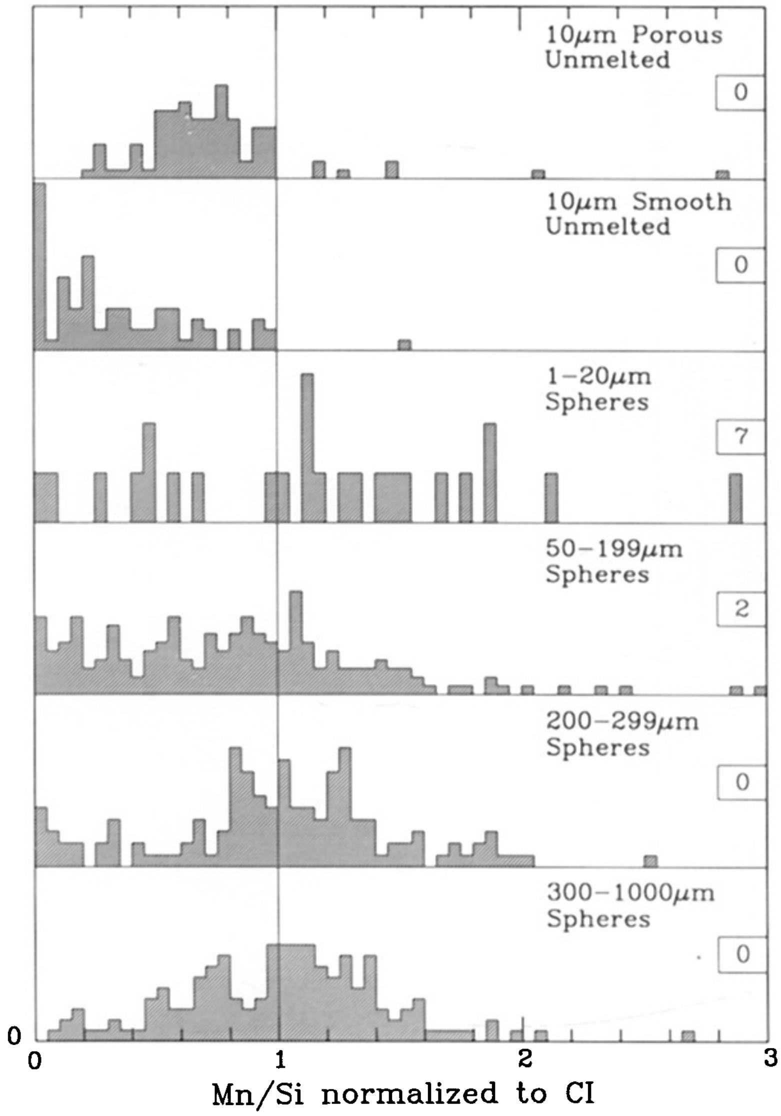

FIG. 9. Ratio distributions of Mn/Si (atom) (normalized to CI) for stony cosmic spherules grouped by size and for the two major classes of chondritic stratospheric micrometeorites, "smooth" and "porous." Mean CM ratio is shown by the dashed line. The number inside of the box indicates the number of spheres that plot outside of range.

have existed for this to happen. Metal formation by reduction is a common process observed in laboratory heating experiments on C-rich chondrites, and partially heated stratospheric micrometeorites have been observed to be covered with metal beads that appear to be produced by reduction (Brownlee *et al.*, 1983). Reduction and separation (or evaporation) of an immiscible siderophile phase from C1/C2 material has been observed during heating and vaporization experiments (Hashimoto *et al.*, 1979; King, 1983; Ekambaram *et al.*, 1984; Yakovlev *et al.*, 1985). Although there is no compelling evidence from this study for the origin for siderophile depletion, we favor a model where metal is formed and lost during atmospheric entry (Kyte, 1983; Brownlee *et al.*, 1984). If this process occurs, it must occur for almost all of the spherules because all but a few have siderophile depletion. If the metal droplets are ejected, then they could be the major source of the type-I cosmic spherules. Czajkowski (1987) provides arguments that this may not be the case and the type-I spherules may have other origins, such as metallic meteoroids.

An alternate possibility for the Ni-Cr correlation is that Ni- and Cr-rich phases may have been associated with each other in the precursor meteoroids. Zolensky and Krot (1996) have described an association of suflides and chromite in Allende.

Precursor Groups

The elements not depleted during the atmospheric entry process provide direct clues to the composition of the parent materials of the spherules. Because the volatiles are depleted, any "matching" with chondrite classes must rely on the relatively refractory elements, including Si and Mn, which do not appear to be strongly effected by entry processes. From the distributions of these elements, the spherules can be grouped into four families: (1) chondritic; (2) high-Fe, low-Mn particles; (3) coarse-grained precursor; and (4) olivine.

The major clan has a chondritic elemental composition that is basically consistent with CM chondrites and probably represents the melt product of material with a grain size much smaller than the recovered sphere sizes. The other groups have important deviations from chondritic compositions, but their compositions are consistent with derivation by melting of coarse-grained materials composed of a few grains of minerals that are common in chondrites. The nonchondritic composition particles could be samples of nonchondritic parent bodies, but it is possible that they are simply coarse-grained components of bodies with bulk undifferentiated compositions. These are not totally distinct groups because there is some overlap between the olivine and the coarse-grained precursor groups. The olivine group is primarily a subset of the coarse-grained precursor group.

Chondritic Group–These spheres have median values of Mg/Si, Al/Si, Ca/Si, Ti/Si, and Mn/Si that are close to CI bulk composition. Extensive vapor fractionation in these particles seems to be ruled out because of the moderate sharpness of the Mg/Si, Mn/Si, and Al/Si distributions. As mentioned previously, if fractionation of these elements had occurred, one would expect that the Mg/Si distribution would have an Si depleted tail due to loss of Si in the most strongly heated particles. The fractionation of the refractory lithophiles Al, Ca, Ti in chondrites is well known (Ahrens *et al.*, 1969) and it provides a basis for classifying different chondrite groups (Kallemeyn and Wasson, 1981; Wasson, 1985). The refractory lithophile fractionation is believed to be the signature of different degrees of incorporation of either high-temperature condensates or refractory residues (Grossman, 1972; Larimer, 1979). The means of the Ca, Al, Ti, and Mg histograms for the spherules are significantly higher than bulk values for ordinary chondrites, which indicates that the spheres are not derived from ordinary chondrites. They also are lower than CV chondrites, which indicates that this class cannot be a major source. Viable sources are CIs, CMs, and CRs.

Figure 15 shows that Ca and Al are correlated in cosmic spherules as they are in bulk chondrites (Ahrens *et al.*, 1969). The correlation is far from perfect, but there is general agreement with the solar abundance line in Fig. 15. The Al/Ca correlation was pre-

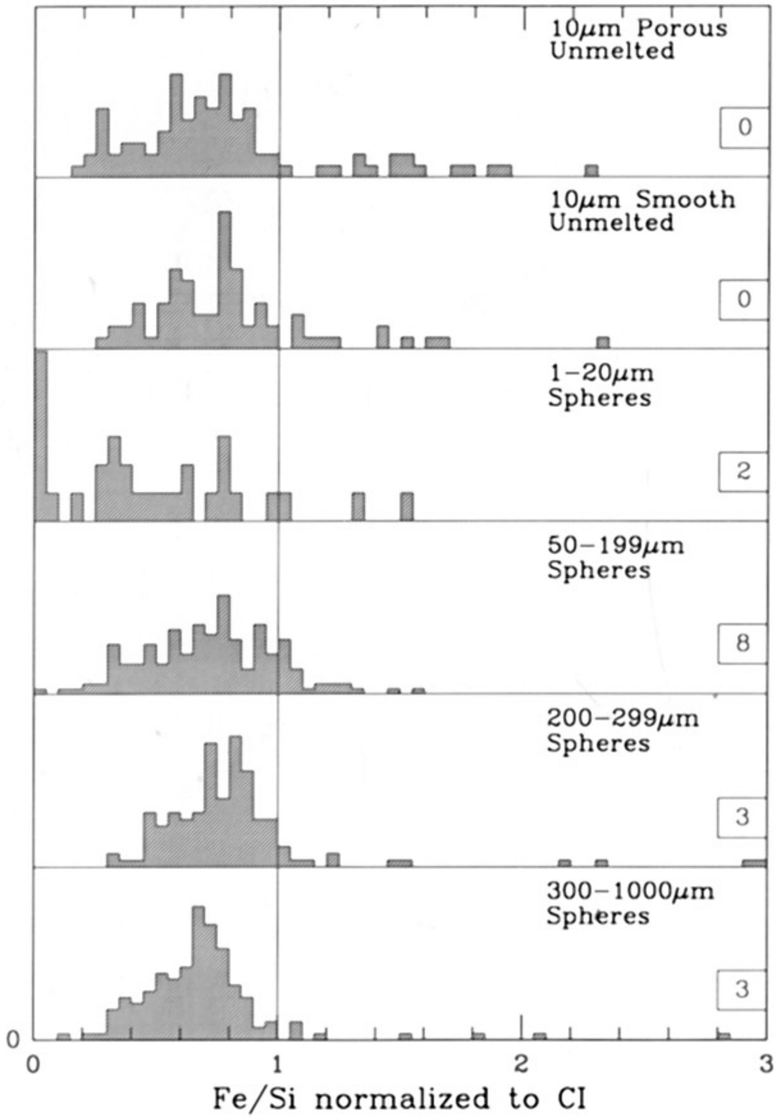

FIG. 10. Ratio distributions of Fe/Si (atom) (normalized to CI) for stony cosmic spherules grouped by size and for the two major classes of chondritic stratospheric micrometeorites, "smooth" and "porous." The number inside of the box indicates the number of spheres that plot outside of range.

