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THE $^3He/^4He$ RATIO IN A CLAY FROM THE K-T BOUNDARY HOKKAIDO, JAPAN

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Abstract: We measured the He content and the $^3He/^4He$ ratio of a K-T boundary clay from Hokkaido. If some meteoritic debris which escaped total melting or evaporation at the K-T event remains in the clay, it may be possible to observe some ^3He in it. However, we could determine only the upper limits of the $^3He/^4He$ ratois ($< 6.2 \times 10^{-6}$ for a bulk sample) because of the small amount of ^3He. Three alternatives are considered to explain the result.

1. Introduction

It is well-known that drastic extinctions of many species occurred at the Cretaceous-Tertiary (K-T) transition about 65 million years ago. In 1977, ALVAREZ *et al.* collected clay from the K-T boundary at Gubbio in Italy and detected anomalous Ir contents up to about 9 ppb (ALVAREZ *et al.*, 1980). While cosmic materials such as CI chondrites contain about 500 ppb Ir (*e.g.*, CROCKET *et al.*, 1967), the Earth's crust is depleted in Ir (about 0.03 ppb, CROCKET and KUO, 1979). Hence, ALVAREZ *et al.* (1980) concluded that the Ir anomaly was caused by impact of a meteorite of about 10 km in diameter. Since then, several workers have measured Ir in K-T boundary clays from all over the world (*e.g.*, KYTE *et al.*, 1980; GANAPATHY, 1980; SMIT and HERTOGEN, 1980; ORTH *et al.*, 1981). By 1986, Ir anomalies were detected at 75 localities (ALVAREZ, 1986). Therefore, we can conclude that the Ir anomaly is a worldwide phenomenon.

Two hypotheses have been proposed to account for the origin of the Ir anomaly: Impact of cosmic materials (*e.g.*, ALVAREZ *et al.*, 1980; HSÜ, 1980; GANAPATHY, 1980) and volcanic eruption (*e.g.*, OFFICER and DRAKE, 1983). The amount of Ir distributed over the Earth due to the K-T event is estimated to be 63×10^{-9} g/cm^2 corresponding to 32×10^{10} g for the entire Earth (ALVAREZ *et al.*, 1982). In the first hypothesis, a meteorite with CI composition and 10 km diameter can explain the estimated amount of Ir. The hypothesis of a volcanic eruption was postulated because Ir-rich particles were collected at vents in Kilauea volcano in Hawaii (ZOLLER *et al.*, 1983; OLMEZ *et al.*, 1986). OLMEZ *et al.* (1986) estimated the amount of Ir emitted by a large scale volcanic eruption to be 3 gIr/10^6 m^3 of magma. During the Cretaceous-Tertiary transition, the Deccan trap in India was active. By estimating the volume of magma from this event to have been 10×10^6 km^3, these authors calculated that 3×10^{10} g Ir must have been emitted from the Deccan, which is about one order of magnitude less than the Ir amount at the

K-T boundary estimated by ALVAREZ *et al.* (1982). However, considering the uncertainty in these estimates, we cannot rule out totally the hypothesis of a volcanic eruption.

It seems to us that more information, especially from isotopic data, is needed to understand the origin of the mass extinction at the K-T boundary. Noble gas isotopic data have been reported by EUGSTER *et al.* (1985) and by LEWIS and WOLBACH (1986) who studied a K-T boundary clay form Stevns Klint in Denmark. EUGSTER *et al.* (1985) measured all noble gases of the clay. They focused mainly on He isotopic ratios of residue which remained after etching by HCl and HF. They measured the ^{3}He/^{4}He ratios of the residue by stepwise heating and found values up to 6×10^{-5}. They attributed the high ratios to terrestrial sources, such as outgassing of primordial ^{3}He or ^{6}Li$(n, \alpha)^3$H reaction. LEWIS and WOLBACH (1986) also treated the clay from New Zealand in addition to the clay from Denmark. They analyzed Xe in the residue, which was obtained by etching with HF and HCl followed by oxidation by HNO_3 or $HClO_4$. Their aim was to detect CCF-Xe (carbonaceous chondrite fission Xe), characteristic component in meteorites. However, they could not detect CCF-Xe. Both groups could not draw any definite conclusion from their noble gas data.

In order to find isotopic evidence which may help us to understand the K-T event, we focused in this work on ^{3}He: the ^{3}He/^{4}He ratios in extra-terrestrial materials are significantly higher than those in terrestrial materials. For example, He-A which is representative of the primordial He in meteorites has ^{3}He/^{4}He ratio of about 1.4×10^{-4}, and solar wind He has a ratio of 4×10^{-4} (*e.g.*, OZIMA and PODOSEK, 1983). On the other hand, the ^{3}He/^{4}He ratios in terrestrial materials are lower than those of extra-terrestrial materials. For example, that of air is 1.4×10^{-6}. Many terrestrial samples contain a large amount of ^{4}He which is produced from radiogenic decay of U and Th. That is, the ^{3}He/^{4}He ratios in extra-terrestrial materials are distinct from those in terrestrial materials. Furthermore, abundance of He in the Earth is several orders of magnitude lower than the cosmic abundance (BROWN, 1952). As a result, helium becomes an extremely sensitive indicator of incorporation of extra-terrestrial materials in terrestrial materials.

