Platinum metals and microstructure in magnetic deep sea cosmic spherules

Ph. Bonté, C. Jéhanno, M. Maurette, D. E Brownlee

► To cite this version:

Ph. Bonté, C. Jéhanno, M. Maurette, D. E Brownlee. Platinum metals and microstructure in magnetic deep sea cosmic spherules. *Journal of Geophysical Research*, 1987, 92 (B4), pp.E641-E648. 10.1029/JB092iB04p0E641 . hal-03545787

HAL Id: hal-03545787

<https://hal.science/hal-03545787>

Submitted on 27 Jan 2022

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Platinum Metals and Microstructure in Magnetic Deep Sea Cosmic Spherules

PH. BONTÉ AND C. JÉHANNO

Centre des Faibles Radioactivités, Laboratoire Mixte CEA-CNRS, Gif-sur-Yvette, France

M. MAURETTE

Laboratoire René Bernas, Orsay, France

D. E. BROWNLEE

Department of Astronomy, University of Washington, Seattle

Instrumental neutron activation analysis was used to determine the concentrations of Ir, Fe, Ni, Co, Cr, and Sc in 16 "iron" and 8 "chondritic" magnetic deep sea spherules with sizes of about 200 μm . With the exception of two iron spheres, high iridium concentrations were found in each sphere, thus confirming their extraterrestrial origin. Moreover, the "depth profile" of the residual mass of iridium was monitored in individual spheres by comparing the variations of the intensities of the γ ray lines of iridium, cobalt, and iron during a very gradual sequential polishing. Each sharp but partial discontinuity, observed only in the Ir profiles, reflects the intersection of a polished section with a tiny Ir-rich nugget. These profiles show that such nuggets are much more common in both the iron and the chondritic spheres than previously thought. We found new types of disequilibrated clusters of micrometer-sized nuggets of platinum metals. All types of nuggets, which were characterized with a scanning electron microscope and an energy dispersive X ray spectrometer, seem to be associated with magnetite. The compositions of the nuggets, as well as the fractionation patterns for Ir, Fe, Ni, Co, and Sc in the spheres, suggest that most of the Ir-rich iron spheres originate from iron-rich bodies.

INTRODUCTION

Collections of magnetic spherules ("spheres") extracted from deep sea sediments contain a major component of extraterrestrial spheres with very specific composition and textural features; these include: iron spheres, composed of Fe/Ni oxides, and chondritic spheres, i.e., stony spheres showing a chondritic composition of major elements [Brownlee, 1981]. Some of the characteristic textural features of the spheres have been reported in Figure 1.

Instrumental Neutron Activation Analysis (INAA) of individual deep sea spheres has already been reported; however, no correlated electron microscope and/or electron microprobe study of them was carried out. Ganapathy [1983] compared the INAA analysis of eight glassy spheres collected at the site of the Tunguska event with those of eight chondritic spheres magnetically extracted from deep sea sediments. Yamakoshi [1985] reported INAA data for about 400 deep sea iron spheres that were characterized only by their size, ranging from 20 μm up to 1000 μm . He thus noted the trend of higher Ir concentrations in the smaller iron spheres.

On the other hand, by relying on both a painstaking sequential polishing of iron and chondritic deep sea spheres followed by a direct examination with a scanning electron microscope (SEM) equipped with an energy dispersive X ray system (EDS), Brownlee *et al.* [1984] reported the discovery of beads or "nuggets" of platinum metals that they found in iron but not in chondritic deep sea spheres. They concluded that nuggets were formed by settling in their host iron spheres. These iron spheres in turn were subsequently ejected as "globules" from melted parent bodies with a chondritic composition.

In this paper we combine for the first time these two different analytical approaches (i.e., bulk INAA and SEM + EDS analysis), as well as the use of a sequential polishing. Our objective is to further characterize the distribution of platinum metals in individual deep sea cosmic spheres and to correlate these distributions with the microstructure of the spheres and the concentration of other siderophile (Ni, Co, and Cr) and lithophile (Cr and Sc) elements. The important work of Raisbeck *et al.* [1984, 1985] has already demonstrated that the parent bodies of a vast majority of the cosmic deep sea spheres are constituent particles of the micrometeorite flux. Thus the present work should help in understanding how the characteristics of the cosmic spheres reflect those of their initial micrometeorite parent bodies in space, after a "reprocessing" resulting from ablation in the atmosphere and terrestrial weathering.

