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PIXE ANALYSIS OF MAGNETIC SPHERULES IN PALEOZOIC-MESOZOIC BEDDED CHERT

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Abstract: Particle Induced X-ray Emission (PIXE) was applied to the elemental characterization of magnetic microspherules collected from the Paleozoic and Mesozoic bedded chert in Southwest Japan. Comparison of the titanium and chromium contents of the spherules with the magnetic components of meteorites and volcanic ash showed that this technique offers promising potential as a new method for distinguishing between spherules of terrestrial and extraterrestrial origin.

1. Introduction

Elemental characterization in geochemical and cosmochemical investigations often requires relatively rapid analytical techniques with high sensitivity and multi-element capability. Although several analytical advances have been made over the decades, the problem of analyzing micro-sized samples with high precision is yet to be resolved. Magnetic microspherules offer a typical sample, where elemental analyses are fundamental for fingerprinting their origin.

It is difficult to determine the origin of microspherules. Their typical surface texture strongly implies a cosmic origin, compared with spherules collected from modern deep sea cores, and it is possible that most of the spherules are actually of extraterrestrial origin. An additional difficulty in attempting to determine their origin is to elimination of the possibility of volcanic origin. We had been using EPMA to study magnetic spherules collected from radiolarian chert (Fig. 1), but were hampered by its limited penetration capability, especially for titanium and chromium analyses (IWAHASHI *et al.*, 1991). Recently, we found that proton beam used in PIXE analysis provides a deeper penetration depth, making it an important technique of *in situ* analysis (JOHANSSON and CAMPBELL, 1989).

2. Sample Preparation and Measurement

2.1. *Sample preparation*

To provide a standard profile for extraterrestrial sample, the magnetic components of six meteorites were analyzed: ALH-77294,86 (H5), Y-74371,87(H4),

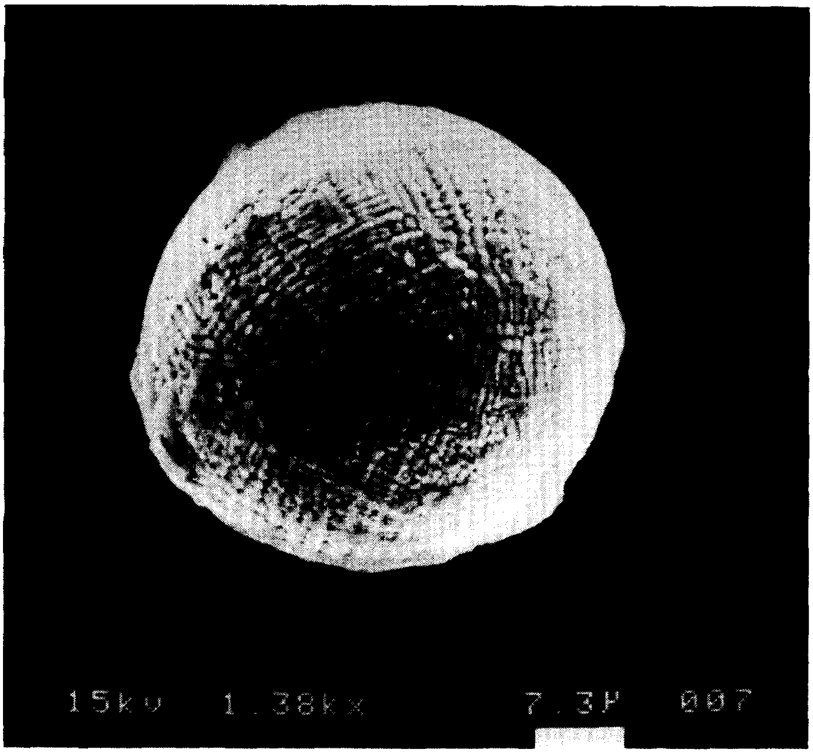

Fig. 1. Photograph of spherules collected from the Cretaceous chert.

