Reports

Silicate Spherules from Deep-Sea Sediments: Confirmation of Extraterrestrial Origin

Abstract. *Silicate spherules produced by atmospheric melting of meteoric bodies are probably the most common form of extraterrestrial material on the earth. It has never been possible to positively identify such particles although it has been known for more than a century that silicate spherules of suspected extraterrestrial origin are present in deep-sea sediments. One such spherule has been identified as definitely extraterrestrial since its abundances of nonvolatile trace elements closely match those of primitive solar system material.*

Spherules of presumed extraterrestrial origin were first discovered in deep-sea sediments more than a century ago (*1*). Although both iron (I) and stony (S) types of spherules were found, most contemporary studies have dealt with the type I variety. Millard and Finkelman (*2*) have shown that many of the type I spheres are almost certainly of cosmic origin because they contain both wüstite ($Fe_{1-x}O$), a metastable oxide indicative of the ablation of metallic iron, and metal cores with Fe, Ni, and Co ratios similar to those in iron meteorites. The type I spherules are apparently solidified droplets produced by the atmospheric ablation of iron meteoroids (*3*). Type S spheres have been discussed in modern literature (*1, 4*), but in general they have been neglected because direct evidence that they are extraterrestrial has been lacking. We report here the use of highly sensitive techniques for trace element analysis on individual particles to demonstrate that at least some type S spheres are bona fide extraterrestrial material.

In our study neutron activation techniques are used to determine the trace element composition of single particles. In earlier studies the trace element approach has been used on bulk samples to evaluate the meteoritic content both in abyssal sediments and in lunar soils. On the earth's surface a number of elements (Re, Os, Ir, Ni, Pd, and Au), often referred to as metal-loving elements or siderophiles, are depleted by factors of 10^{-2} to 10^{-4} relative to the cosmic abundances (*5*). Since these elements should be present in undifferentiated meteoroids in approximately unaltered cosmic proportions, an enrichment in a given sample is a measure of the amount of cosmic debris present in it. Analysis of Os and Ir in Pacific Ocean sediments by Barker and Anders (*6*) yielded a value of 1.2×10^{-8} g cm^{-2} year^{-1} for the terrestrial accretion rate of cosmic debris. Although this trace element approach yielded an estimate of the amount of cosmic debris in sediments, the chemical composition of the debris remained totally unknown. This shortcoming is due mainly to the fact that not many elements possessing different chemical and physical properties are depleted in the oceanic sediments so as to signal the composition of a small component of cosmic debris in bulk sediment.

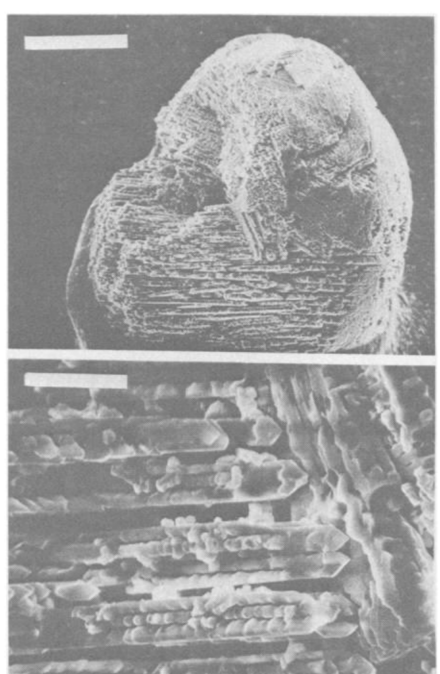

Fig. 1. Particle 3 is very similar to the many type S spheres recovered from the sediment. The exterior morphology appears to be the result of the quenching of a chondritic melt followed by some etching in the sediment. Scale bar (top), 100 μm; scale bar (bottom), 10 μm.

The first clue to the composition of cosmic debris came from the chemical analysis of lunar soils (*7, 8*). Surface rocks on the moon are significantly depleted (relative to the cosmic abundances) in the elements in the middle and on the right side of the periodic table (*7*). Several elements from these groups were found to be enriched in the lunar soil as a result of the presence of cosmic debris. The composition of the cosmic debris matched very well with the composition of primitive solar system material; this result confirmed earlier suggestions (*9*) that a large part of interplanetary debris is primitive solar system material. The amount of interplanetary dust falling on the moon, 2×10^{-9} g cm^{-2} year^{-1}, determined by the chemical method, is in good agreement with estimates based on satellite and photographic meteor data (*10*).