EXPERIMENTAL METHODS

The cosmic spherules analyzed in this work were extracted by magnetic raking from west Pacific surface clays 0–100,000 years old found at depths ~5000 m in the Mariana Trough. We analyzed 16 "iron" and 8 "stony" particles in the 100 to 400 μm size fraction, all showing spherical shape already suggesting a melting by ablation in the atmosphere. Only the stony spheres were further preselected by checking with the EDS that their major element composition (Mg, Al, Si, Ca, Fe) was roughly chondritic.

Our experimental procedure includes the following successive steps: First, the two types of spheres were enclosed in ultrapure quartz containers. They were then irradiated in the OSIRIS reactor (5 hours; flux: 1.24×10^{14} n/cm²/s) at Pierre Sûe Laboratory. Standards, including USGS rock Al and MAG1, and a 0.80 mg chip of an aluminium wire with 1 ppm Ir (prepared by A. A. Samadi), were irradiated in the same rabbit. After removal each sphere was mounted in epoxy resin, and the γ

Copyright 1987 by the American Geophysical Union.

Paper number 6B7207.
0148-0227/87/006B-7207\$05.00

Fig. 1. SEM micrographs of polished sections of iron and chondritic deep sea spheres. (a) Ir-rich iron sphere A7: the brightest globule is a large "equilibrated" Ir-rich nugget; the darker and brighter zones refer to magnetite and wustite, respectively. (b) Same iron sphere at a higher magnification: "disequilibrated" small nuggets (see the dark arrows) dispersed in the magnetite phase. (c) Same iron sphere: this micrograph is an enlarged view of a tiny nugget showing its unexpected geometrical habit (white arrow). (d) Ir-poor iron sphere 2d: dendrites of magnetite (brightest phase) embedded in a matrix of interstitial glass (darker phase). (e) Chondritic sphere CH25: the glass phase has been deeply etched out in this sphere, leaving only tiny etch canals in which the magnetite crystals are still preserved; the platinum metal nuggets shown in the next micrograph were observed in a near surface zone identified with the white arrow. (f) Same sphere at a much larger magnification: the cluster of about nine small nuggets of platinum metals can be observed as the brightest spots in this high contrast micrograph. The set of white numbers refer to the chemical group of the nuggets, as listed in Table 3. (g) Chondritic sphere CH14: a very regular "barred" texture, frequently observed in the chondritic spheres, that shows olivine lamellae (bright lamellae), interstitial glass (darker lamellae), and magnetite crystals (brightest phase). (h) Chondritic sphere CH20: a disordered texture of olivine and glass with a low abundance of magnetite crystals was found for this sphere.

TABLE 1. Iron Spheres Data

Name	1a	1b	1c	1d	2a	2c	2d	A3	4a	4b	A5	A6	A7	A8	A11	A14
<i>Energy Dispersive X ray Analysis*</i>																
Mg%				3.5	0.6		1.6									
Al%				0.3	0.2		1.0									
Si%		0.3		4.5	1.0		1.5	0.2								
Ca%		0.2		0.6												
Ti%							0.7						0.9			
Cr%	0.2			0.2			0.6							0.2		
Fe%	66.6	70.3	67.3	57.8	65.4	67.8	62.1	70.0	70.2	70.9	67.7	71.1	62.2	68.6	67.3	69.8
Co%	0.4	0.5	0.6	0.4	0.3		0.5		0.4	0.3	0.5		0.6	0.6	0.2	0.5
Ni%	5.6	1.1	4.6	2.0	4.4	4.9	2.9	2.3	1.9	1.3	4.6	1.4	9.2	3.3	5.3	2.3
<i>Weight†</i>																
μg	58	102	13	98	15	16	70	178	218	84	137	121	246	34	193	98
<i>INAA Data‡</i>																
Sc ppm	<0.4	<0.6	<0.7	1.4	<0.6	<1.1	7.3	<0.1	<0.1	<0.2	<0.3	<0.1	1.1	<0.3	<0.2	<0.3
Ni%	4.9	1.3	5.7	2.5	4.7	6.7	2.7	2.2	7.7	1.3	4.3	1.5	8.9	3.2	5.4	2.0
Co ppm	2460	2400	3910	3000	3240	3180	2180	1820	3030	2350	3320	2600	5140	3410	2210	2580
Cr ppm							8300	266			96	277	1000	1900	1800	570
Ir ppm	11.6	7.0	4.2	2.1	<0.1	6.7	<0.04	12.3	4.1	11.0	5.1	10.1	73.0	7.2	5.6	5.2
Residual Ir§								0.27	<0.04							<0.4
Wustite	x	x	x		x	x		x	x	x	x	x	x	x	x	x
Magnetite	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x
Glass				x	x		x									
Ni Segregation	x		x								x		x	x		
Disequilibrated								x		x			x			
Nuggets																