Y-74115,101(H5), Y-81124,93(H5), Y-74647,70(H5) and La Criolla(L6). For terrestrial samples, eleven magnetic components of volcanic ash and one magnetic component of chert were analyzed. The volcanic ash was collected from Kagoshima Prefecture and the Osaka area. Our bedded chert samples were collected from four other areas in Japan: Gujohachiman in Gifu Prefecture (Permian and Triassic), Ryozen in Shiga Prefecture (Permian and Triassic), Inuyama in Aichi Prefecture (Permian and Triassic), and the Yokonami Peninsula in Kochi Prefecture (Cretaceous). The ages of the specimens were determined by their radiolarian record. The process of sample preparation was as follows. First, a rock sample taken from the bedded chert was put in between two copper plates and crushed by a vice. The crushed powder was then sieved (35 mesh, sieve opening: 420 microns), separating out the bigger fragments (IWAHASHI *et al.*, 1991). Using a hand magnet, the magnetic components were carefully separated from the rock powder. The magnetic components were then transferred to adhesive tape and the spherules were carefully removed with a needle under a microscope. The magnetic components remaining after the spherules were removed were analyzed as the magnetic components of the terrestrial chert.

2.2. *Experimental procedure*

To carry out the samples are mounted on a backing material. The backing material should be as small as possible in order to minimize bremsstrahlung background, and its elemental components should have the lowest possible atomic number in order to minimize both the energy and intensity of bremsstrahlung to ensure that it contributes no characteristic X-rays to the observed spectrum. Furthermore, it should be free of elements such as sodium and fluorine which produce γ-ray back-

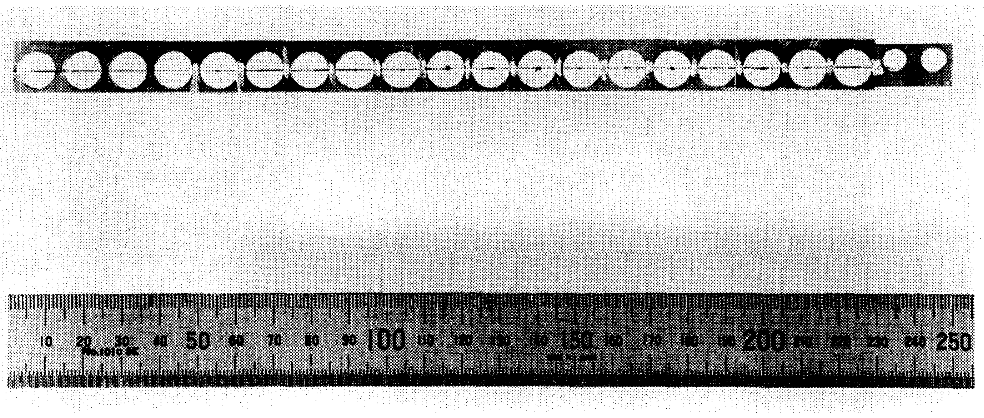

Fig. 2. The sample holder with strained carbon fiber. The samples are mounted on the fiber with collodion.

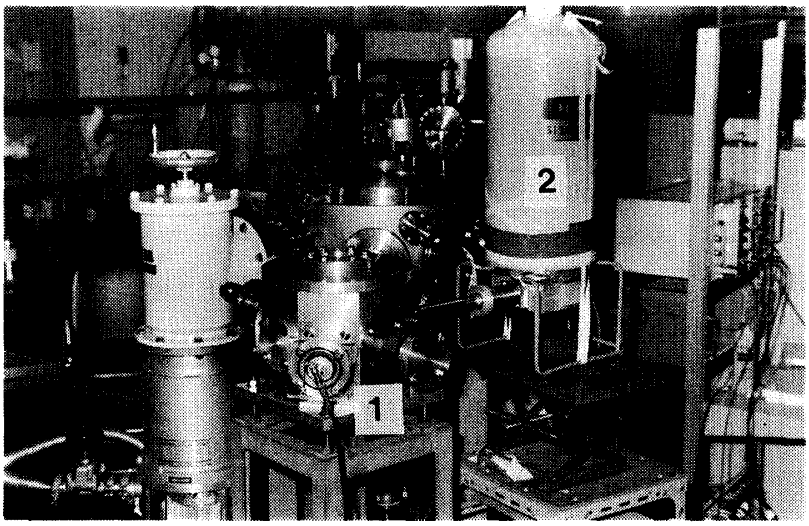

Fig. 3. The experimental arrangement at Ritsumeikan University. "1" is an experimental chamber and "2" a Si (Li) detector.

ground (JOHANSSON and CAMPBELL, 1989). We thus adopted a high-purity carbon fiber approximately 30 μm in diameter for the backing. The fiber was strained on a sample holder with 19 holes (each 10 mm in diameter), and the samples were mounted on the fiber at the center of the hole with collodion. The sample holder with the strained carbon fiber is shown in Fig. 2.