If there is any meteoritic debris in a K-T boundary clay, we may detect some anomalous ^{3}He/^{4}He ratio. It is likely that most noble gases, especially helium, will have been lost at impact. However, it is not entirely unreasonable to expect that a small fraction of meteoritic debris survived without being degassed and we might detect some extra-terrestrial ^{3}He. Therefore, we measured the ^{3}He/^{4}He ratio and the He content in the clay from K-T boundary from Hokkaido.

2. Experimental Procedure

2.1. Sample description

The clay from the K-T boundary was collected at Ikeda-cho, Honbetsu, which is located in the eastern part of Hokkaido in Japan, by the group of Prof. T. SAITO at Yamagata University. He identified the K-T boundary on the basis of foraminifera. Paleomagnetic data show that the clay layer is included in the magnetic reversal zone 29R, which is the same zone as other K-T boundary clays measured in the world. The

width of the clay layer is about 10 cm. Upper and lower layers of clay consist of mudstone. The K-T boundary clay layer is more black and softer than the upper and lower layers. Y. SAITO (private communication, 1986) at the National Science Museum in Tokyo analyzed this clay using a microscope and an electron microprobe and found that most of the minerals are clay minerals with Ba-bearing minerals (barite and romanechite) and a small amount of coarse-grains of quartz. The sedimentation rate was estimated using paleomagnetic information. The mean sedimentation rate for layers including the K-T boundary layer was estimated to be 15 mm/10^3 y. However, the Ba content of the K-T boundary clay is about six to seven times larger than that of the surrounding layers. Ba-bearing minerals are considered to be authigenic. Since they are likely to be generated nearly at a constant rate, the sedimentation rate of the K-T boundary clay is considered to be about one-sixth of that of the surrounding layers, that is, 2.5 mm/10^3 y. Therefore, the total time needed to form the K-T boundary clay is estimated to be forty thousand years. Iridium in this K-T boundary clay was measured by W. ALVAREZ (private communication with T. SAITO, 1986) in Berkely. But he did not detect Ir.

2.2. *Sample preparation*

We prepared three samples of the K-T boundary clay for He isotopic study: a bulk sample, an acid residue and a magnetic fraction. First, the K-T boundary clay was pulverized. An aliquot of the sample was used for a bulk analysis. For chemical treatment, a sample of 301.49 mg was mixed with HF and HCl. The sample was put into a teflon container which was enclosed in a stainless steel cylinder, and baked at 80°C for 16 h followed by 120°C for 24 h. Then the residue was rinsed with distilled water. By this treatment we obtained 79.41 mg of acid residue which corresponds to 26% of the original clay mass. The third sample was a magnetic fraction of the clay. We intended to check whether the clay contains a significant amount of IDPs (Interplanetary Dust Particles) which continuously fall on the Earth (*e.g.*, OZIMA *et al.*, 1984). IDPs are enriched in magnetic fractions of deep sea sediments (MERRIHUE, 1964; TILLES, 1966; AMARI and OZIMA, 1985). From a sample of 308 g of the K-T boundary clay, only 0.49 mg of a magnetic fraction was collected. These three samples we redried in an oven at 120°C and packed into aluminum foils.

2.3. *Mass spectrometry*

Helium analyses were performed using a "Nuclide" mass spectrometer, which is a 60 degree deflection sector mass spectrometer with a double collector. The resolution of the mass spectrometer is about 600, which is sufficient to resolve ^{3}He from HD and H_3. Noble gases were extracted using a resistance-heated high temperature furnace, which was originally designed by TAKAOKA (1976). The samples were heated at 1510°C for 30 min. Extracted gases were purified by a Ti-furnace at about 800°C to remove active gases. Activated charcoal at liquid nitrogen temperature was used to trap noble gases except for He and Ne. Then He and Ne were introduced into the mass spectrometer. For ^{3}He an electron multiplier and for ^{4}He a Faraday collector were used. The typical hot blank of ^{3}He and ^{4}He was 1×10^{-13} cm^{3}STP and 8×10^{-9} cm^{3}STP, respectively.

3. Results and Discussions

In Table 1 we summarize the experimental results on He isotopic ratios and He contents. The ^{3}He content is nearly the same as ^{3}He in hot blanks. Therefore, we could determine only the upper limits of ^{3}He/^{4}He ratios and ^{3}He contents. The observed ^{4}He can be attributable to a product of radiogenic decay from U and Th.

Table 1. Helium in samples from the K-T boundary Hokkaido.

Sample	Weight (mg)	^{3}He/^{4}He (10^{-6})	^{3}He (10^{-12} cm^3 STP/g)	^{4}He (10^{-7} cm^3 STP/g)
Bulk	103.10	<6.17	<1.62	2.61 ± 0.24
Acid residue	49.22	<14.7	<3.56	2.41 ± 0.22
Magnetic fraction	0.49	<34.9	<339	97.3 ± 8.9

From He data alone, we cannot draw any definite conclusion. However, considering the fact that Ir is not detected in the clay, we can consider three possibilities: (1) Meteoritic debris or emitted particulates from volcanic eruption did not reach Hokkaido. (2) Ir-bearing materials are distributed heteorgeneously over the whole layer ($\sim$10 cm) and we collected the sample from a part which does not contain excess Ir. (3) Noble gases of cosmic origin were degassed at the impact event or lost by diffusion.

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