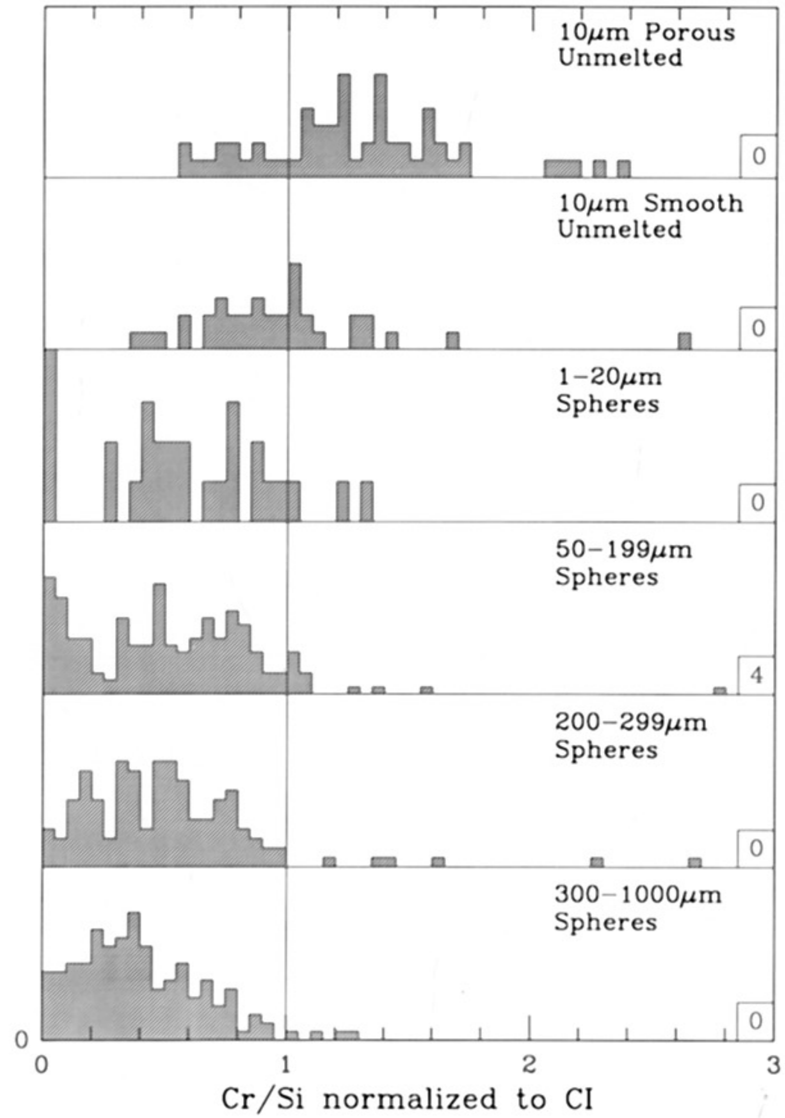

FIG. 11. Ratio distributions of Cr/Si (atom) (normalized to CI) for stony cosmic spherules grouped by size and for the two major classes of chondritic stratospheric micrometeorites, "smooth" and "porous." The number inside of the box indicates the number of spheres that plot outside of range.

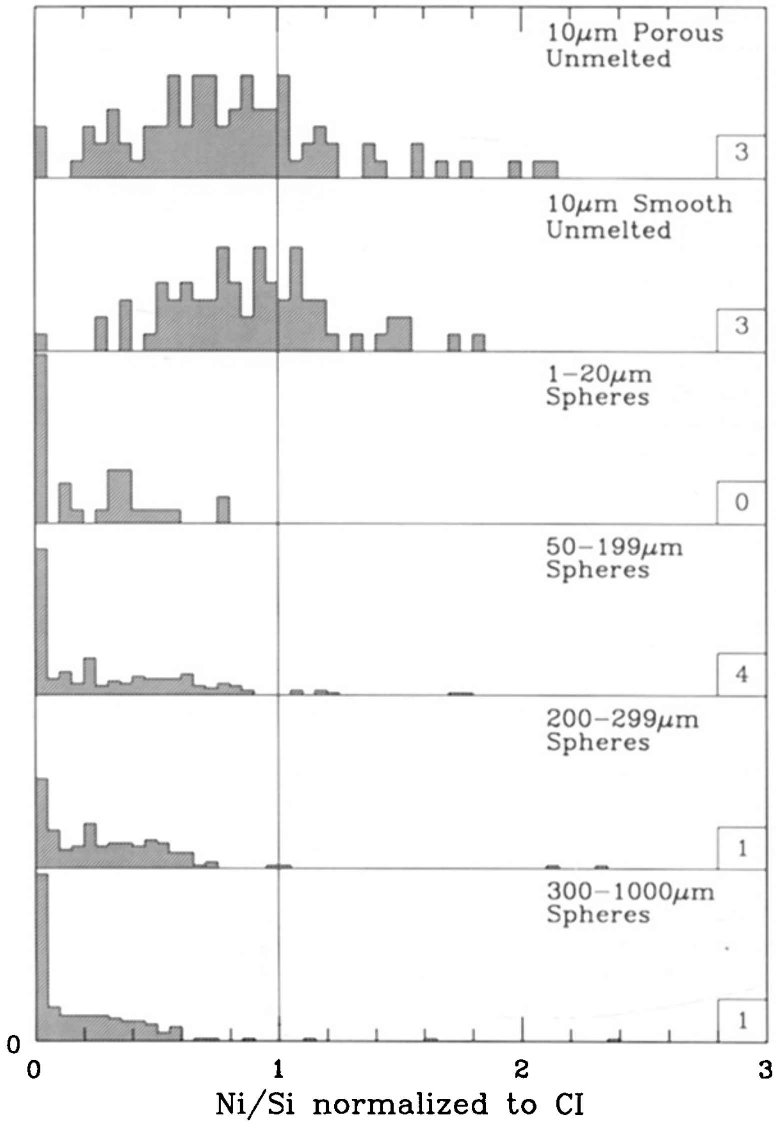

FIG. 12. Ratio distributions of Ni/Si (atom) (normalized to CI) for stony cosmic spherules grouped by size and for the two major classes of chondritic stratospheric micrometeorites, "smooth" and "porous." The number inside of the box indicates the number of spheres that plot outside of range.

viously noted for unetched deep-sea spheres by Blanchard *et al.* (1980) for the Antarctica spheres by Koeberl and Hagen (1989) and the unmelted 10 μm CS class of micrometeorites (Schramm *et al.*, 1989). However, the data in Fig. 15 also show that there is an asymmetry in the dispersion about the CI Ca/Al ratio. Nearly 10% of the spheres have depleted Ca but have Al in the normal range. There are only two spheres with low Al and uncorrelated Ca depletion. This effect is likely related to parent body processing. As seen in Fig. 4, the matrix of CI and CM chondrites is highly depleted in Ca (McSween and Richardson, 1977). CI chondrites contain veins of Ca and Mg sulfates and carbonates formed during aqueous alteration (leaching and redeposition) in the CI parent bodies (Richardson, 1978; Kerridge and Bunch, 1979). The vein material may contain 10–25% of the total Mg, and virtually all of the Ca is in carbonates (Kerridge, 1976). Kerridge reports Mg abundances in Orgueil phyllosilicates (matrix) compared to Orgueil bulk of 0.8, abundances in Mn of 0.6, and abundances in Ca of 0.08. The veins and matrix separations have scales of ~100 μm. We see depletions and enrichments of Ca in the spherules to be of the right order of magnitude to be explained by inhomogeneous sampling of veined and unveined matrix material. The wide dispersion seems to diminish with increasing size (Fig. 6), which indicates that the scale of the sampling is becoming larger than the heterogeneity. This effect has also been described by Engrand *et al.* (1995). The Ca effects are also seen in the stratospheric IDPs where there is a definite difference between the "porous" and "smooth" subtypes (Fig. 8).

Nonchondritic Particles–Most cosmic spheres have approximately chondritic proportions for nonvolatile and nonsiderophile elements, and their most probable origin is by melting of a fine-grained polymineralic precursor material whose cumulative composition was chondritic. This composition is the natural result of random mixture of large numbers of primitive grains whose sizes are much smaller that the aggregate whole. However, some spheres significantly deviate from chondritic composition and could not have been derived simply from random mixtures of fine-grained material with undifferentiated bulk elemental composition. On the basis of the abundances of the analyzed spheres, we identify the following nonchondritic groups.

