Neutron activation analysis of silicate spherules from oceanic sediments

HIROSHI NAGASAWA¹, KAZUO YAMAKOSHI² and HIDEO HIGUCHI³

Department of Chemistry, Gakushuin University, Mejiro, Toshima-ku, Tokyo 171,¹
Institute for Cosmic Ray Research, Tokyo University, Tanashi, Tokyo 188,²
and Japan Chemical Analysis Center, Chiba,³ Japan

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A technique of neutron activation analysis was developed for nondestructive analysis of small extraterrestrial grain samples of less than 1 mg. The features of the technique are (1) use of glass standards made from geochemical standard rocks (JB-1 and BHVO-1) and (2) use of a small aluminum plate on which samples and standards are precisely mounted for gamma-ray counting.

Twelve silicate spherules obtained from dredged deep-sea sediments were analyzed for trace and major elements by applying the above method of neutron activation and electron microprobe analysis. The results show that most of the silicate spherules analyzed have marine origin except for a 0.7 mm glassy spherule of meteoritic origin reported in the previous paper (NAGASAWA *et al.*, 1979).

INTRODUCTION

The spherules from oceanic sediments have recently become recognized as an important source of extraterrestrial information besides meteorites and lunar samples (SHIMAMURA *et al.*, 1978; GANAPATHY *et al.*, 1978; BROWNLEE *et al.*, 1978, 1979; NAGASAWA *et al.*, 1979; YAMAKOSHI *et al.*, 1980). These spherules, compared with meteorites, may comprize wider varieties of cosmic materials, because cosmic materials which originally have small sizes or friable structure are to be found more likely as spherules than meteorites. Such cosmic materials may include extrasolar materials such as meteor debris or interstellar dust etc.

To investigate the origin and processes of formation of the spherules and to obtain effectively extraterrestrial or extrasolar information from the tiny spherules, individual spherules must be analyzed by nondestructive methods for physical and chemical properties. Determination of density by Stokes' method (e.g. HUNTER and PARKIN, 1960) or heavy liquids and observation of size and structure by optical or electron microscope are useful methods for

observing physical properties of the spherules. Nondestructive chemical analyses, electron microprobe analysis and instrumental neutron activation analysis (INAA), are important methods of investigation of the spherules.

Among trace elements the rare earth elements (REE) provide effective tool to investigate the extraterrestrial silicate samples (BOYNTON, 1975, 1978; NAGASAWA and ONUMA, 1979). In the terrestrial igneous processes REE behave similarly with regular variations parallel to atomic number with an exception of Eu which shows anomalous behavior under reducing conditions. During cosmochemical processes evaporation of REE could take place under low-pressure, high-temperature conditions to produce fractionation accompanied by anomalies of Ce, Yb and possibly of Tm, in addition to those of Eu. Because the extent of the anomalies depends on the oxygen fugacity in the atmosphere, the REE abundance patterns of the spherules would provide information on chemical composition and temperature of the ambient atmosphere in which the spherules were formed.

Compositions of stable isotopes also provide effective tools to investigate extraterrestrial

samples (e.g. CLAYTON *et al.*, 1973; LEE *et al.*, 1976; LUGMAIR *et al.*, 1978). Precise determinations of isotopes, however, require destructive analytical methods. Thus, small samples, in particular, must be analyzed by nondestructive chemical analyses before isotope studies.

We have developed a technique of INAA which can effectively be applied to the chemical analysis of the spherules before final destructive analysis for isotope compositions. The features of the technique are (1) use of glass standards made from geochemical standard rocks (JB-1 and BHVO-1) and (2) use of a small aluminum plate on which samples and standards are precisely mounted for gamma-ray counting. Excellent reproducibility of geometry obtained for neutron irradiation and gamma-counting of either the samples or standards greatly reduced the errors inevitably associated with the use of a powder standard for INAA of small samples.

In a previous paper (NAGASAWA *et al.*, 1979) we have reported the results of INAA of 4 silicate spherules including a 0.7mm glassy spherules of meteoritic origin. In this paper, we report the results of INAA of our glass standards and of 13 additional spherules and 3 mineral grains from red clay from the North Pacific, together with some results of electron microprobe analysis. Results of observations of physical and mineralogical properties of the spherules are also given.