*Values below 0.2 are not considered.

†Calculated from EDS analysis (Fe content) and INAA (weight of iron).

‡Chromium was not detectable because of the long delay between irradiation and counting.

§After removing major nuggets.

rays of ^{192}Ir , ^{51}Cr , ^{59}Fe , ^{58}Co , ^{46}Sc , and ^{60}Co were measured with an HP Ge detector (FWHM 1.8 keV at 1332 keV; relative efficiency: 20%). For each sphere these γ ray lines can be related to the absolute weights of Ir, Cr, Fe, Ni, Sc, and Co, respectively, by means of the standards (INAA results in Tables 1 and 2). Second, about 20% to 30% of each sphere was ground off, and a new counting was performed that yielded the residual

weights of each element. Then each polished section was studied with a JEOL JSM-840 scanning electron microscope equipped with both two solid-state detectors for Z-contrast image and a LINK energy dispersive X ray spectrometer for quantitative elemental analyses. Major element compositions were thus determined on a large ($50\text{ }\mu\text{m} \times 50\text{ }\mu\text{m}$) surface. With appropriate standards, the accuracy of the analyses varied from 1% to 30%,

TABLE 2. Chondritic Spheres Data

Name	CH10	CH12	CH13	CH14	CH20	CH21	CH24	CH25
<i>Energy Dispersive Analysis*</i>								
Mg%	15.9	8.0	20.0	16.2	24.3	20.9	14.4	14.3
Al%	1.3	3.8	0.7	1.0	1.7	1.6	1.2	1.5
Si%	19.9	8.6	16.4	17.8	16.4	17.7	11.9	17.2
Ca%	2.1	0.2	0.5	1.7		1.4	0.2	1.5
Ti%		0.5						
Cr%	0.3	0.5		0.4		0.3	0.6	0.3
Mn%	0.4				0.6	0.3	0.3	0.6
Fe%	17.8	42.9	21.4	21.9	14.8	15.7	33.9	24.1
<i>Weight†</i>								
μg	327	113	180	214	141	174	125	162
<i>INAA Data</i>								
Sc ppm	9.9	9.4	5.4	8.2	4.6	8.8	4.8	6.1
Ni ppm	2730	3340	1960	12000	400	2440	10300	6280
Co ppm	120	400	330	450	26	300	530	300
Cr ppm	1970	4250	990	3950	540	1850	4520	2200
Ir ppb	10	2970	54	353	220	378	374	296

*Values below 0.2 are not considered.

†Calculated from EDS analysis (Fe content) and INAA (weight of iron).

depending on elemental concentration (LINK results in Tables 1 and 2). From the Fe concentrations we calculated the weight of each sphere and then all minor element concentrations using INAA results. Third, some spheres were next sequentially polished in order to remove micrometer-thick layers from their surface. Gamma ray measurements of Ir, Co, and Fe conducted after each polishing step yielded the "depth profiles" of the residual weight of each element. Simultaneously, many SEM and EDS observations were made during this tedious polishing procedure, including specific observations of the one polished section that did show a discontinuity in the Ir profile (we show below that this section does in fact intersect an Ir-rich nugget). Finally, a few spheres were further polished for determining whether any residual iridium remained when all the nuggets had been removed.