High-Fe, Low-Mn Particles–As shown in Fig. 16, there is a substantial number of particles with very high Fe contents. These Fe-rich particles that are composed of glass and magnetite are the G petrographic class discussed previously, and they occur in all size ranges and sources of collection. The Fe-Mg-Si ternary diagrams (Fig. 16) show that the Fe-rich particles lie on a mixing line between chondritic composition (the main cluster) and Fe, which suggests that the spheres could be simply an oxidized mixture of chondritic composition material with either a metal or sulfide. Clearly, this is not the case, however, as is illustrated in Fig. 17. The high-Fe particles have very low-Mn/Si ratios, which indicates that the silicate component does not have a chondritic composition. As a note of caution on the Mn data, most of the Mn measurements for the highest Fe/Si points are near or below probe detection limits. We rule out vaporization of Mn because of the lack of any evidence of Mn/Si fractionation in Fig. 9. Figure 16 illustrates that the particles lie on a line with Fe and enstatite end members and that subtracting Fe, the spheres have an enstatite normative composition. We believe that the most likely precursor of the G spheres is a mixture of enstatite and either metal or sulfide. It is significant that there is no evidence for the existence for Fe-rich spheres on the forsterite-Fe tie line, and apparently the high-Fe component is exclusively associated with Fe-poor pyroxene. Bates (1986) has studied the minor element composition of G spheres and finds that the particles are most similar to the metal silicate fractions of enstatite chondrites (or achondrites), although Ca abundances and other considerations show there is not an exact "match." Enstatite in E chondrites does have the very low-Mn/Si ratios seen in the G particles because Mn in these highly reduced objects is concentrated in sulfides. If it is possible to really match the G type with a particular chondrite class, it will probably have to be done with other data such as trace-element composition

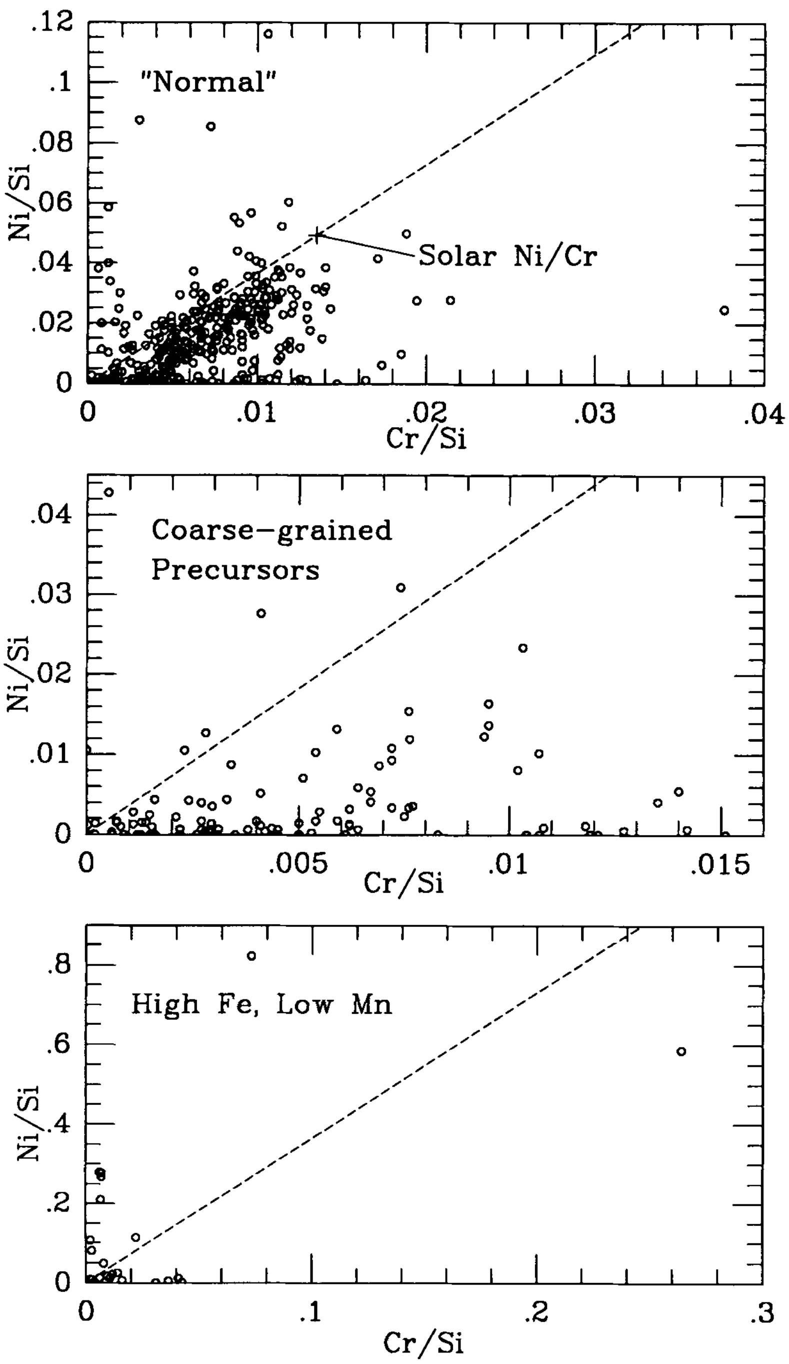

FIG. 13. Nickel *vs.* chromium (atom), normalized to Si, for the three compositional classes of stony spheres: "normal" chondritic, those with coarse-grained precursors, and those with high Fe and low Mn relative to solar composition. The solar Ni/Cr ratio is shown by the dashed line. Note the different ranges for each group.

or O isotopes. The G spheres are a very interesting class of spherule that appear to have a very different origin than the typical S spherules. It could be that they are samples from a distinct enstatite-metal-rich asteroid type or they could be nebular products that exist as millimeter sized components in finer-grained matrix material and could be the source of the more common sphere types.

The Coarse-grained Precursor Particles–The Fe/Si *vs.* Mn/Si diagram (Fig. 17) shows the presence of a nonchondritic group of particles above the main group of chondritic ones. We have called these coarse-grained precursors only because rare unmelted stratospheric IDPs with similar compositions are coarse-grained particles whose elemental compositions are dominated by one or two minerals. The precursors of the nonchondritic spherules could in fact be fine-grained, but their composition still would have to be constrained by a very limited number of phases. We define the coarse-grained precursor group by particles that fall into the circles scribed in Fig. 17. This definition is crude and somewhat arbitrary, but it does inscribe a population that is distinct from the "normal" group in the Fe-Mn distribution. The particles in the coarse-grained precursor region have higher than average Mn/Fe ratios; they also tend to have lower than chondritic Al/Si and Ca/Si abundances. Figure 13 shows that they have systematically lower Ni/Cr ratios than normal spherules, which suggests that the precursor is silicate dominated without associated metal or sulfide. In Fig. 16b and c, it is seen that this subgroup is responsible for an appreciable amount of the scatter from the core of nearly constant Mg/Si ratios for the entire set of spherules with moderate Fe contents. Removal of the coarse-grained precursor particles from the Al/Si distribution removes the asymmetry from the main peak seen for "all spheres" producing the "normal" group, which in fact has a nearly gaussian Al/Si distribution (Fig. 18). The Mg/Si median of this high-Mn group is consistent with CI/CM chondrites, but the dispersion of the distribution is larger as seen in Fig. 16b.

Olivine (Low Al)–Examination of the Al/Si histograms in Figs. 7 and 18 shows that the distribution is bimodal (at least), with the second peak of ratios <25% of bulk CI. The low-Al particles could not have started with an appreciable amount of chondritic composition material in them. Chondritic material would bring with it an Al/Si ratio of ~0.09; a mixture of this material with Al/Si <0.01 would indicate that no more than ~10% chondritic material was present in the low-Al spheres. The low-Al particles were evidently dominated by a single phase or phases that contained very low Al. Identification of the mineral in question is rather easy. The Mg-Fe-Si ternary diagrams show compositions for all 500 spherules in Fig. 16c compared with those with Al/Si ratios <0.03 in Fig. 16a. The majority of the low-Al particles have olivine normative compositions scattering around the fayalite-forsterite line. The low-Al characteristic of these particles is due to the inability of olivine to incorporate Al into its structure. The half dozen particles that are distinctly above the olivine line could be mixtures of olivine and either pyroxene or a low-Al glass.

Two-thirds of the low-Al particles are also included in the coarse-grained precursor group defined by the Fe-Mn plot in Fig. 7 and shown in Fig. 16b. In this sense, the low-Al group is mainly a subset of the coarse-grained precursor. There is a hint of a positive correlation between the Fe and Mn for the olivine particles, which is qualitatively consistent with the observations of Steele *et al.* (1985) of the MnO-FeO systematics in relict olivine grains in some deep-sea spherules. Cosmic spherules exist in which large mineral grains have survived entry without completely melting, and a substantial fraction of these relict mineral grains are forsteritic oli-

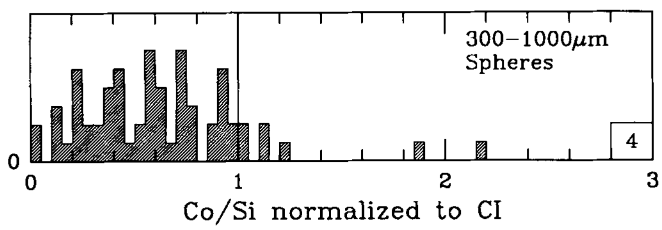

FIG. 14. Ratio distributions of Co/Si (atom) (normalized to CI) for stony cosmic spherules. Cobalt was measured in 67 spheres that were all >350 μm in size. The number inside of the box indicates the number of spheres that plot outside of range.

vine. The grains are usually surrounded by melted material of nominal S spherule composition. It is not hard to extrapolate from this situation to one where the relict grain has melted—a situation that would produce a particle with the signature of an olivine plus a small admixture of chondritic material. The two peaks of the Al/Si histogram are well separated, with the "olivines" near detection limits and the "solar" composition material near 0.09. There appears to be little mixing of the two components.