SAMPLE DESCRIPTION

Two tons of cobble-clay mixture containing ferromanganese nodules were collected by dredging the bottom of the middle North Pacific Ocean between (17°17'N, 176°18'W) to (17°18'N, 176°21'W) at about 4,000m depth.^{a)} More than 10 thousand silicate spherules ranging from 70 to 800 μ m in diameter were collected by hand-picking with a fine needle from a 700-g, +200-mesh fraction of red clay sample

separated from the cobble-clay mixture.

Most of the spherules are classified into the following 4 types:

Type 1. Pale brown to brownishwhite, opaque "ping-pong ball" spherules with shiny surface, spherical shape, accounting for less than 5% of the total spherules. (Samples #2, #6, #16, #17, #26).

Type 2. "Meat ball" spherules with color and shape essentially similar to type 1, but with a rough surface, spherical or oblong spherical shape. (#56).

Type 3. Color essentially similar to types 1 and 2, but with a rough surface, more irregular shape due to presence of large crystals just below the surface. Types 2 and 3 account for more than 90% of the total spherules. (#A, #B, #C, #55, #80).

Type 4. Glassy, colorless and transparent, perfect spherical, less than 0.5% of the total spherules.

Only one typical type 4 spherule was found from the sediment sample and analyzed by INAA. However, more than 70 spherules of this type were found in other sediment samples. The distribution of the type 4 spherules appears heterogeneous among different sediment samples. Study of these additional type 4 spherule samples is now under way.

Densities of the spherules were measured by Stokes' method (HUNTER and PARKIN, 1960). Average density of 13 spherules of type 1 - 3 was 2.53 (Appendix), while that of type 4 (#G) was 3.0 which is considerably higher than those of type 1 - 3 spherules.

Magnetic spherules were found from the red clay sample in addition to the silicate spherules. Chemical composition and description of the magnetic spherules will be published elsewhere (NOGAMI *et al.*, 1980; YAMAKOSHI *et al.*, 1980). Euhedral mineral grains of phillipsite, quartz and magnetite were also found from the sample.

^{a)} Sample Code, Station-40 (KH-67-5), collected with a beam-trawl net during the cruise of Hakuho-Marui of Ocean Research Institute, University of Tokyo.

ANALYTICAL

Glass standards Silicate glass standards were prepared for INAA of small scale samples by melting JB-1 (Geol. Survey of Japan) and BHVO-1 (U.S. Geol. Survey) standard rock basalts. About 10g each of JB-1 and BHVO-1 powders were melted in Pt crucibles at about 1,350°C for 15 min under atmospheric condition, and cooled rapidly by dropping into deionized water. The inner parts of the cracked blocks of the quenched glass were selected and crushed to small chips of less than 1mg in weight. The crushed chips were washed with deionized water and used for standards. Homogeneity of the glass standards were checked by repeated analysis of the chips by INAA, the results of which are shown in Table 1.

As shown in Table 1, standard deviations of repeated analysis are 1 to 2% where standard deviations of counting rate are about 1 or smaller. This indicates that chemical heterogeneity of the sample does not exceed 2%. Since lower (or higher) values tend to appear repeatedly for the same samples as seen in Table 1, the observed 1 to 2% deviations appear to be due to difference in geometry and/or error from weighing or loss of weight of the samples during handling. Thus, chemical heterogeneity of the standards must be much smaller, possibly less than 1%. Although conventional heating method without control of O₂ fugacity etc. was used for melting the standards, the obtained glasses showed excellent chemical homogeneity for standards at the 100µg level. We determined chemical compositions of the glass standards separately at 10mg scale using BCR-1 as standard, because we do not have adequate standards for the samples of less than 1mg in weight. Good agreement was obtained between the values of the glass and original powder standards (Table 2). The possible loss of Na by evaporations is negligible.