INAA RESULTS

Iridium Concentrations

With the exception of two iron spheres in which iridium was below our detection limit (indicated as upper limits in Table 1), all iron and chondritic spheres found in the size fraction investigated in this work show a peculiar clustering of high iridium concentrations before polishing. These high iridium contents confirm an extraterrestrial origin, which was already demonstrated for similar types of spheres of a slightly larger size ($\sim 500 \mu\text{m}$) by very difficult measurements of their ^{26}Al and ^{10}Be concentrations [Raisbeck *et al.*, 1984, 1985, 1986; Yiou *et al.*, 1985]. In the 14 iron spheres in which Ir was detectable, 13 spheres yielded iridium concentrations that are very narrowly clustered within a factor of 6 (2.1 to 12.3 ppm) and one sphere gave a much higher value (73 ppm). In the set of eight chondritic spheres, five spheres gave values (220, 296, 353, 374, and 378 ppb) that are close to that (473 ppb) quoted for the CI chondrite Orgueil [Anders and Ebihara, 1982], and only three spheres departed from this trend in showing either lower (10 and 54 ppb) or higher (2970 ppb) iridium concentrations.

Element Fractionation

Using our INAA results (Tables 1 and 2) and data for the Orgueil meteorite, we represent each sphere on a $K(X/Y) = (X/Y)/(X/Y)_o$ diagram where our value, X/Y , of the concentration ratio (in mass) of elements X and Y is stated relative to Orgueil (subscript o). In this paper we only report on a semilogarithmic scale the abundance ratios obtained for $X = \text{Ir, Co, Ni, Cr, and Sc}$ in the iron and chondritic spheres, by choosing iron as the reference element Y.

Ir-rich iron spheres (Figure 2a). For the 14 Ir-rich spheres, Ir is enriched ($K = 1.5\text{--}50$) with regard to Co and Ni, which show only small variations around the normal chondritic ratio. The two lithophile elements (Cr and Sc) are strongly depleted, and this trend seems to be more pronounced for Sc ($K < 8 \cdot 10^{-2}$) than for Cr ($1.10^{-2} < K < 2 \cdot 10^{-1}$). The lack of Cr measurements for eight spheres is due to the long delay between irradiation and counting.

Chondritic spheres (Figure 2b). While abundance ratios for Ir are widely scattered, the other siderophile elements (Co, Ni) show a roughly similar depletion pattern with $K(X/\text{Fe})$ ranging from 4.5×10^{-2} to about 0.9. The two lithophile elements (Cr and Sc) have normal abundance ratios ranging from about 0.45 up to 1.8, with Cr showing the trend of being slightly depleted with regard to Sc. Sphere CH14 is clearly chondritic with the five abundance ratios near 1.

Ir-poor iron spheres (Figure 2a). Their different depletion patterns are still related to those of the other spheres, as one of them (sphere 2a) looks similar to that of the Ir-rich iron spheres, while the other one (sphere 2d) rather fits the trend observed for the chondritic spheres.

The Ir Depth Profiles and the Hunt for Platinum Metal Nuggets

For all Ir-rich spheres, the γ ray measurements both before and after the first major single polishing step that leaves 70% to 80% of the initial mass show generally two distinct evolutions for Ir: Either Ir weight is unaffected upon polishing (Figure 3a), or this element is no longer detectable. This fast initial step of the polishing procedure already indicates that Ir is always concentrated in a discrete phase (i.e., "nugget") and not homogeneously dispersed in the host spheres.

For the spheres showing no Ir loss, this first step was followed up by the tedious sequential polishing, which could only be applied to a few spheres so far. We thus observed that Ir shows a depth profile different from that of the other elements, represented by Co in Figures 3a and 3b. While the weight of Co steadily decreases upon polishing, that of Ir first keeps a constant value and then undergoes a sharp discontinuity. These depth profiles indicate that Ir is concentrated in tiny Ir-rich nuggets. They also give an important guideline for finding these nuggets with the SEM. Indeed, as long as the Ir plateau is observed, the nuggets are still below the polished section; but when a partial discontinuity is observed, this indicates a nugget is intersecting the polished section of the sphere, having been partially ground away. Such a section was carefully examined with the SEM for nuggets and when a nugget is found, it is analyzed by EDS.