ORIGIN

Quench textures and incorporation of terrestrial O (Clayton *et al.*, 1986) imply that the majority of spheres are rapidly cooled droplets of meteoroids that melted during atmospheric entry. It has been suggested that some spheres can obtain their spheroidal shapes in space (Parkin *et al.*, 1983), although an example of this has yet to be found. Atmospheric entry calculations (Love and Brownlee 1991), the mass distribution of interplanetary material (Kyte and Wasson, 1986), and the high ratio of cosmogenic $^{26}Al/^{10}Be$ (Raisbeck *et al.*, 1985; Nishiizumi *et al.*, 1991) all suggest that typical cosmic spherules are samples of meteoroids intermediate in size between conventional meteorites and micrometeorites. Typical spherules are melt droplets of meteoroids on the order of a factor of two larger than the collected spherule. Some spherules must be ablation spray from larger meteorite producing bodies, but these should be very rare because of the relatively small cumulative mass of centimeter sized and larger objects entering the atmosphere and because droplets released from larger bodies are systematically more strongly heated than those that enter as initially small particles. Debris from larger bodies is released deeper in the atmosphere where the higher air density leads to proportionately greater heating and vaporization.

The spherules are a sampling of small Earth-crossing meteoroids that in turn are samples of asteroids and comets, the major particulate-generating bodies in the solar system. There are strong selection effects that influence both the successful transportation from asteroidal and cometary parent bodies and survival of atmospheric entry. In general, these selection effects are considerably different than those involved in producing conventional meteorites. Poynting-Robertson (PR) drag is a process that causes all particles external to 1 AU to evolve towards Earth-crossing orbits. This nongravitational effect permits a much larger population of asteroids and comets to

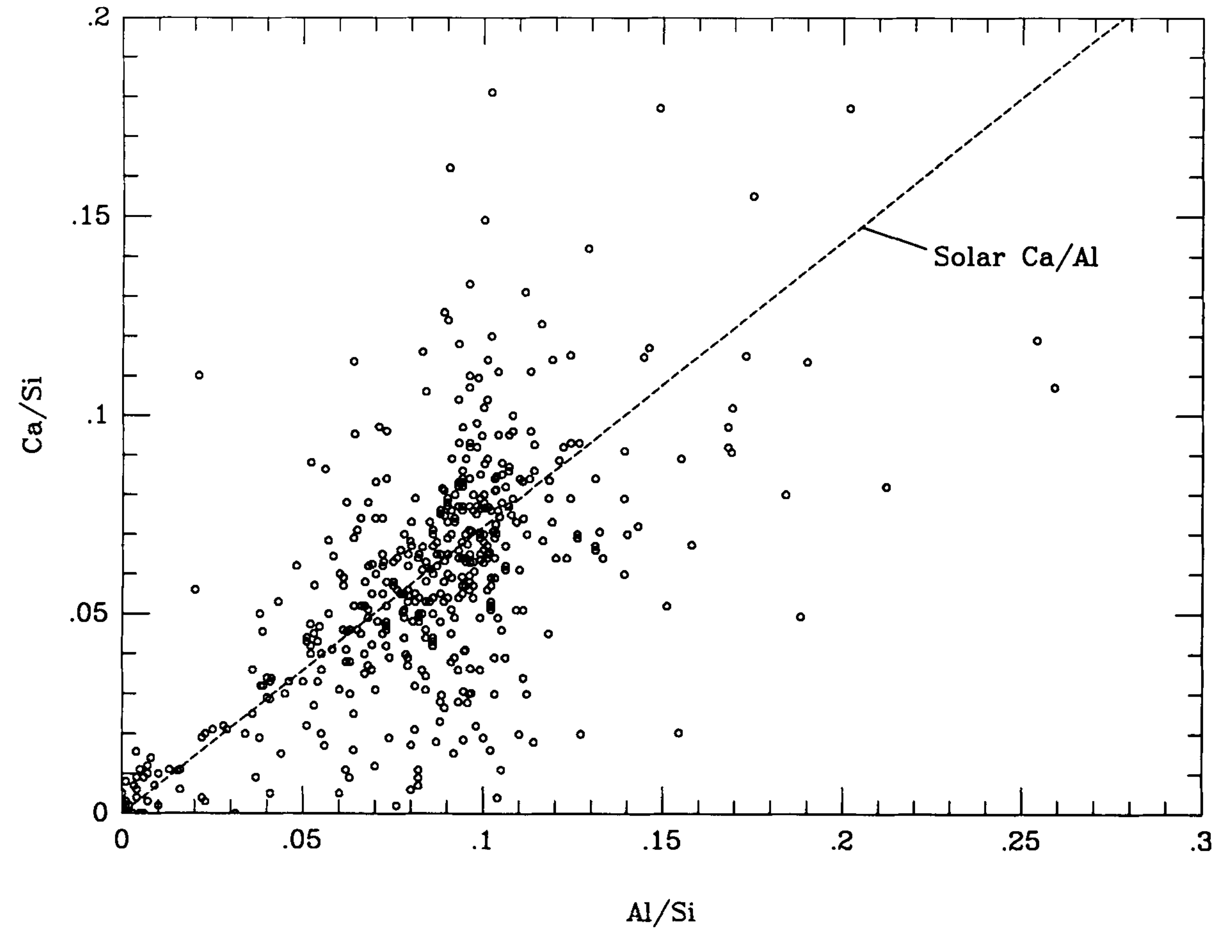

FIG. 15. Calcium *vs.* aluminum (atom), normalized to Si, for stony cosmic spherules. The solar Ca/Al ratio is shown for comparison.

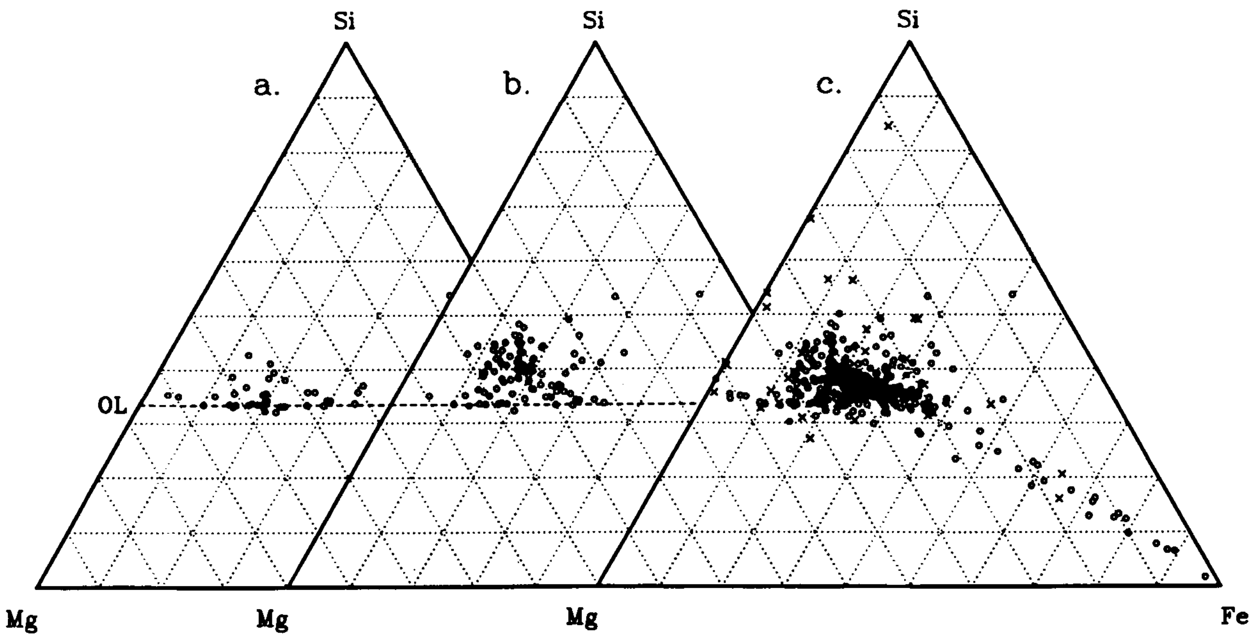

FIG. 16. Magnesium-silicon-iron atom ratios for (a) spheres with atomic Al/Si < 0.03, (b) spheres that have coarse-grained precursors, and (c) all stony cosmic spherules. Spheres <20 μm in size are indicated by Xs.

produce Earth-crossing dust than the conventional meteorites. The PR spiral time from the asteroid belt to 1 AU is ~100,000 and 10^6 years, respectively, for 100 μm and 1 mm particles (Grun *et al.*, 1985). During such transport, however, particles are exposed to collisions and estimated destruction lifetimes are shorter than PR lifetimes for particles >200 μm (Grun *et al.*, 1985). Collisional destruction is most important for large asteroidal dust particles that must survive a long period of orbital decay before reaching Earth. The $>10^6$ year cosmic-ray exposures of cosmic spherules (Nishiizumi *et al.*, 1991) is consistent with exposure times that exceed predicted collisional lifetimes. It is probable that many of the spherule precursors experienced several communition episodes during transit to the inner solar system.

One might expect that the majority of cosmic spherules would have cometary origins except that atmospheric entry provides a filter that very strongly discriminates against particles with high entry velocities and elliptical comet-like orbits. Spherules >100 μm that survive without extreme volatilization are rare ones that entered with a velocity close to the escape velocity and at a low incidence angle. At 14 km/s^{-1} entry velocity and 45° entry angle, vaporization is >90% for 300 μm particles; and for the 20 km/s^{-1} or higher entry velocity for cometary orbits, vaporization is much higher (Love and Brownlee, 1991). This degree of mass loss (Yada *et al.*, 1996) is consistent with isotopic fractionation seen in type-I cosmic spherules (Nyquist *et al.*, 1995). Entry calculations indicate that nearly all spherules >70 μm are asteroidal due to the strong velocity dependence of vaporization. This prediction could be incorrect if there is a significant source of low-eccentricity, low-inclination comet dust (Liou and Zook, 1996; Flynn, 1996a) or if only negligible numbers of particles survive PR transport from the asteroid belt.