Analytical procedures The samples, both standards and spherules, were weighed by a Cahn electrobalance (Model G), sealed in fused quartz

tubes, and irradiated at total neutron fluxes of about 3×10^{18} neutrons/cm² in JRR-2 or JRR-3 reactor of Japan Atomic Energy Research Institute for determination of isotopes with half lives longer than 15hr (²⁴Na). The irradiated samples were taken out from the quartz tubes and mounted on Al sample holders (20×40×1mm thickness with a 4mm hole at a position 10mm from each of three sides), thus eliminating background activities from impurities in the quartz tubes. By positioning the solid samples at the center of the hole on the Al-holder by a plastic tape, good efficiency and reproducibility were obtained for counting at about 5mm distance from the end of the detector housing. Counting was done with a Ge(Li)-detector and a pulse height analyzer at about 7 days and 40 days after irradiation. Some of the spherules were analyzed by electron microprobe analyzer for major element compositions.

IDENTIFICATION OF "COSMIC" SPHERULES
BY REE ABUNDANCES

Most straightforward way of identifying an extraterrestrial material is to find out if the chemical composition of the material is identical with one of those which are already known as extraterrestrial, typically meteoritic. In fact, GANAPATHY *et al.* (1978) and GANAPATHY and BROWNLEE (1979) showed that some spherules from deep-sea sediments and dust particles collected by U-2 airplane at high altitude have chemical compositions very similar to those of C-1 chondrites. However, extraterrestrial materials which have not been known as meteorites or accessible planetary materials are more important than those identical with those already known, in the sense that they provide more information on unaccessible space. Furthermore, even a known meteoritic material could have undergone cosmochemical fractionation of elements to a substantial degree by partial volatilization. NAGASAWA *et al.* (1979) reported that a glassy silicate spherule from deep-sea sediment have chemical compositions which

Table 1. Results of repeated analysis of the glass standards^{a)}

	JB-1 glass										BHV-1 glass									
	1	2	3	4	5	6	7	8	σ^b (%)	σ^c (%)	1	2	3	4	5	6	7	8	σ^b (%)	σ^c (%)
La	1.00	0.99	0.99	1.01	1.01	1.01	1.00	1.00	0.67	0.5	0.98	0.96	1.03	1.01	1.01	0.98	1.00	1.00	2.1	2
Ce	0.95	0.98	1.03	1.01	0.98	1.06	1.00	0.99	3.4	2	0.98	0.98	1.01	1.04	0.98	1.00	1.00	1.01	2.0	3
Sm	1.02	0.99	1.00	1.01	1.01	0.98	1.00	1.00	1.0	0.7	0.99	0.98	0.99	1.01	1.00	1.01	1.00	1.00	0.89	0.5
Eu	1.01	0.99	1.00	0.98	0.96	1.02	1.02	1.03	2.4	2	0.99	0.98	0.99	1.02	1.03	1.01	0.99	0.99	1.6	1.5
Tb	0.87	0.92	0.91	1.00	0.92	1.31	0.92	1.16	15	10	0.97	0.93	1.08	1.00	1.09	1.11	0.86	0.96	8.5	10
Yb	1.03	0.98	1.01	1.04	1.02	0.95	0.98	0.99	2.8	4	1.00	0.96	1.01	1.06	1.04	1.03	0.96	0.97	3.9	4
Lu	0.99	1.00	1.04	0.96	0.97	1.03	1.06	0.95	4.0	5	0.96	1.03	0.93	0.90	1.10	1.07	0.99	1.01	6.9	6
Sc	0.99	0.98	0.99	1.02	1.00	1.00	1.02	1.00	1.4	0.4	0.98	0.98	1.00	1.02	1.01	1.00	1.00	1.00	1.3	0.2
Fe	0.99	0.96	1.01	1.01	0.98	1.01	1.04	1.00	2.2	1	0.98	0.98	0.97	1.03	1.00	1.00	1.00	1.00	1.8	0.5
Co	0.99	0.98	0.98	1.01	1.01	1.01	1.01	0.99	1.4	1.5	1.00	1.00	0.99	1.03	1.00	1.01	0.99	0.99	1.4	0.8
Cr	0.95	0.98	0.94	1.02	1.09	0.97	0.98	1.06	5.1	0.8	0.97	1.00	1.01	1.01	1.00	0.99	1.01	1.02	1.5	1
Th	1.03	0.94	0.99	0.98	0.97	1.00	1.00	1.10	4.9	3	1.29	0.88	0.86	1.04	0.96	1.10	0.97	0.92	14	20
Hf	—	—	—	—	—	—	—	—	—	—	0.98	0.99	1.02	1.02	1.05	0.98	0.96	0.99	3.1	5
Na	1.00	0.97	0.99	1.03	1.01	0.98	1.01	1.02	2.2	1	0.97	0.99	0.99	1.01	0.99	1.01	1.02	1.01	1.8	1

a) Values are expressed as the average of 8 analyses = 1.

b) Standard deviation calculated for 8 analyses.

c) Standard deviation of counting statistics for individual values.