The lunar work demonstrated that the average elemental composition of interplanetary material falling onto the moon (and the earth) is a primitive undifferentiated material distinctly different from common meteorites and also from the type I spherules. For the lunar work, however, only an averaged composition can be obtained because infalling meteoroids are largely destroyed when they impact the lunar surface with full cosmic velocity. The meteoritic material is in unrecognizable forms, perhaps as thin coatings on lunar soil grains. Entry into the earth's atmosphere is a far more gentle process, and analyzable fragments survive, often as spherical droplets of melted meteoroids. Successful analysis of these spheres can lead to a detailed characterization of the types of bodies in the earth-crossing meteoroid complex.

The spheres that we analyzed are part of a collection of over 700 spherules (>100 μm) extracted from 100 kg of box core samples of Pacific red clay taken in the mid-Pacific at a depth of 5 km. The sediment was loaned by the National Oceanic and Atmospheric Administration Domes project. We separated the

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spherules from the sediment, using a magnetic extractor suspended in an agitated slurry of sediment and water. The separation process was very efficient for even weakly magnetic particles > 100 µm. We expect that most cosmic spherules can be collected by this process because ablation during entry produces magnetite in silicate materials containing even small amounts of Fe (*11*, *12*). Although many classic type I spheres, similar to those described by Finkelman (*13*), were found, over half the recovered spheres were of the S type. The concentration of > 400-µm spheres was approximately 10 parts per billion in the sediment. Most of the recovered type S particles are assemblages of micrometer-sized magnetite and olivine crystals (1 to 50 µm) with glass intercrystal filling material. Figure 1 shows such a particle (particle 3), consisting of large olivine bars and some micrometer-sized magnetite. As measured by x-ray analyses in the scanning electron microscope (SEM), the major element compositions of the particles are usually qualitatively similar to chondritic abundances except for S, which is highly depleted. In mineral content, elemental composition, and texture, the spherules match criteria predicted to be diagnostic for the identification of debris produced by the ablation of primitive meteoric bodies (*11*). A detailed description and interpretation of the spherules is presented elsewhere (*14*).

Table 1. Abundances of trace elements in three spheres recovered from Pacific Ocean sediments. Sample codes and sample weights are as follows: particle 1, RC-2C83, 107 µg; particle 2, RC-2C34, 65 µg; and particle 3, RC-2D1, 78 µg. Uncertainties for the three particles represent 2 σ counting statistics (σ is the standard deviation). Abbreviations: ppb, parts per billion; ppm, parts per million.

Element	Particle 1	Particle 2	Particle 3	C1 chondrites (*21*)
Ir (ppb)	35.2 ± 1.5	285 ± 10	535 ± 4	514
Ru (ppb)	69 ± 134	542 ± 181	1210 ± 195	690
Sc (ppm)	14.4 ± 0.2	3.85 ± 0.12	8.90 ± 0.19	6.4
Fe (%)	30.4 ± 0.3	38.6 ± 0.4	41.8 ± 0.4	18.7
Co (ppm)	460 ± 5	289 ± 3	452 ± 4	483
Ni (%)	2.92 ± 0.18	≤0.02	1.02 ± 0.10	1.03
Cr (ppm)	2206 ± 8	246 ± 4	2139 ± 11	2,250
Au (ppb)	1.8 ± 5.2	1.4 ± 3.7	7.6 ± 4.2	152
Zn (ppm)		28.3 ± 3.3	19.0 ± 4.1	303
Sr (ppm)			6.2 ± 1.9	8.6
Os (ppb)			541 ± 115	480
Sb (ppb)			208 ± 151	138
Cs (ppb)			14.5 ± 2.8	192
Ag (ppb)			13.8 ± 6.0	182
Se (ppb)			40 ± 54	19,500