A process associated with atmospheric entry that probably does not appreciably effect the population of surviving spherules is fragmentation. Fragmentation does provide a very strong filter for survival of particles >1 cm. This prevents friable objects, such as typical cometary materials (Verniani, 1969), from surviving atmospheric entry to become conventional meteorites. For millimeter sized and smaller bodies that produce the bulk of the spherules, fragmentation does not provide a selection effect because all but the weakest materials melt to form spherules before they fragment. The ram pressure on a nonablating millimeter sized meteoroid that is frictionally heated to a uniform internal temperature of T, is given by:

$$P_{ram} = \frac{8\pi\sigma T^4}{V}$$

The instantaneous velocity is V and σ is the Stefan-Boltzman constant. A melting point of 1500 K and minimum entry velocity implies a maximum ram pressure of only 6×10^3 dyn/cm^{-2} before a particle melts. Faster particles melt at even lower ram pressure. This "melting pressure" is lower than the typical crushing strength of cometary meteors (Verniani, 1969), so we do not believe that strength provides a selection effect favoring any particular particle type. The primary reason why small particles melt before they fragment is that their interiors are uniformly heated to melting. Larger particles support strong internal temperature gradients and retain solid, crushable interiors when the exterior is molten.

A further effect that enhances the asteroidal contribution is gravitational focusing of particles approaching Earth on low-inclination, low-eccentricity orbits (Flynn, 1988). These arguments suggest that nearly all of the >100 μm spherules in this study are asteroidal. Because transport times and entry velocities are similar and because strength selection (during entry) is not a factor, it appears that the spherules should be a representative sample of large dust particles liberated by collisions in the asteroid belt. Near-Earth asteroids probably are not important contributors because their cumulative surface area is small. There should be some preference for survival of particles generated in the inner regions of the belt, due to shorter PR spiral times, and for particles with properties that enhance PR drag and collisional survival. The 500 analyzed spherules must be samples of an appreciable number of parent asteroids; but it is not known, however, how representative they are of the overall asteroid population. It is possible that the analyzed samples were derived from 500 different asteroids distributed over the asteroid belt. At

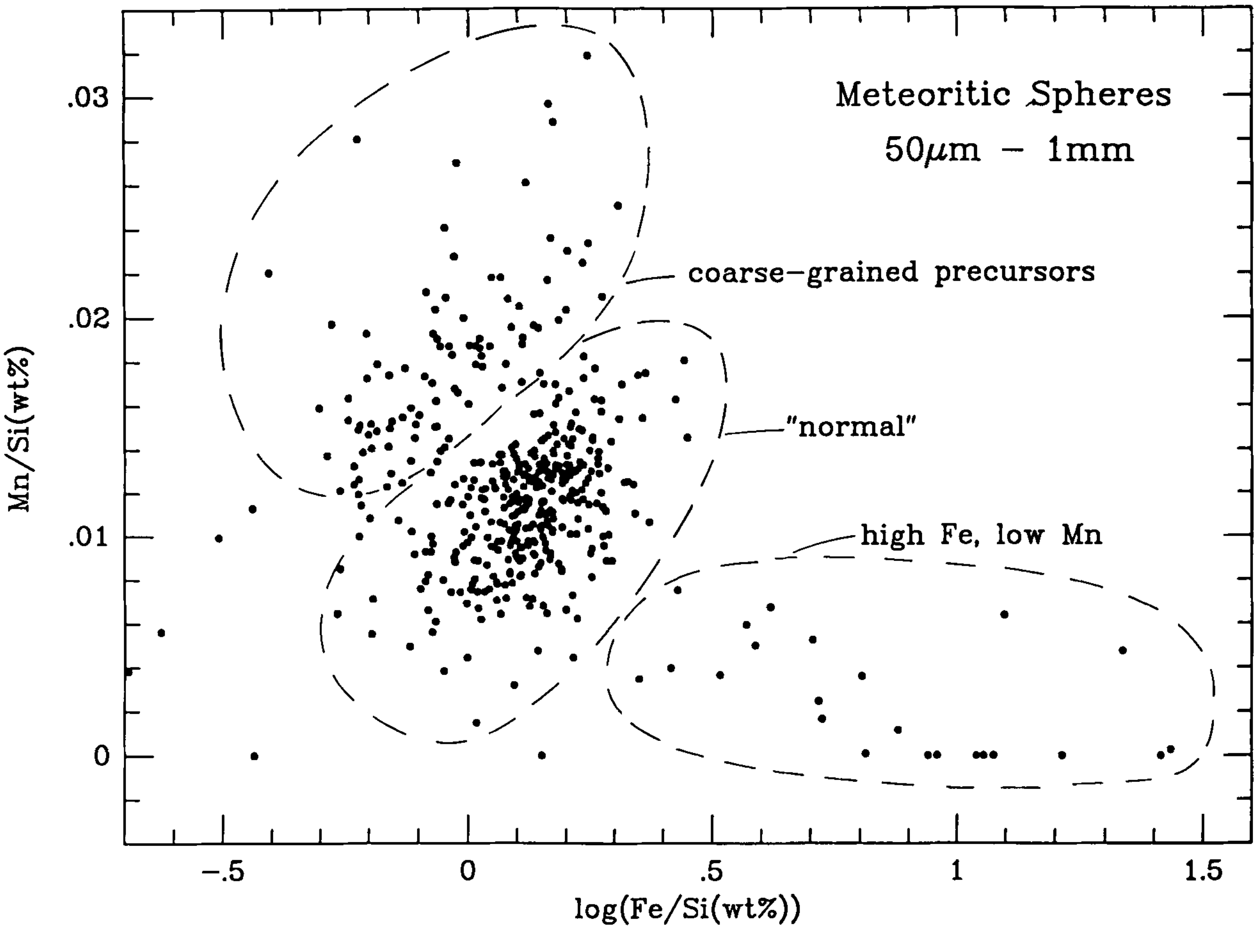

FIG. 17. Manganese *vs.* iron normalized to Si (wt%) plot showing the three compositional groupings of cosmic spherules: the "normal" chondritic spheres, spheres with coarse-grained precursors, and high-Fe, low-Mn spheres (G type).

the other extreme, it is possible that just a few sources could dominate the sample. For example, Dermott *et al.* (1996) have suggested that >50% of the small particles impacting the Earth could be derived from the Themis and Koronis asteroid families. Dust from these two sources is clearly seen in the IRAS dust bands. Although they do not dominate the interplanetary population, their importance at Earth is amplified by strong gravitational concentration. If major collisions are important producers of the millimeter sized meteoroid population, then it is likely that their contributions will vary with time. This could, in principle, be studied by analysis of spherules from deep-sea cores or ancient sediment deposits.

Relationship to Chondrites and Asteroid Types

Type-S asteroids dominate the main belt asteroid interior to 2.5 AU, and C types are the most common beyond this distance. The spheres should contain representative compositional data for both types. Unfortunately, the relative contribution from C- and S-type asteroids is not well known. It is likely that S-type asteroids are a significant source (>20%) of spherule-producing particles, and it is possible that they constitute as much as 50%. These rough estimates are appropriate whether the spherules are derived from 500 parent bodies or whether an appreciable fraction of them came from the Koronis (S-type) and Themis (C-type) families (Flynn, 1996b).

There has been considerable debate about the nature of S asteroids and their relationship to chondrites. On one side, it has been suggested that the S asteroids are ordinary chondrites (OC) whose spectral reflectance differs from OCs due to the effects of "space weathering" (Chapman, 1996). An alternate suggestion is that the S asteroids are differentiated objects that melted by processes that preferentially effected asteroids in the inner portion of the belt dominated by S asteroids (Bell *et al.*, 1991). The spherule data do not appear to support either of these propositions. The spherule data are consistent with the bulk of millimeter sized asteroidal meteoroids being derived from a material with a CM-like elemental composition at the millimeter size scale. The peaks of the distributions in Fig. 4 differ from OC composition, although it is difficult to securely estimate or place an upper limit on the OC contribution. The peaks and shapes of the Mg, Al, Ca, and Ti histograms in Fig. 4 appear to be inconsistent with a OC contribution >25%, and it is possible that the OC contribution is much less. In a study of unmelted mineral grains in 427 Antarctic micrometeorites, in the 100 μm to 400 μm size range, Walter *et al.* (1995) found that only 1% of the particles were mineralogically related to ordinary chondrites. Bulk analysis of thousands of type-S deep-sea cosmic spherules yielded a mean O-isotopic composition consistent with CM chondrites and not OCs (Clayton *et al.*, 1986). An association with differentiated meteorites is also not apparent. The nearly chondritic composition of typical spheres is inconsistent with derivation from differentiated objects. It is possible, however, that some or even many of the coarse-grained precursor and olivine particles could have come from differentiated bodies. Approximately 15% of the spherules fall into this group. About 5% of the particles belong to the high-Fe, low-Mn group.