Table 2. INAA results for spherules and mineral grains^{a)}

Sample number	# 2	# 6	# 16	# 17	# 26	# 55	# 56	# 80	# A	# B	# C	# G	# M1	# M5	# MA	# MC
Type	1	1	1	1	1	1	2	2	3	3	3	4	M	M	M	M
Weight (μg)	950	857	538	242	531	309	419	174	565	610	518	722	386	260	189	229
La	19.6	13.1	17.1	25.9	25.6	16.5	11.4	30.0	32.6	23.3	38.5	1.46 (3.6)	.52 (8.1)	.88 (13)	.40 (20)	.4
Ce	39.3	31.5	78.0	75.9	141	48.6	44.2	33.0	30.7	43.7	49.7	.20	2.41 (12)	7.93 (7.7)	7.95 (9.4)	1.7
Sm	4.86	3.24	3.41	6.82	6.51	4.13	2.59	7.78	8.47	5.67	10.3	.83	.87 (2.4)	.045 (4.4)	.045 (15)	.02 (25)
Eu	1.04	.734	.89	1.53	1.35	.97	.69	1.84	2.07	1.30	2.36	.33 (4.4)	.024 (19)	.076 (14)	—	.02
Tb	1.8	1.3	.69 (13)	1.46 (15)	2.3	.91 (16)	.50 (11)	1.42	1.45	.9 (20)	1.78	.31 (29)	—	—	—	—
Yb	1.74	1.23	1.59	2.43	2.71	1.39	1.13 (3.9)	3.36 (2.6)	3.41	2.18	4.33	.92 (4.6)	.055 (24)	.4	.12	.22
Lu	.270	.181	.218	.384	.382	.219	.160	.462 (3.1)	.497	.298	.600	.146	.034 (8.0)	.02	.02	.01
Sc	4.14	2.63	4.07	5.20	4.68	3.12	2.46	5.22	18.9	4.40	5.16	31.9	.075 (3.7)	3.57	3.03	1.75
Fe as FeO%	.844	1.66	1.36	1.64	1.68	1.17	1.24	1.01	7.24	1.26	1.05	.80	.020 (15)	.561	.538	.206
CO	7.29	10.8 (8.5)	8.86	21.8	89.5	11.1	10.1	10.5	15.1	11.2	8.4	.41	.53 (6.3)	2.96	2.11	1.37 (6.5)
Na as Na ₂ O%	5.35	6.10	6.73	3.711	5.47	6.13	4.46	5.58	3.12	5.75	5.67	.17 (29)	.028 (15)	5.60	4.52	3.21
Cr	11 (10)	10 (12)	15 (8.6)	25 (10)	16 (9.7)	16 (15)	27.3	11 (13)	42	11 (8.0)	17	.66	3 (10)	3.7 (19)	3.6 (24)	3.4
Th	1.2 (14)	1.4 (13)	2.0 (6.8)	1.9 (11)	2.1 (17)	1.3 (11)	.94 (9.7)	1.8 (9.7)	2.0	2.4	1.9	.66	—	—	—	—

a) ppm, unless otherwise noted.

Accuracy of the data are approximately equal to the (%) value for 8 analyses in Table 1.

Larger errors are indicated in parentheses.

have possibly been derived from those of chondrite by evaporation loss of volatile elements and Ce on heating at the time when the original material entered the earth's atmosphere.

The idea proposed by GANAPATHY and ANDERS (1974) can be applied to identifying extraterrestrial materials which have cosmochemically fractionated chemical composition. They showed pairs of elements which are similar in crystal chemical properties but differ in cosmochemical properties (volatility) are useful to estimate the difference in chemical compositions of the terrestrial planets. An extraterrestrial material once experienced a cosmochemical process would become enriched or depleted in one of the elements in the pair relative to the average earth's material to the degree which cannot be explained by crystal chemical processes.