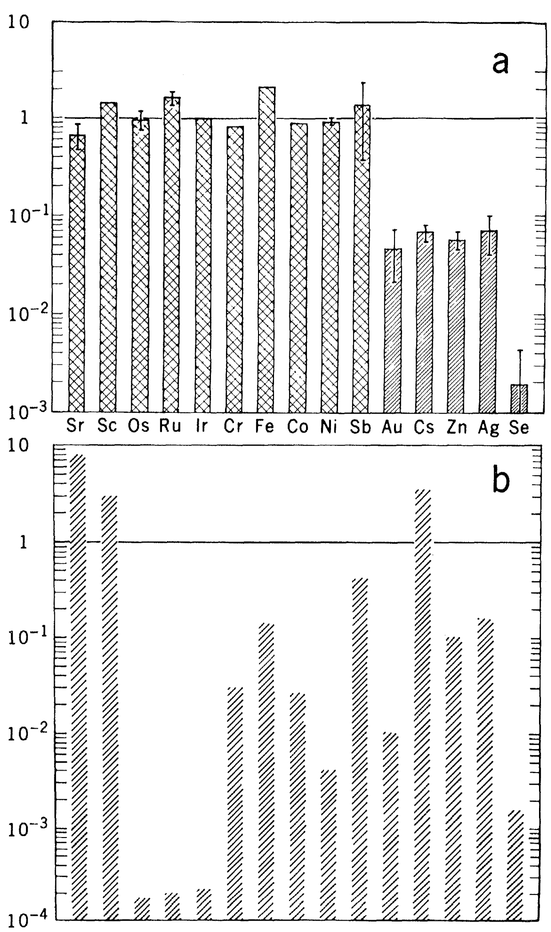

Fig. 2. (a) Composition of particle 3 relative to cosmic abundances. (b) Composition of the earth's crust relative to cosmic abundances. The first ten elements listed, which possess markedly differing chemical properties, are not only present in particle 3 in cosmic proportions but also are present in abundances very close to cosmic values. These results demonstrate conclusively that particle 3 is of extraterrestrial origin. Note the contrast in composition for the earth's crust, largely comprised of continental and oceanic basalts.

The three spheres that were subjected to neutron activation analysis were selected from the collection because of their large size and because their surface compositions of Fe, Mg, Si, Ca, Ni, and Cr were similar to cosmic abundances. On the basis of SEM examination, the surfaces of all three spheres appeared very similar. Prior to analysis, the spherules were ultrasonically cleaned in water, 2-propanol, and Freon and then sealed in quartz tubes. The samples (and standards of known elemental content) were irradiated with 2.2 mmole of thermal neutrons. The abundances of Sc, Cr, Fe, Co, Ni, Zn, Ru, Ir, and Au were determined nondestructively by gamma-ray counting (*15*). For Se, Sr, Ag, Sb, Cs, and Os, gamma-ray counting was done after extensive radiochemical purification of these elements (*16*). The standards were processed radiochemically only after the counting of the samples had been completed so that there was no possibility of cross-contamination.

The elemental abundances found for these three particles are shown in Table 1; for a direct comparison, the abundances in C1 chondrites (a group of undifferentiated meteorites that best represent the cosmic abundance of chemical elements) are also included. Of the three particles, particle 3 shows excellent resemblance to C1 chondrites. The relative abundances of all the nonvolatile elements in this particle are very similar to those of C1 chondrites. Elements that are moderately volatile have lower abundances. Whether this depletion is caused by ablation during atmospheric entry or was established earlier will be discussed below. For particle 2, the abundances of siderophile elements, such as Ir and Ru, are low by a factor of 2. There is also a large-scale depletion of Ni and Cr in particle 2. Although particle 1 contains more

Ir than is found in oceanic basalts, the absolute content is lower by a factor of 15 as compared with C1 chondrites. The ratio of Ru to Ir, 2.04 ± 0.16, for all three particles is slightly higher than the cosmic value of 1.34. Particles 1, 2, and 3 have the same physical attributes; all three particles are spherical, weakly magnetic, and have the same surface composition of major elements. However, they are quite different in their trace element compositions. We know of no physicochemical processes in the solar nebula that could deplete the abundances of Ir and Ru alone in particle 1 and Ni and Cr in particle 2 without affecting the abundances of many other elements. Could it be that particle 1 is extraterrestrial in origin, but that its Ir and Ru contents have been depleted either during atmospheric entry or during residence in the sediment?