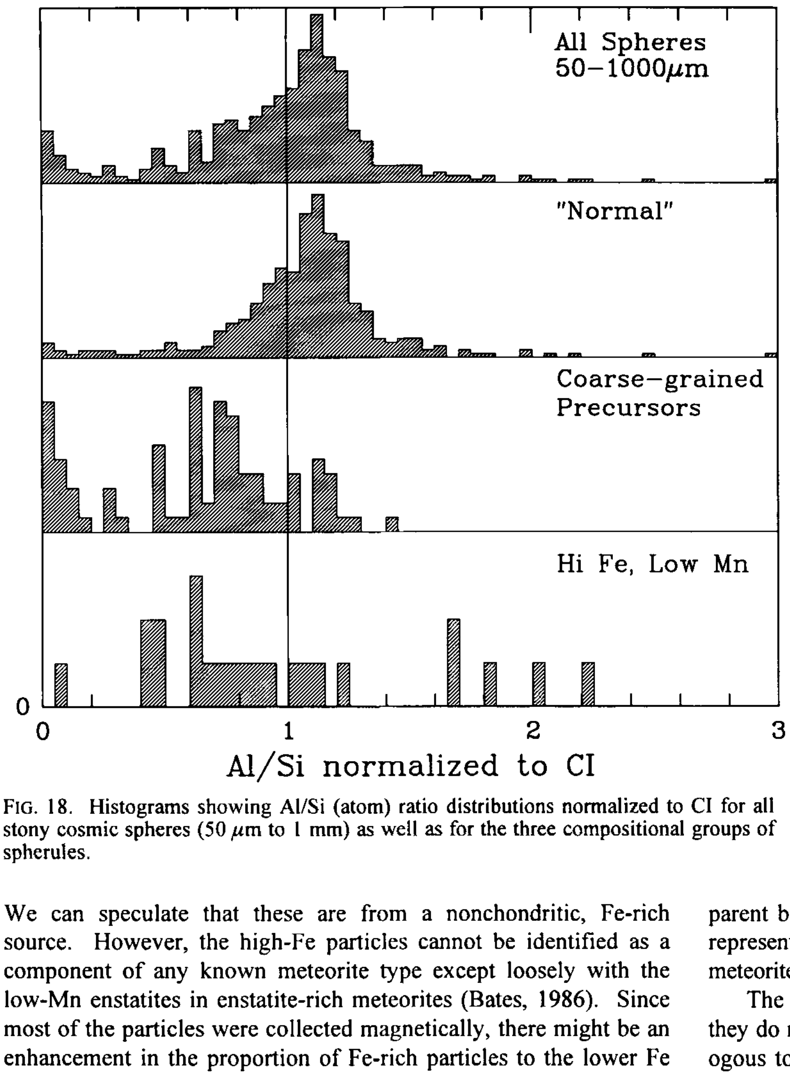

FIG. 18. Histograms showing Al/Si (atom) ratio distributions normalized to CI for all stony cosmic spheres (50 μm to 1 mm) as well as for the three compositional groups of spherules.

We can speculate that these are from a nonchondritic, Fe-rich source. However, the high-Fe particles cannot be identified as a component of any known meteorite type except loosely with the low-Mn enstatites in enstatite-rich meteorites (Bates, 1986). Since most of the particles were collected magnetically, there might be an enhancement in the proportion of Fe-rich particles to the lower Fe (chondritic) particles. If so, we can at least say that their contribution is not >5%. Future work involving O isotopes or cosmic-ray exposure ages may yield a more quantitative link between the nonchondritic spherules and their parents.

The composition of the spherules is also inconsistent with the possibility that a significant fraction of them could have been produced by atmospheric melting of chondrules. The chondrule/matrix ratio is very high in many unequilibrated ordinary chondrites and it is possible that a population of weakly bound unequilibrated ordinary chondrites could collisionally fragment in space to form a population of millimeter sized meteoroids dominated by "naked chondrules." Chondrules are, however, strongly depleted in Fe (Scott *et al.*, 1982) and typically plot below the Fe/Si peak in Fig. 4 and to the left of the main cluster of spherules in the Fe-Mg-Si ternary diagrams in Fig. 16.

The peaks in the element distributions of Fig. 4 show a best correlation with CM chondrite bulk composition, and it is clear that the most common parental materials of stony cosmic spherules are compositionally related to carbonaceous chondrites. Because C-type asteroids are the dominant reflectance class in the asteroid belt, we assume that this material is representative of the C-type asteroids. The peaks of the "undepleted" elements show systematic offsets from CI and very large offsets from CI matrix. For all of these elements, there is a better match with CM. The "match" with CM is better but because the most definitive volatile elements are lost during atmospheric entry, it is not clear that the implied CI-VS-CM distinction is fully significant. It is, however, very clear that the data are very incompatible with actual CI chondrites *vs.* material with CI-like elemental composition. The bulk of the fine-grained matrix in CIs is highly depleted in Ca, due to redistribution by internal parent body processes (McSween and Richardson, 1977). The strong Ca depletion is not seen in the spherule data. It is possible that there could be CI-like objects in the solar system that have not experienced the parent body processing seen in existing CI specimens and would not show this internal redistribution. Oxygen isotope data for the spherules are inconsistent with CI prevalence but are consistent with origin from CMs (Clayton *et al.*, 1986). The dominance of CM-like material as inclusions in HED meteorites (Zolensky *et al.*, 1996) is further evidence that CM-like material is common in the asteroid belt. The implication of CM-like does necessarily indicate that the spherule parents and probably most C asteroids are directly related to CM chondrites. While particles mineralogically identical to CM chondrites have been positively identified among 10 μm extraterrestrial particles collected in the stratosphere, they are very rare (Bradley and Brownlee, 1991). Both CM and CI chondrites have been extensively modified by aqueous alteration, and it is entirely possible that the asteroid belt could contain materials with CI and CM elemental composition but with different mineralogical composition. An interesting possibility is that CI and CM chondrites unaltered by parent body aqueous alteration might be highly friable and underrepresented or even unrepresented as centimeter sized and larger meteorites.

The abundance histograms of Fig. 4 are also significant in that they do not show clear quantization of meteoroid compositions, analogous to specific Al/Si ratios that would be seen for analysis or a random collection of chondritic meteorites. If bulk compositions of all recovered meteorites were plotted in this way, they would show separate peaks corresponding to Al/Si ratios for H, CM, E, and CV chondrite groups. The lack of well-defined subpeaks is either due to the limited range of sources that dominate the spheres, blurred composition distinctions due to the small sample masses analyzed or, most interestingly, that the parental elemental compositions are not quantized like chondrites but show a broad continuum range.

Cosmic Abundances

The analyzed sample of 500 individual particles is potentially a wide sampling of asteroidal materials, and the abundances should be given some consideration as providers of information on cosmic abundances. Of the elements analyzed, only Mg, Si, Al, Mn, and Ti appear to have been unaltered during atmospheric entry or by parent body processes. The peaks of these element distributions shown in Fig. 4 are indicative of the bulk composition of the sources of cosmic spherules, and they may coincide with solar composition. It is arguable whether peak or average values are the most appropriate to use for comparison purposes. We assume that the peaks in Fig. 4 represent average compositions of millimeter volumes of fine-grained primitive material from the spherule progenitors. The peaks of the selected element set normalized to Si show systematic small offsets from CI, but the most conspicuous is for Mn. The Mn abundance is a good match with CM but considerably lower than CI. If the spherules have sampled hundreds of primitive asteroids, then it is possible that this well-formed peak is a reasonable approximation of the solar ratio. The Mn/Si abundance of CI chondrites is unusual because it is higher than all other chondrites. The matrix point count data of McSween and Richardson (1977) suggest, however, that Mn in CI chondrites has been disturbed by aqueous alteration. The matrix values of Mn/Si average 47% lower than bulk. Like Na, Ca, and S, it is evident that Mn was mobilized inside CI parent bodies, and it is not clear that the bulk Mn/Si values from the few CI meteorites that have been analyzed truly represent the best determination of the solar Mn/Si. We cannot prove that Mn has not been depleted relative to Si during the spherule formation process or during terrestrial storage. However, the well formed peak and the lack of systematic effects with spherule size suggest that Mn is well preserved in stony spherules. We suggest that future data from meteorites as well as comet and asteroid missions be examined with the possibility that CI Mn abundances overestimate solar composition.

SUMMARY

Relative to chondritic proportions, nearly all of the spherules are depleted in siderophiles and volatiles. This depletion appears to have occurred during atmospheric entry. With the exception of volatiles and siderophiles, the average composition of the suite of stony cosmic spherules is most similar to CM meteorites based on the ratios of Mg/Si, Al/Si, Ca/Si, Ti/Si, Mn/Si, and Fe/Si. Three subgroups of stony cosmic spherules are recognized. The largest group is similar in composition to CM chondrites. These particles must have been derived from fine-grained parents and it is likely that this data are indicative of the bulk elemental composition of C-type asteroids. The second group consists of particles with higher than average Mn/Si ratios and lower than average Al/Si and Ca/Si values. This group is interpreted to have had coarse-grained precursors and contains the majority of the particles that had olivine precursors. The third group is distinguished by high-Fe content and low-Mn/Si ratios. The silicate portions of these particles have lower than chondritic Mg/Si, Al/Si, Ca/Si, and Mn/Si ratios, thus precluding a simple chondritic plus Fe mixing model. The best matches for the silicate portions are with the silicates from pyroxene-rich meteorites. The second and third groups are derived from coarser-grained or mineralogically simple parental materials. They may be related to S-type asteroids, or it is possible that many are just large mineral grains or inclusions broken out of fine-grained matrix materials. The compositional data are not consistent with the possibility that a significant fraction of millimeter sized spherules reaching the Earth are chondrules.