For the purpose of identifying an extraterrestrial material which experienced a high temperature event such as condensation in the primitive solar nebula, a set of REE can be a useful indicator. Among REE Ce, Eu, Yb and possibly Tm show exceptionally high volatility compared with other REE under certain cosmochemical conditions. Loss or enrichment of these elements by cosmochemical fractionation can be seen as anomalies in the REE patterns, REE abundances plotted in terms of relative values to the chondritic average against REE atomic number (or ionic radius). The values for these elements expected for the material if the material did not experienced cosmochemical fractionation can be obtained by interpolation of the patterns. The observed and the interpolated values for these elements serve as perfect pairs for identifying the extraterrestrial spherules. The volatilities of Ce, Eu, Tm and Yb depend on the oxygen partial pressure in the atmosphere (BOYNTON, 1975, 1978; NAGASAWA *et al.*, 1979); Ce is volatile only in oxygen-rich atmospheres, while Eu, Tm and Yb are volatile in hydrogen-rich, or low-oxygen-partial-pressure atmospheres. In addition, light REE tend to be more volatile compared with

heavy REE.

REE are among the most refractory members of the elements. A lower temperature cosmochemical process can only produce uniform enrichment of REE due to evaporation of more volatile elements, such as Mg, alkali or ion group elements etc. Meteoritic spherules which were produced by heating and melting of the meteorites can be identified by their relative REE abundances in their similarity to the chondritic values even if their major element compositions have been changed significantly due to cosmochemical fractionation by the heating episode.

Another important change in REE abundances can be expected in *extra-solar* spherules, if present; if REE in the materials were produced by nucleosynthetic processes which are different from that produced solar REE, the REE abundance patterns in the material can be totally unrelated to those in the solar system in terms of geo-or cosmochemical fractionations.

Fresh "cosmic" spherules, in most cases, should have characteristic REE abundance patterns as discussed above. However, burial under ocean bottom for a long time interval could change their chemical compositions by interaction with sea-water. Ce, in particular, can be dissolved selectively by sea-water to produce negative Ce anomaly (LUDDEN and THOMPSON, 1979). Abundances of light REE, particularly of La, can also be affected by glass-water interaction. The rate of glass-water interaction appears to vary widely depending on environmental conditions; glassy rinds of ocean-floor basalts have been shown to be palagonized completely in 4m.y., whereas fresh glass has been found in DSDP samples which are several tens of m.y. old (THOMPSON, 1973; LUDDEN and THOMPSON, 1979). Thus, to identify "cosmic" spherules samples must be carefully inspected microscopically for alteration. Since major element composition of chondrite samples must be significantly different from those of terrestrial silicate samples, major element composition of the spherules must be studied in comparison

Table 3. Major element compositions of silicate spherules (%)

Sample number	#16*	#56*	#A*	#G*	#A1			#A2		#A3		#A4	
Type	1	2	3	—	3			3		2		1	
Al ₂ O ₃	16.3	10.8	15.3	8.5	63.7	66.3	59.6	65.2	65.8	64.7	73.0	50.1	65.7
Fe as FeO	1.36	1.24	7.24	.80	20.9	21.4	19.4	20.8	21.7	21.9	23.6	12.7	22.1
MgO	5.3(13)	2.4(28)	—	32	.23	.55	.82	.72	.36	.51	.59	5.7	3.0
CaO	.9(26)	.6	3.3(11)	6.7(6.6)	.23	.22	.34	.35	.34	.20	.20	.13	.82
Na ₂ O	6.73	4.46	3.12	.17(29)	.64	.74	.75	1.35	.81	.30	.28	.25	.22
K ₂ O	—	—	—	—	7.4	7.2	8.0	5.3	6.8	2.2	1.2	1.7	3.0
MnO	.43(6.3)	.037(6.6)	.052(5.6)	.028	5.0	4.6	4.5	4.0	4.3	5.3	2.7	3.1	5.2
					.09	.06	.003	.7	0	.03	0	1.2	.11

Data by INAA (NAGASAWA *et al.*, 1979). Reproducibility for INAA values of Al₂O₃, MgO, CaO and MnO are 3, 10, and 5 (%), respectively. Those for FeO and Na₂O are indicated in Table 1. Larger statistical errors are indicated in parentheses.

with those of terrestrial silicates.