These Ir depth profiles show that nuggets are much more frequently formed in cosmic spheres than previously thought. Indeed, the existence of nuggets of platinum metals in iron spheres was already directly inferred from SEM observations by Brownlee *et al.* [1984]. These authors found that about half the iron spheres contain a single platinum metal nugget with sizes of $5\text{--}10 \mu\text{m}$, and that in their examination of polished sections of ~ 1000 chondritic spheres no nugget was observed. All of the 14 Ir-rich iron spheres investigated in our work contain at least one nugget, and sphere A7 with 73 ppm of iridium shows two nuggets (Figure 3b). In addition, the initial part of the Ir profiles indicates that nuggets also exist in each one of the 8 chondritic spheres analyzed so far, and we succeeded in finding them in sphere CH25 (Figures 1e and 1f). We also show below from direct SEM observations that both types of spheres contain new families of smaller platinum metal nuggets that are frequently depleted in Ir and are thus not detectable in the Ir profiles (Figure 1c). We finally infer that iridium (and probably the other platinum metals) has been very efficiently collected in most of the Ir-rich nuggets, as this element cannot be detected in the spheres after the loss of their platinum metal nugget. However, in one iron sphere (A3 in Table 1) we still detected about 2% of the initial mass of Ir after the removal of its major nugget.

SEM OBSERVATIONS AND EDS ANALYSES

Microstructure of the Spheres

Fourteen iron spheres show a rather similar structure. In these spheres, magnetite (Fe_3O_4) and wustite (FeO) are the two major

Fig. 2. Fractionation patterns noted for Ir, Co, Ni, Cr, and Sc in (a) 16 iron and (b) 8 chondritic deep sea spheres. K values represent the abundance ratio: $K = (\text{element}/\text{Fe})_{\text{spherule}}/(\text{element}/\text{Fe})_{\text{Oguchi}}$. Upper limits in the concentrations of Ir and Sc in the iron spheres have been reported as downward arrows.

phases, and no chondritic material can be directly observed with the SEM. The nature of these phases was determined in one sphere from Debye-Scherrer X ray diffraction patterns. We found that wustite always contains a higher concentration of Ni than magnetite by factors of 1.3 up to 2. Both phases are clearly separated on SEM micrographs, with wustite appearing as the brighter phase (Figures 1a and 1b) as a result of a higher average atomic number. The grain boundaries between the two phases contain frequently very tiny and needle-shaped segregations of Ni (Figure 1c).

The chondritic spheres are generally made of olivine crystals and interstitial residual glass that contains a variable amount of tiny magnetite crystals (Debye-Scherrer patterns). The spheres show diverse structures that range from a well-ordered barred texture (Figure 1g), dominated by long and relatively large olivine

lamellae separated by interstitial glass loaded with magnetite crystals, to the extreme example of the highly disordered and magnetite-poor structure found in sphere 1d (Figure 1h).

Three spheres that were initially classified as iron spheres are rather "stony iron" objects somewhat intermediate between these two major classes of deep sea spheres. They all contain a minor fraction of Mg, Al, and Fe-rich silicates; this is now directly observable with the SEM (see the darker minor phase in Figure 1*d*). Two of them (spheres 1*d* and 2*a*) show only a single oxidized phase of Fe/Ni alloys, which gives a good example of dendritic growth (Figure 1*d*). The third sphere (2*a*) exhibits a unique "intestine"-folded configuration of magnetite and wustite. Sphere 2*d* (Figure 1*d*) was broken before counting. This might explain its low Ir concentration if the nugget was embedded in the lost broken fragment.

Fig. 3. Depth profiles of ^{192}Ir and ^{60}Co . (a) For the chondritic sphere CH25 the initial weight of iridium did not change during the first polishing step, and a cluster of nuggets (Figure 1f) intersected the polished section when $\sim 95\%$ of the mass of the sphere was ground away. (b) For the iron sphere A7, a nugget was completely lost during the first polishing step, and a second nugget (Figure 1a) was found on the surface when $\sim 60\%$ of the mass of the sphere had been ground away.