Although the spherules are strongly modified during atmospheric entry, they retain important information. Terrestrial weathering is a factor, but modified portions are easily distinguished from unweathered material. The work here shows that cosmic spherules can provide valuable information on asteroids that compliments information from meteorites. The spherule data are important because they provide a less biased sampling of main-belt asteroids. The distribution of meteoroid types implied by the spherules is very different from meteorite falls that are dominated by ordinary chondrites. This work suggests that millimeter to centimeter sized meteorites should be collected and investigated to see if there is a transition of meteoroid types between conventional meteorites and submillimeter cosmic spherules and IDPs. The spherules used in this work were limited both in the time interval at which they fell and by their magnetic properties. Future spherule studies might search for temporal variations in the meteoroid complex and better define the meteoroid subgroups. It is likely that the subgroups and their relation to asteroids and meteorites could be better defined using isotopic signatures, cosmic-ray exposure ages or trace-element composition. To fully utilize spherules as a least-biased sample of Earth-crossing meteoroids, it is also important to use particles collected in a totally nonselective manner, such as is done in the South Pole water well (Taylor *et al.*, 1996).

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REFERENCES

AHRENS L. H., VON MICHAELIS H., ERLANK A. J. AND WILLIS J. P. (1969) Fractionation of some abundant lithophile element ratios in chondrites. In *Meteorite Research* (ed. P. M. Millman), pp. 166–173. Springer-Verlag, New York, New York.

ANDERS E. AND GREVESSE N. (1989) Abundances of the elements: Meteoritic and solar. *Geochim. Cosmochim. Acta* **53**, 197–214.

ARMSTRONG J. T. A. AND BUSECK P. R. (1975) Quantitative chemical analysis of individual microparticles using the electron microprobe. *Anal. Chem.* **47**, 2178–2192.

ARNDT P., BOHSUNG J., MAETZ M. AND JESSBERGER E. K. (1996) The elemental abundances in interplanetary dust particles. *Meteorit. Planet. Sci.* **31**, 817–834.

BATES B. A. (1986) The elemental composition of stony extraterrestrial particles from the ocean floor. Ph.D. thesis. University of Washington. 199 pp.

BATES B. A. AND BROWNLEE D. E. (1984) The elemental composition of extraterrestrial stony deep sea spheres (abstract). *Lunar Planet. Sci.* **15**, 40.

BELL J. F., DAVIS D. R., HARTMANN W. K. AND GAFFEY M. J. (1991) Asteroids–The big picture. In *Asteroids II* (eds. R. Binzel, T. Gehrels and M. S. Mathews), pp. 921–945. Univ. Arizona Press, Tucson, Arizona.

BLANCHARD M. B., BROWNLEE D. E., BUNCH T. E., HODGE P. E. AND KYTE F. T. (1980) Meteoroid ablation spheres from deep sea sediments. *Earth Planet. Sci. Lett.* **46**, 178–190.

BONTE P., JEHANNO C., MAURETTE M. AND BROWNLEE D. (1987) Platinum metals and microstructure in magnetic deep sea cosmic spherules. *Lunar Planet. Sci. Conf.* **17th**, *J. Geophys. Res.* **92**, 641–648.

BRADLEY J. P. AND BROWNLEE D. E. (1991) An interplanetary dust particle linked directly to type CM meteorites and an asteroidal origin. *Science* **251**, 549–552.

BROWNLEE D. E. (1981) Extraterrestrial component in deep sea sediments. In *The Sea* (ed. C. Emiliani), pp. 733–762. J. Wiley, New York, New York.

BROWNLEE D. E., TOMANDL D. A. AND OLSZEWSKI E. O. (1977) Interplanetary dust: A new source of extraterrestrial material for laboratory studies. *Proc. Lunar Planet. Sci. Conf.* **7th**, 149–160.

BROWNLEE D. E., PILACHOWSKI L. B. AND HODGE P. W. (1979) Meteorite mining from the ocean floor (abstract). *Lunar Planet. Sci.* **10**, 157.

BROWNLEE D. E., OLSZEWSKI E. O. AND WHEELOCK M. M. (1982) A working taxonomy for micrometeorites (abstract). *Lunar Planet. Sci.* **12**, 71.

BROWNLEE D. E., BATES B.A. AND BEAUCHAMP R. H. (1983) Meteor Ablation Spherules as Chondrule Analogs. In *Chondrules and Their Origins* (ed. E. A. King), pp. 10–25. Lunar and Planetary Institute, Houston, Texas.

BROWNLEE D. E., BATES B. A. AND WHEELOCK M. M. (1984) Extraterrestrial platinum group nuggest in deep sea sediments. *Nature* **309**, 693–695.

CHAPMAN C. R. (1996) S-type asteroids, ordinary chondrites, and space weathering: The evidence from Galileo's fly-bys of Gaspra and Ida. *Meteorit. Planet. Sci.* **31**, 699–725.

CLAYTON R. N., MAYEDA T. K. AND BROWNLEE D. E. (1986) Oxygen isotopes in deep sea spherules. *Earth Planet. Sci. Lett.* **79**, 235–240.

CZAJKOWSKI J. (1987) Cosmo and geochemistry of the Jurrasic hardgrounds. Ph.D. thesis. Univ. California San Diego. 418 pp.

DERMOTT S. F., GROGAN K., GUSTAFSON B. A. S., JAYARAMAN S., KORTENKAMP S. J. AND XU Y. L. (1996) Sources of interplanetary dust. In *Physics, Chemistry and Dyamaics of Interplanetary Dust, ASP Conf. Series 104* (eds. B. A. S. Gustafson and M. S. Hanner), pp. 143–153. Astron. Soc. of the Pacific, San Francisco, California.

EKAMBARAM V., GROSSMAN L. AND KING E.A. (1984) Chemical studies of volatilization residues of chondrules (abstract). *Lunar Planet. Sci.* **15**, 240.

ENGRAND C., MAURETTE M., KURAT G. AND WALTER J. (1995) Electron microprobe analyses of Antarctic micrometeorites and interplanetary dust particles collected in the stratosphere (abstract). *Lunar Planet. Sci.* **26**, 375–376.

ESAT T. M., BROWNLEE D. E., PAPANASTASSIOU D. A. AND WASSERBURG G. J. (1979) Magnesium isotopic composition of interplanetary dust particles. *Science* **206**, 190–197.

FLYNN G. J. (1988) The near-earth enhancement of asteroidal over cometary dust. *Proc. Lunar Planet. Sci. Conf.* **20**, 363–371.

FLYNN G. J. (1988) Atmospheric entry heating of micrometeorites. *Proc. Lunar Planet. Sci. Conf.* **19**, 673–682.

FLYNN G. J. (1996a) Sources of 10 micron interplanetary dust: The contribution from the Kuiper belt. In *Physics, Chemistry and Dynamics of Interplanetary Dust, ASP Conf. Series 104* (eds. B. A. S. Gustafson and M. S. Hanner), pp. 171–175.

FLYNN G. J. (1996b) Are the S-type asteroids the parent bodies of ordinary chondrite meteorites?: Evidence from the interplanetary dust recovered from the Earth's stratosphere (abstract). *Lunar Planet. Sci.* **27**, 365.

GANAPATHY R., BROWNLEE D. E. AND HODGE P. W. (1978) Silicate spherules from deep sea sediments: Confirmation of extraterrestrial origin. *Science* **201**, 1119–1121.

GROSSMAN L. (1972) Condensation in the primitive solar nebula. *Geochim. Cosmochim. Acta* **36**, 597–619.

GRUN E., ZOOK H. A., FECHTIG H. AND GIESE R. H. (1985) Collisional balance of the meteoritic complex. *Icarus* **62**, 244–272.

HASHIMOTO A. (1983) Evaporation metamorphism in the early solar nebula-evaporation experiments on the melt FeO-MgO-SiO_2-CaO-Al_2O_3 and chemical frationations of primitive material. *Geochim. J.* **17**, 111–145.

HASHIMOTO A., KUMAZAWA M. AND ONUMA N. (1979) Evaporative metamorphism of primitive dust material in the early solar nebula. *Earth Planet. Sci. Lett.* **43**, 13–21.

HODGE P. W. (1981) *Interplanetary Dust.* Gordon and Breech, New York, New York. 280 pp.

JEHANNO C., BOCLET D., BONTE PH., CASTELLARIN A. AND ROCCHIA R. (1988) Identification of two populations of extraterrestrial particles in a jurasic hardground of the southern Alps. *Proc. Lunar Planet. Sci. Conf.* **18**, 623–630.

JESSBERGER E. K., BOHSUNG J., CHAKAVEH S. AND TRAXEL U. G. (1992) The volatile element enrichment of chondritic interplanetary dust. *Earth Planet. Sci. Lett.* **112**, 1–4.

KALLEMEYN G. W. AND WASSON J. T. (1981) The compositional classification of chondrites–I. The carbonaceous chondrite groups. *Geochim. Cosmochim. Acta* **45**, 1217–1239.

KERRIDGE J. F. (1976) Major element composition of phyllosilicates in the Orgueil carbonaceous meteorite. *Earth Planet. Sci. Lett.* **29**, 194–200.

KERRIDGE J. F. AND BUNCH T. E. (1979) Aqueous activity on asteroids: Evidence from carbonaceous meteorites. In *Asteroids* (ed. T. Gehrels), pp. 745–764. Univ. Arizona Press, Tucson, Arizona.

KING E. A. (1983) Reduction, partial evaporation, and splattering: Possible chemical and physical processes in fluid drop chondrule formation. In *Chondrules and Their Origins* (ed. E. King), pp. 180–187. Lunar and Planetary Institute, Houston, Texas.

KOEBERL C. AND HAGEN E. H. (1989) Extraterrestrial spherules in glacial sediment from the Transantarctic Mountains, Antarctica: Structure, mineralogy, and chemical composition. *Geochim. Cosmochim. Acta* **53**, 937–944.