PIXE analysis was performed using the 1.3 MeV proton beam from the Compact Disktron accelerator (Physitec Co. Ltd., Tokyo, Japan) at Ritsumeikan University. The proton beam enters the aluminum scattering chamber through a collimator (2 mm in diameter). The intensity of the beam current during each run was monitored by a Faraday cup. The typical current on the target was 3 nA. The characteristic X-rays from the sample were detected by a Si (Li) detector. The signal was fed to a multichannel analyzer through an amplifier, and analyzed by a NEC PC-9801 computer with an EMCA analysis program (SEIKO EG&G Co.). The irradiation time was typically 10–20 min.

The X-ray spectra are processed by an appropriate program which substracts the average experimental background and evaluates the correction of escape peak by Fe and Ti using the standard reference samples, Fe, Ti and titanium-stainless steel (Ti 5%, Mn 2%, Cr 10.5%, Ni 18%, Si 1% and Fe 63.5%). Errors associated with PIXE data are the standard deviations expected from counting statistics.

The experimental arrangement is shown in Fig. 3.

3. Results and Discussion

A typical PIXE spectrum of the spherules is shown in Fig. 4. The spectrum is characterized by a number of distinct peaks. These compositional peaks correspond to elements such as Fe, Cr, Ti and Mn. Although Ni and Co are considered to be elements typically present in extraterrestrial material, they were not found in these samples. As this is a necessary but not sufficient condition, it may be that the origin of microspherules from the Paleozoic-Mesozoic chert nevertheless have an interstellar origin. There are, however, serious difficulties with this approach which we have covered in another study (MIONO, 1991).

The Ti/Fe and Cr/Fe ratios of the magnetic components of the volcanic ash, chert, meteorite and spherules are summarized in Table 1, and are plotted on a diagram of Ti/Fe vs. Cr/Fe in Fig. 5.

From our analytical results, it was found that titanium and chromium are indicator elements for clearly eliminating a volcanic origin, as is evident from Fig. 5. When it is considered that the titanium content depends on the temperature of crystallization, it is quite reasonable result that volcanic ash contains a larger amount of titanium than extraterrestrial material. Consequently, the Ti/Fe and Cr/Fe ratios are fundamental for distinguishing between terrestrial and extraterrestrial origin. A similar suggestion has been reported by BORNHOLD and BONARDI (1979) and GAO

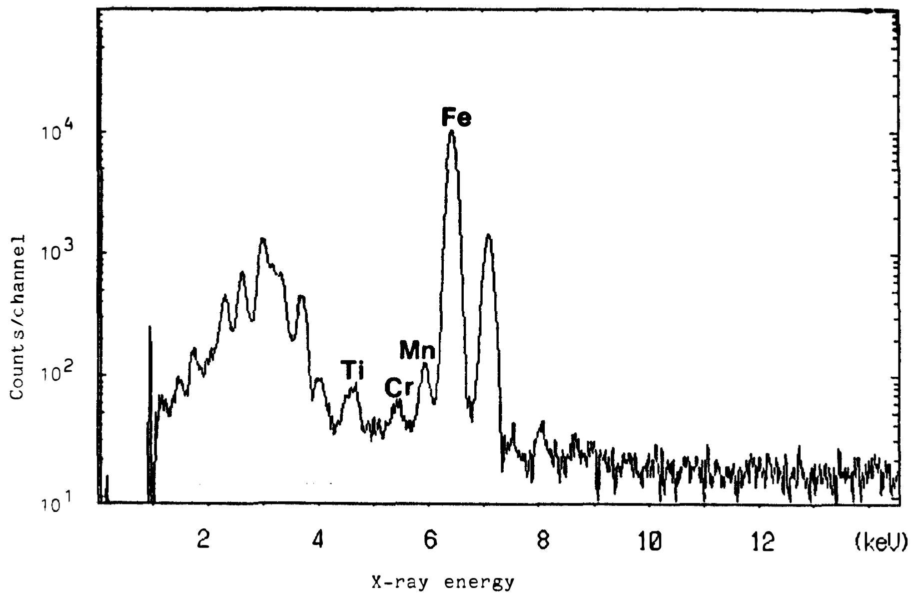

Fig. 4. A typical PIXE spectrum of the spherule. The spherule is Spherule 1 in Table 1.