We prepared the following check-list for identification of "cosmic" spherules.

- #1. Similarity of REE abundance pattern to those in meteorites.
- #2. Anomalies of Ce, (Eu), Tm and/or Yb.
- #3. Irregular REE pattern which cannot be expected from crystal chemical or cosmochemical fractionation of the solar REE.

The criterion #1 accounts for a meteoritic origin of a spherule; #2 accounts for an origin as a high temperature condensate in a primitive solar nebula or in a supernova, or an evaporation residue of meteoritic material or cosmic dust etc.; #3 indicates an extrasolar origin. In applying the above check-list, alteration effect must be taken into consideration.

RESULTS AND DISCUSSION

The results of INAA of the spherules are listed in Table 2 and those of major element analysis are listed in Table 3. The major and trace element compositions of type 1 - 3 spherules are fairly similar, while the type 4 spherule #G shows major and trace element compositions which are substantially different from those of type 1 - 3 spherules: spherule #G is enriched in Mg, Ca and Sc and depleted in most other analyzed elements compared with type 1 - 3 spherules.

Type 1 - 3 spherules Major and trace element compositions of type 1 - 3 spherules in Tables 2 and 3 are similar and are indistinguishable from those of oceanic sediments (SVERDRUP *et al.*, 1942; WILDEMAN and HASKIN, 1965). The similarity of the spherules and oceanic sediments in chemical compositions is best demonstrated by their REE abundance patterns shown in Fig. 1. The REE patterns of type 1 - 3 spherules are parallel with each other with differences in absolute abundances of up to a factor of about 5, and fall approximately within the range of those of oceanic sediments observed by WILDEMAN and HASKIN (1965). Thus, REE abundances, together with major element compositions, indicate marine origin of the spherules (NAGASAWA *et al.*, 1979).

Most of the type 1 - 3 spherules show negative or positive Ce anomalies. As discussed in the previous paper (NAGASAWA *et al.*, 1979), the Ce anomalies appear to indicate interaction between the spherules and the ocean water which is depleted in Ce possibly due to existence of Ce as Ce⁴⁺ (GOLDBERG *et al.*, 1963). The observed variations in size and polarity of the Ce anomalies were explained by variable ratios of Ce⁴⁺-rich, REE³⁺-poor phase to Ce⁴⁺-poor, REE³⁺-rich phase in the spherules. The observed variation of the absolute REE abundances can also be accounted for by the variable ratios of REE-rich to REE-poor phases. Since micro-manganese nodules are common in the sediments

Fig. 1. REE and Sc abundances of the silicate spherules normalized to chondritic average values plotted against REE atomic number. Broken lines indicate REE abundances for NASC (HASKIN and PASTER, 1979). Spotted area indicates the range of values for oceanic sediments determined by WILDEMAN and HASKIN (1965).

along with the spherules, and are expected to have high Ce content (PIPER, 1974), a Ce-rich component which is similar to those in the manganese nodules is possibly present in the spherules to produce the positive Ce anomalies. Phillipsite (M5 in Table 2) showed positive Ce anomaly. However, Ce concentrations are too low to explain the Ce anomalies in the spherules. Although REE concentrations in mordenite is not known, there is no particular reason to believe that mordenite has much higher Ce content compared with phillipsite.

Similarity of the relative REE abundance patterns in the spherules to that of the North-American Shele Composite (NASC) HASKIN and PASTER, 1979) which approximates REE supplied to the ocean water shows that REE, except Ce, are in amorphous phase rather than in

mineral phase, since minerals fractionate REE by the crystal structure-ionic size controlled mechanism (MATSUI *et al.*, 1979).