KORDESH K. M., MACKINNON I. D. R. AND MCKAY D. S. (1983) A new classification and database for stratospheric dust particles (abstract). *Lunar Planet. Sci.* **14**, 389.

KYTE F. T. (1983) Analysis of Extraterrestrial Materials in Terrestrial Sediments. Ph.D. thesis, Univ. California at Los Angeles. 152 pp.

KYTE F. T. AND WASSON J. T. (1986) Accretion rate of extraterrestrial matter–Iridium deposited 33 to 67 million years ago. *Science* **232**, 1223–1229.

LARIMER J. W. (1979) The condensation and fractionation of refractory lithophile elements. *Icarus* **40**, 446–454.

LIOU J-C. AND ZOOK H. A. (1996) Comets as a Source of Low Eccentricity and Low Inclination Interplanetary Dust Particles. *Icarus* **123**, 491–502.

LOVE S.G. AND BROWNLEE D. E. (1991) Heating and thermal transformation of micrometeoroids entering the Earth's atmosphere. *Icarus* **89**, 26–43.

LOVE S. G. AND BROWNLEE D. E. (1993) A direct measurement of the terrestrial mass accretion rate of cosmic dust. *Science* **262**, 550–553.

MAURETTE M. (1993) *Hunting for Stars.* McGraw Hill, New York, New York. 185 pp.

MAURETTE M., HAMMER C., BROWNLEE D. E., REEH N. AND THOMSEN H. H. (1986) Placers of cosmic dust in the blue ice lakes of Greenland. *Science* **233**, 869–872.

MAURETTE M., JEHANNO C., ROBIN E. AND HAMMER C. (1987) Characteristics and mass distribution of extraterrestrial dust from the Greenland ice cap. *Nature* **328**, 699–702.

MAURETTE M., POURCHET M., BONNY PH., DE ANGELIS M. AND SIRY P. (1989) A new collection of micrometeorites extracted from 100 tons of artificially melted blue ice, near Cap-Prudhomme in Antarctica (abstract). *Lunar Planet. Sci.* **20**, 644.

MCSWEEN H. Y. AND RICHARDSON S. M. (1977) The composition of carbonaceous chondrite matrix. *Geochim. Cosmochim. Acta* **41**, 1145–1161.

MILLARD H. T. AND FINKELMAN R. B. (1970) Chemical and mineralogical compositions of cosmic and terrestrial spherules from marine sediment. *J. Geophys. Res.* **75**, 2125–2133.

MURRAY J. AND RENARD A. F. (1883) Report on the deep sea deposits. *Reports Challenger*, 327–336.

NISHIIZUMI K. (1983) Measurement of ^{53}Mn in deep sea iron and stony spherules. *Earth Planet. Sci. Lett.* **63**, 223–228.

NISHIIZUMI K., ARNOLD J. R., FINK D., KLEIN J. AND MIDDLETON R. (1991) Exposure history of individual cosmic particles. *Earth Planet. Sci. Lett.* **104**, 315–324.

NISHIIZUMI K., ARNOLD J. R., BROWNLEE D. E., CHAFFEE M. W., FINKEL R. C. AND HARVEY R. P. (1995) ^{10}Be and ^{26}Al in individual cosmic spherules from Antarctica. *Meteoritics* **30**, 728–732.

NYQUIST L. E., SHIH C. Y., WIESMANN H., BROWNLEE D. E., XUE S., HALL G. S. AND HERZOG G. F. (1995) Chromium, nickel, and iron in deep sea spheres (abstract). *Meteoritics* **30**, 558.

PAPANATASSIOU D. A., WASSERBURG G. J. AND BROWNLEE D. E. (1983) Chemical and isotopic study of extraterrestrial particles from the ocean floor. *Earth Planet. Sci. Lett.* **64**, 341–355.

PARKIN D. W AND TILLES O. (1968) Influx measutements of extratrrestrial material. *Science* **159**, 936–946.

PARKIN D. W., SULLIVAN R. A. L AND ANDREWS J. N. (1980) Further studies on cosmic spherules from deep sea sediments. *Phil. Trans. Roy. Soc. London* **297**, 495–518.

PARKIN D. W., SULLIVAN R. A. L. AND BULL R. K. (1983) Cosmic spherules and asteroidal collisions. *Geophys. J. R. Astr. Soc.* **75**, 473–491.

PRESPER T., KURAT G., KOEBERL C., PALME H AND MAURETTE M. (1993) Elemental depletions in Antarctic micrometeorites and Arctic cosmic spherules: Comparison and relationships (abstract). *Lunar Planet. Sci.* **24**, 1177.

RAISBECK G. M., YIOU F., KLEIN J., MIDDLETON R. AND BROWNLEE D. (1985) Al–26/Be–10 in deep sea spherules as evidence of cometary origin. In *Properties and Interactions of Interplanetary Dust, Proc. IAU Colloquium No. 85* (eds. R. H. Giese and P. D. Lamy), pp. 169–174. Reidel, Dordrecht, The Netherlands.

RAISBECK G. M., YIOU F., BOURLES D. AND MAURETTE M. (1986) ^{10}Be and ^{26}Al in Greenland cosmic spherules: Evidence for irradiation in space as small objects and a probably cometary origin (abstract). *Meteoritics* **21**, 487–488.

RICHARDSON S. M. (1978) Vein formation in the C1 carbonaceous chondrites. *Meteoritics* **13**, 141–159.

ROBIN E. (1988) Des poussieres cosmiques dans les cryoconites du Groenland: Nature, origine et applications. Ph.D. thesis, Univ. d'Orsay, France. 131 pp.

ROBIN E., JEHANNO C. AND MAURETTE M. (1988) Characteristics and origin of Greenland Fe/Ni cosmic grains. *Proc. Lunar Planet. Sci. Conf.* **18th**, 593–598.

ROBIN E., CHRISTOPHE MICHEL–LEVY N., BOURNOT–DENISE M. AND JEHANNO C. (1990) Crystalline micrometeorites from Greenland Blue Lakes. *Earth Planet. Sci Lett.* **97**, 162–176.

ROBIN E., BONTE PH., FROGET L., JEHANNO C. AND ROCCHIA R. (1992) Formation of spinels in cosmic objects during atmospheric entry–A clue to the Cretaceous-Tertiary boundary event. *Earth Planet. Sci. Lett.* **108**, 181–190.

SCHRAMM L. S., BROWNLEE D. E. AND WHEELOCK M. M. (1989) Major element composition of stratospheric micrometeorites. *Meteoritics* **24**, 99–112.

SCOTT E. R., TAYLOR G. J. AND KEIL K. (1982) Origins of ordinary and carbonaceous type 3 chondrites and their components (abstract). *Lunar Planet. Sci.* **13,** 704–705.

STEELE I. M., SMITH J. V. AND BROWNLEE D. E. (1985) Minor-element signature of relic olivine grains in deep sea particles–A match with forsterites from C2 meteorites. *Nature* **314,** 297–299.

TAYLOR S. AND BROWNLEE D. E. (1991) Cosmic spherules in the geologic record. *Meteoritics* **26,** 203–211.

TAYLOR S., LEVER J. AND HARVEY R. (1996) A New Source of Micrometeorites: The South Pole Water (abstract). *Lunar Planet. Sci.* **27,** 1319.

VERNIANI F. (1969) Structure and fragmentation of meteoroids. *Space Sci. Rev.* **10,** 230–261.

WALTER J., KURAT G., BRANDSTÄTTER F., KOEBERL C. AND MAURETTE M. (1995) The abundance of ordinary chondrite debris among Antarctic micrometeorites (abstract). *Meteoritics* **30,** 592.

WARREN J. L. AND ZOLENSKY M. E. (1994) Collection and curation of interplanetary dust particles recovered from the stratosphere. In *Workshop on the Analysis of Interplanetary Dust Particles, AIP Conf. Proc. 310* (ed. M. Zolensky), pp. 245–253. Lunar and Planetary Institute, Houston, Texas.

WASSON J. T. (1985) *Meteorites: Their Record of Early Solar System History*. W. H. Freeman, New York, New York. 267 pp.

WASSON J. T. AND KALLEMEYN G. W. (1988) Composition of chondrites. *Phil. Trans. Roy. Soc. London* **A325,** 535–544.

YADA T., SEKIYA T., NAKAMURA T. AND TAKAOKA N. (1996) Numerical simulation of I-type spherule formation (abstract). *Lunar Planet. Sci.* **27,** 1463.

YAMAKOSHI K. (1984) Chemical compositions of magnetic, stony spherules form deep sea sediments determined by instrumental neutron activation analysis. *Geochem. J.* **18,** 147–152.

YAMAKOSHI K. (1994) *Extraterrestrial Dust, Astrophysics and Space Science Library* vol. 181, Terra Scientific, Tokyo, Japan. 214 pp.

YAKOVLEV O. I., FAINBERG V. S., SHAPKIN A. I. AND RAMENDIK G. I. (1985) Melt evaporation under fast heating conditions (abstract). *Lunar Planet. Sci.* **16,** 924.

ZOLENSKY M. E. AND KROT A. N. (1996) Mineralogical and Compositional Study of an Allende Dark Inclusion (abstract). *Lunar Planet. Sci.* **26,** 1503–1504.

ZOLENSKY M. E., WEISBERG M. K., BUCHANEN P. C. AND MITTLEFEHLDT D. W. (1996) Mineralogy of carbonaceous chondrite clasts in HED achondrites and the Moon. *Meteorit. Planet. Sci.* **31,** 518–537.