Table 1. The ratios of Ti, Cr, Mn, and Ni to Fe. Volcanic ash samples were collected from the Osaka area (Nos. 1–10) and Kagoshima Prefecture (No. 11). Mag. comp. of chert and spherules were collected from Inuyama (Nos. 1–3) and Yokonami (Nos. 4, 5) samples. Errors represent one standard deviation.

	Mn/Fe×0.01	Ni/Fe×0.01	Ti/Fe×0.01	Cr/Fe×0.01
ALH-77294,86	1.119±0.028	3.361±0.083	0.244±0.008	1.004±0.022
Y-74371,87	0.073±0.007	5.140±0.102	0.095±0.005	0.145±0.008
Y-74115,101	0.825±0.024	9.463±0.140	0.080±0.004	0.129±0.008
Y-81124,93	0.601±0.020	3.197±0.079	0.096±0.005	0.236±0.011
Y-74647,70	0.058±0.006	4.710±0.096	0.095±0.005	0.195±0.010
La Criolla	0.430±0.018	7.917±0.128	0.124±0.005	0.613±0.017
Volcanic ash 1	0.914±0.340	—	18.405±0.114	0.096±0.009
Volcanic ash 2	1.562±0.030	—	31.754±0.121	0.040±0.004
Volcanic ash 3	0.937±0.087	—	46.471±0.608	—
Volcanic ash 4	1.241±0.029	—	32.360±0.129	0.009±0.002
Volcanic ash 5	0.799±0.025	—	9.783±0.061	0.090±0.007
Volcanic ash 6	0.274±0.013	—	5.833±0.040	0.113±0.009
Volcanic ash 7	0.196±0.196	—	18.602±0.083	0.062±0.005
Volcanic ash 8	0.353±0.058	—	30.634±0.459	0.271±0.042
Volcanic ash 9	1.463±0.018	—	30.011±0.068	—
Volcanic ash 10	1.172±0.033	—	35.245±0.163	0.011±0.002
Volcanic ash 11	0.601±0.020	—	5.630±0.040	0.166±0.009
Mag. comp. chert	0.825±0.024	0.169±0.018	4.410±0.035	0.148±0.008
Spherule 1	0.394±0.017	—	0.128±0.005	0.109±0.007
Spherule 2	0.312±0.051	—	0.049±0.011	0.242±0.040
Spherule 3	0.588±0.113	—	0.444±0.057	0.776±0.109
Spherule 4	0.419±0.060	—	0.109±0.017	0.186±0.033
Spherule 5	6.260±0.536	—	0.262±0.062	41.392±1.490

—: Not detected.

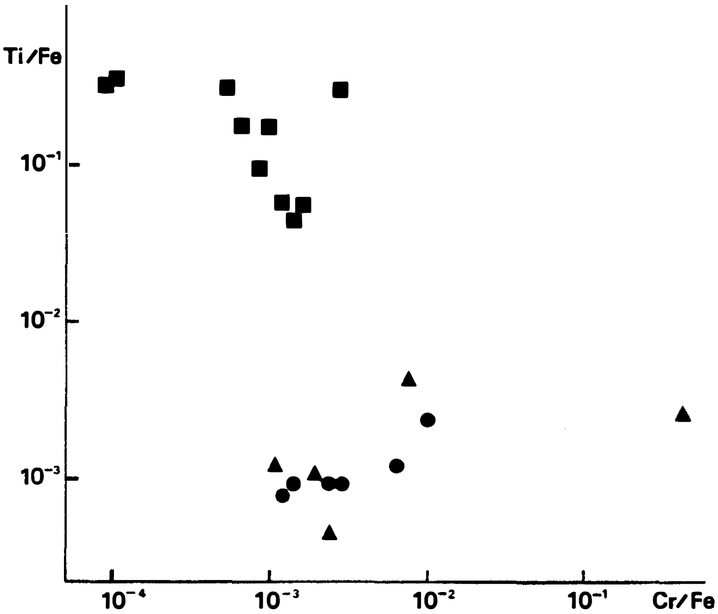

Fig. 5. A plot of Ti/Fe vs. Cr/Fe ratios.
▲ *spherule.*
■ *magnetic components of chert and volcanic ashes.*
● *magnetic components of meteorites.*

et al. (1987). However, we found that PIXE allows much more quantitative analysis and seems to be offer a firm basis for establishing the extraterrestrial origin of the individual microspherules we examined from the Paleozoic-Mesozoic bedded chert.

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