Mineral compositions of the spherules determined by powder X-ray diffraction pattern also indicate the marine origin of the spherules. The X-ray pattern showed lines^{a)} correspond to those of gismondite, a zeolite with a chemical formula of $(Ca,K,Na)Al_2Si_2O_8 \cdot 4H_2O$. The X-ray powder patterns suggest that small amounts of phillipsite, $(Na,K,Ca)_5Al_5Si_{11}O_{32} \cdot H_2O$ also exist. These minerals are usually associated with materials originated under marine conditions, but have not been found in cosmic materials such as meteorites. Major element compositions determined by point analysis with an electron microprobe analysis (Table 3) do not agree well with the compositions of either gismondite or phillipsite, although the most abundant cations, Na, K, Ca, Al and Si are the same as in both minerals. The disagreement may be due to the presence of zeolite minerals as small grains. Line scan of electron microprobe across the sample surface, in fact, indicated short scale variations of chemical compositions.

The above discussion indicates the type 1-3 spherules are mixtures of mineral phases, mostly zeolites, and amorphous phases produced under marine environment in contact with ocean water. However, the possibility remains that some of the spherules have cores of extraterrestrial origin, on which outer terrestrial layers have grown in marine environment. The growth mechanism might well be the same as those for manganese nodules.

Type 4 spherule Type 4 spherule was very rare in the deep sea sediment sample. Only one large glassy spherule was found from the sample and found to be extraterrestrial in origin (NAGASAWA *et al.*, 1979) on the basis of criteria #1 of the extraterrestrial material discussed in the previous section. The observed large negative

a) Lines at 7.48 (s), 4.18 (s), 3.23 (vs), 2.99 (w), 2.72 (s), and 1.79 (w) (d in Å) correspond to major lines expected for gismondite, where vs, s and w denote very strong, strong and weak lines, respectively.

Ce anomaly in the spherule G satisfies the criteria #2. The anomaly appears to be due to the evaporation loss by heating when the original meteoritic material entered the earth's atmosphere.

Some other oceanic sediment samples we recently studied have much higher concentrations of type 4 spherules. We found spherules of various colors, such as green or yellow, as well as transparent ones with sizes from a few to a few tens of microns. Analysis of the spherules are now under way.

Mineral grains Results of INAA of mineral grains are shown in the last 4 columns in Table 2. M1 shows very low trace element concentrations suggesting M1 to be quartz crystal. The observed trace elements are expected to be in surface contaminants or material attached to the crystal.

M5 is a phillipsite identified by X-ray pattern. REE concentrations in M5 is very low with the exception of Ce which is enriched by factor of 3 or more compared with other REE on the basis of chondrite-normalized abundances. PIPER (1974) reported high REE abundances in phillipsite with relative abundances similar to those in ocean water, i.e. enrichment of light REE with a large negative Ce anomaly. The observed large discrepancy in REE abundances between the PIPER's values and the present data suggests that REE are not only in the crystal sites replacing major cations but also adsorbed in the cavities in the zeolite structure. Some of the mineral grains had semi-spherical shape which were first misclassified as type 4 by observation under microscope.

SUMMARY

The glasses prepared from JB-1 and BHVO-1 were found to have excellent homogeneity which is appropriate as standard for INAA of small scale samples of less than 1 mg. By use of the glass standards, small samples, possibly as small as 10 μ g, can be analyzed for REE and other

trace elements by INAA with accuracies normally available for mg-scale samples, say, less than 5% for 7 REE (La, Ce, Sm, Eu, Tb, Yb and Lu) and Sc.

Chemical composition, together with mineral composition, indicate that most of the silicate spherules classified as types 1, 2 and 3 have marine origin, whereas a type 4 glassy spherule #G is meteoritic in origin.

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APPENDIX

Densities of the spherules measured by Stokes' method^{a)} (HUNTER and PARKIN, 1965).

Number	Diameter (μm)	Density (g/cm^3)
Group 1 - 3		
1	790	2.31
8	800	2.35
10	650	2.40
47	580	2.45
48	490	2.65
55	610	2.76
56	485	2.66
65	515	2.36
69	430	2.51
86	515	2.47
90	490	2.51
107	445	2.52
113	395	2.95
		av. 2.53
Group 4		
G	780	3.04

a) Density d was calculated by Stokes' equation: $d = d' + 18Vn/gD^2$, where d' is the density of glycerin (g/cm^3), V is the terminal velocity (cm/sec) measured dropping the spherule in glycerin, D is the diameter of the spherule (cm) and n is the viscosity of glycerin (poise).