Platinum Metal Nuggets in Four Iron Spheres and One Chondritic Sphere

In the Ir-rich iron spheres the SEM and EDS analyses define three major groups of nuggets. We found the two families of "large" nuggets previously observed by others: (1) large globules, with diameters of $\sim 50\ \mu\text{m}$ of almost pure nickel [Brownlee, 1981], that we found to be real platinum metal nugget (lines 1 and 2 in Table 3) containing all the Ir of the spheres; and (2) Ir-rich spherical nuggets (Figure 1a), with smaller sizes of

5 and $20\ \mu\text{m}$, that were first reported by Brownlee *et al.* [1984] and that show the typical "equilibrated" compositions reported in lines 3 and 4 in Table 3. But we also found a new family of micrometer- and submicrometer-sized nuggets showing specific properties. They are abundant (Figure 1b), always found in the magnetite phase, and some have a geometrical habit (Figure 1c). Moreover, they all show a "disequilibrated" composition (lines 5 and 6 in Table 3) in that they only contain the most volatile Pt-metals (Pt, Ru, and Rh). These small nuggets cannot be generally revealed from the Ir-profiles, as they are

TABLE 3. Platinum Metal Compositions of Nuggets

Element (Wt %)	Fe	Ni	Os	Ir	Ru	Pt	Rh	Pd
<i>Iron Spheres</i>								
4a Ni globule	10.1	88.8		0.006*				
2c Ni globule	8.2	91.2		0.2*				
A8 nugget	3.1	9.0	21.7	19.5	16.6	27.1	2.8	
A7 nugget	5.9	4.2	28.8	18.4	14.6	25.8	2.3	
A3 small nugget	28 [†]	21			2.1	43.4	4.5	
A7 small nugget	22.4 [†]	20.8			3.5	44.8	7.6	
<i>Chondritic Sphere CH25</i>								
Nugget 1	7.0	36.5	<1	5.5	11.9	25.6	4.0	8.4
Nugget 2	7.7	2.7	4.2	19.5	25.4	38.4	1.7	
Nugget 3	3.4	0.4	61.8	20.2	10.5	2.7		

Energy dispersive X ray analysis; values below 0.2 are not considered.

*Calculated from INAA data and globule diameter.

[†]Partially due to the matrix.

depleted in this element. All types of nuggets in the iron spheres are associated with the magnetite and not with the wustite phases.

In the chondritic sphere CH25 a cluster of at least nine micrometer-sized nuggets was discovered near the deeply weathered top surface of this sphere after removing 95% of its mass (see the white arrow in Figure 1e). Each nugget exhibits a specific composition that is highly disequilibrated and that looks different from those noted for the disequilibrated small nuggets in the iron spheres. In particular, an unexpectedly high concentration of palladium (a highly volatile platinum group element) was found in nugget 1 (line 7 in Table 3). The compositions of the other nuggets have been tentatively classified in two additional chemical groups that are listed in lines 8 and 9 in Table 3. The nuggets again seem to be associated with the segregations of magnetite. Indeed, with the exception of their higher "Z" brightness on SEM micrographs, they look rather similar to the magnetite crystals, with regard to both their preferential localization in the constituent interstitial glass of the spheres and their size and geometrical habit (Figure 1f). In a deep sea chondritic sphere, F. Kyte (personal communication, 1986) found one nugget containing all six platinum metals. We note that the bulk analysis of the cluster of nuggets found in CH25 would give a rather similar composition.

DISCUSSION

Correlations Between Microstructure and Chemical Composition

Thirteen Ir-rich iron spheres present the typical texture of wustite and magnetite reported in Figures 1a and 1b. Three types of distribution of platinum metals can be observed: They can be concentrated in a single big Ni-core (4a), in one or two nuggets (A3), and in small "disequilibrated" nuggets (A3, 4b, and A7). The existence of a large Ni-core in sphere 4a accounts for the different Ni concentrations determined by INAA or EDS (Table 1). All spheres in this group are strongly depleted in Cr and Sc (Figure 2a).