Three obvious processes could potentially alter the abundances of ablation particles: (i) selective volatilization during entry, (ii) separation and loss of a metal phase when the particles are molten, and (iii) leaching in the sediments. Of these, leaching is the most complex and difficult to assess. Examination of polished sections of type S spheres has shown that the three major mineral phases in type S spheres, olivine, glass, and magnetite, are attacked preferentially. In most cases the glass has been partially to totally etched out, taking with it elements strongly concentrated in the glass, such as Al and Ca and probably several trace elements as well. Magnetite does not show evidence for degradation, but in some particles the centers of olivine grains near spherule boundaries have been etched out. The low volatility and low solubility of the depleted elements in particles 1 and 2 argue against a simple depletion by volatilization or leaching.

Particle 3 has the attributes of an extraterrestrial particle. We have compared the elemental abundances for this particle to cosmic abundances (*17*) by normalizing the data to the cosmic Ir value (Fig. 2). The first ten elements listed are present in this particle in their cosmic proportions. The mean for these ten elements relative to the cosmic abundances is 1.19 ± 0.43. This result indicates that these elements, which possess markedly different chemical properties, are not only unfractionated from one another but are present in particle 3 in abundances very close to cosmic values. The fact that elements, such as Ir, Ru, and Os, that are depleted in terrestrial basalts (Fig. 2b) by factors of 10^{-3} to 10^{-4} and elements, such as Sc and Sr, that are enriched by factors of 3 to 8 are all present in cosmic proportion in particle 3 provides strong evidence that this particle is of extraterrestrial origin and that it has been preserved intact all this time. The moderately volatile element Sb is commonly depleted by a factor of 3 in ordinary chondrites in relation to C1 chondrites. However, in particle 3, Sb is present in cosmic proportion.

For this particle, the last five elements listed in Fig. 2 are underabundant relative to the cosmic values. All these elements are moderately volatile. They are depleted in all undifferentiated meteorites (with the exception of C1 chondrites), presumably as a result of loss during chondrule formation (*18*). These elements are depleted in ordinary chondrites relative to C1 chondrites by the following factors: Au (1.6), Cs (7), Zn (12), Ag (5), and Se (5). This depletion could come from a combination of leaching or volatilization. It is known that Au forms complexes in aqueous systems. However, the most water-soluble element, Cs, is not severely depleted in relation to Ag, Zn, and Au. Heating experiments on primitive chondrites show substantial loss of Zn and Ag at temperatures around 1000°C (*19*). The spherules have been completely melted and must have been heated above 1200°C for a period of time on the order of 10 seconds. Perhaps the depletion of volatile elements may be better understood when more particles of various sizes have been analyzed.

The chondritic abundance pattern in particle 3 is conclusive evidence that the particle is extraterrestrial and was generated by a chondrite-like meteoroid. Although the existence of such particles has long been suspected, this is the first time they have been positively identified. We expect that future trace element analyses of similar spherules will provide a means of studying the elemental composition of the earth-crossing meteoroid complex. Although the spheres that we studied appear to have been modified by atmospheric entry and residence in the sediment, it may be possible in future analyses to be more selective and choose particles with minimal alterations. For example, examination of the interior structure of 150 type S spheres has shown that roughly 10 percent contain unmelted relict grains and Ni-bearing sulfides. These particles obviously have been exposed to only minimal heating and accordingly their volatile element contents may not have been altered by atmospheric entry. The real value of these spherules is that they make it possible to analyze millimeter-sized samples of fragile meteoroid types which do not produce meteorites.

Whereas only strong cohesive meteoroids can survive atmospheric entry to become meteorites, presumably all types of meteoroids produce spherules. A major goal of this type of research is the chemical characterization of millimeter-sized meteoroids. Meteor studies have shown that most millimeter-sized meteoroids are fragile bodies with proven cometary origin (*20*).

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