Two other iron spheres (1d and 2d) with a dendritic texture (Figure 1d) show the least depleted composition in lithophile elements. This is related to the existence of a minor glassy phase. They are probably the G-type spherules classified by *Blanchard et al.* [1980].

A correlation between microstructure and chemical composition is not found in the chondritic spheres. For example, spheres CH14 and CH20 show very different textural features (Figures 1g and 1h) that correspond to two different depletion patterns, but their iridium content is similar (Figure 2b).

Constraints on the Origin of the Ir-rich Cosmic Spheres

It was previously argued that iron spheres originate from a process of Fe/Ni globule ejection from a chondritic melt [*Brownlee et al.*, 1984]. *Brownlee* [1981] found small (<50 μm sized) globules in the near-surface region of a few chondritic spheres and/or small cavities with similar shapes and sizes. These were interpreted to result from the ejection of the Fe/Ni globules from a parent chondritic melt formed upon ablation in the atmosphere. The lost globules were postulated to form iron cosmic spheres.

Yiou et al. [1985] recently proposed a quite different origin for the iron spheres. They measured saturation values for the concentrations of ^{10}Be (a strongly lithophile element) in five iron spheres (size $\sim 500\ \mu\text{m}$) that are similar to saturation values

measured for iron meteorites. This shows that iron spheres with sizes only slightly larger than those investigated in our work can only originate from an iron-rich body and not from a chondritic melt that should have kept the strongly lithophile element.

In deep sea sediments the abundance of the iron spheres with sizes $>100\ \mu\text{m}$ is roughly similar to that of the chondritic spheres in the same size range [*Brownlee*, 1981]. Consequently, if each one of the chondritic spheres ejects one iron sphere on the average, we should have found a high depletion of iron and iridium, as well as no platinum metal nugget in the chondritic spheres. As these trends were not observed, we believe that the conclusion of *Yiou et al.* [1985] about the formation of the iron spheres from Fe-rich bodies also extends to the slightly smaller size fraction investigated in the present work.

There is possibly additional information in the depletion pattern of other trace elements. For example, such bodies would show a much narrower range of Ir concentrations than that observed in iron meteorites, which covers 4 orders of magnitude range [*Mason*, 1971]. Moreover, if iron spheres did originate from iron meteorites and not from pallasites, the concentrations of Cr and Sc should have been about 100 times smaller than the values reported here. Therefore the iron-rich parent bodies of the spheres are probably different from iron meteorites in that they contain a minor fraction of chondritic material. This conclusion applies particularly to spheres 1d and 2d, which not only yield the highest concentrations of Sc but also show direct evidence with the SEM for a silicate phase (Figure 1d).

SUMMARY AND FUTURE PROSPECTS

Platinum metal nuggets are much more frequently formed in both iron and chondritic deep sea cosmic spheres than previously thought. Their formation process is still poorly understood. On the one hand, the large "equilibrated" nuggets have likely been formed by a single process, such as settling in a molten phase formed upon ablation in the atmosphere. However, this process of segregation must be extremely efficient and fast, in order to collect all Ir initially present in the parent bodies of the spheres over the short thermal pulse that they experience during the ablation process. Furthermore, this single process is not expected to yield the highly disequilibrated family of nuggets reported here. Indeed, both results are hard to reconcile with usual concepts of "classical" metallurgy (A. Lesoulte, personal communication, 1986).

For the iron spheres our measurements would also extend to a slightly smaller size fraction the earlier conclusions of *Yiou et al.* [1985], pertaining to the existence of iron-rich parent bodies for the iron spheres. Correlations between microstructure and minor and trace element fractionation in individual cosmic spherules should soon yield additional clues about such parent bodies, when we consider other important trace elements such as Au and W.

However, these preliminary inferences are based on several assumptions that still have to be checked. In particular, we assume that the initial concentrations of platinum metals in the parent bodies of the Ir-rich spheres have not been strongly modified during the short pulse heating occurring during their ablation in the atmosphere. As emphasized by F. Kyte in his careful review of our manuscript, these key assumptions are yet unproven. Fortunately they should soon be checked by conducting simulation experiments with solar furnaces at Odeillo, with materials including chunks of chondritic and iron

meteorites, such as Mighei and Negrillos, in which the sequential polishing technique revealed an homogeneous distribution of iridium. The new facilities available there can now deliver thermal pulses with a minimum duration of about 0.1 s, which are much shorter than those previously used by King [1982] at the same facilities for investigating the formation of chondrules. Moreover, the experiments can be conducted in a controlled atmosphere, in which the residual pressure of atomic oxygen can be correctly adjusted so as to assess the possible role of this important atomic species in the ablation "metallurgy" that reprocessed the cosmic spheres from still poorly known parent bodies.

Acknowledgments. We thank F. Kyte for his excellent and very helpful review of this manuscript and G. Raisbeck for very useful comments. This work was mostly supported by two grants from "Action Thématique Programmée de Planétologie" from INSU as well as by fundings from CEA and CNRS. This is CFR contribution No. 794.

REFERENCES

- Anders, A., and M. Ebihara, Solar system abundances of the elements, *Geochim. Cosmochim. Acta*, **46**, 2363–2380, 1982.
- Blanchard, M. B., D. E. Brownlee, T. E. Bunch, P. W. Hodge, and F. T. Kyte, Meteorite ablation spheres from deep-sea sediments, *Earth Planet. Sci. Lett.*, **46**, 178–190, 1980.
- Brownlee, D. E., Extraterrestrial components in deep sea sediments, in *The Sea*, vol. 7, edited by C. Emiliani, pp. 733–762, Wiley, New York, 1981.
- Brownlee, D. E., B. A. Bates, and M. Wheelock, Extraterrestrial platinum group nuggets in deep sea sediments, *Nature*, **309**, 693–695, 1984.
- Ganapathy, R., The Tunguska explosion of 1908: discovery of meteoritic debris near the explosion site and at the South Pole, *Science*, **220**, 1158–1161, 1983.
- King, E. A., Refractory residues, condensates and chondrules from solar furnace experiments (abstract), in *Lunar and Planetary Science XIII*, pp. 389–390, Lunar and Planetary Institute, Houston, 1982.
- Mason, B., *Handbook of Elemental Abundances in Meteorites*, Gordon and Breach, New York, 1971.
- Raisbeck, G. M., F. Yiou, J. Klein, Y. Yamakoshi, and D. E. Brownlee, ^{26}Al and ^{10}Be in deep sea stony spherules; evidence for small parent bodies (abstract), in *Lunar and Planetary Science XIV*, pp. 622–623, Lunar and Planetary Institute, Houston, 1984.
- Raisbeck, G. M., F. Yiou, J. Klein, R. Middleton, and D. E. Brownlee, $^{26}\text{Al}/^{10}\text{Be}$ in deep sea spherules as evidence of cometary origin, in *Properties and Interactions of Interplanetary dust*, edited by R. H. Giese and P. Lamy, pp. 169–174, D. Reidel, Dordrecht, 1985.
- Raisbeck, G. M., F. Yiou, D. Bourles, and M. Maurette, ^{10}Be and ^{26}Al in Greenland cosmic spherules; Evidence for a cometary origin, *Sixth Int. Conf. Geochronology, Cosmochronology and Isotope Geology*, Cambridge, in press, 1986.
- Yamakoshi, K., Further studies on size distribution of siderophile elements concentrations in black magnetic spherules from deep sea sediments, *J. Geomag. Geoelectr.*, **37**, 205–213, 1985.
- Yiou, F., G. M. Raisbeck, and D. E. Brownlee, ^{10}Be in iron type cosmic spherules: Evidence for a differentiated parent body, *Meteoritics*, **20**, 791–792, 1985.
- Ph. Bonté and C. Jéhanno, Centre des Faibles Radioactivités, Laboratoire Mixte CEA-CNRS, 91190 Gif-sur-Yvette, France.
- M. Maurette, Laboratoire René Bernas, 91406 Orsay, France.
- D. E. Brownlee, Department of Astronomy, University of Washington, Seattle, WA 98195.

(Received April 22, 1986;
revised December 24, 1986;
accepted December 24, 1986.)