Measurement of Iridium in the P/T Boundary Layers in Gifu by Neutron Activation Method

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Abstract

Measurement has been made of Ir content in samples collected from P/T boundary layers in Gifu, Japan. The samples were collected from the site where fullerenes have been found. The samples were first crashed into powders and then activated in a nuclear reactor. The gamma ray measurement of the samples was made after cooling for two months. None of the samples analyzed yielded Ir content comparable with the well-known K/T boundary layer at several ppb's. In view of other experiments which yielded negative results, it is tentatively concluded that the P/T boundary does not provided a geological evidence of extra-terrestrial cause in the form of Iridium.

1. Introduction

The Permian/Triassic boundary is dated 250 million years BP. The boundary is well-known for the extinction of many species. In terms of the number of species which became extinct over the boundary, the extinction was even more severe than the Cretaceous/Tertiary boundary where the well known dinosaurs extinction took place. According to Sepkoskii (1996), the percentage of extinct marine genera over the P/T boundary is close to 60%, compared with 40% of the K/T boundary. Although there are a number of geological evidence which support extra-terrestrial event for the K/T boundary, geological evidence for the P/T boundary is rather poor.

For the K/T boundary, there is the well known crater at Chicxulub, Mexico, worldwide Iridium deposit (Kyte & Wasson 1986), extra-terrestrial amino acid (Zahnle & Greenspoon 1990), and so on. In view of the fact that the first extra-terrestrial evidence for the K/T event was the discovery by Alvalez et al (1980) of the Ir in the boundary clay, it is of considerable interest to see if one can detect Ir in the P/T boundary at a level similar to the K/T boundary.

There is a paper by Yi et al (1985), where the authors claimed to have detected Ir in the material collected from southern China. However, they detected Ir from one among the 10 samples for which detection measurement has been made; for the remaining samples, no Iridium has been detected. No mention is made of the experimental procedure nor the probable errors associated with the measurement. Thus, it seems still premature to regard the iridium detection as firmly established. Here we wish to report a measurement intended to verify if the claimed detection may be substantiated when other sites of the P/T boundary are investigated.

2. The boundary layer

In Japan, there are three sites where the P/T boundary layers are exposed. Of these, two are widely acknowledged as genuine P/T boundary. They are at Kinkazan and at Unuma, both in the prefecture of Gifu. The third site in Sasayama, Tanba is somewhat problematical. Although the site in Sasayama, Tanba is the place where Becker et al (2001) collected samples and claim to have detected extra-terrestrial Helium encapsuled in fullerenes. Their claim is questioned by Isozaki (2001). Thus, instead of Tanba, Sasayama, we have chosen Kinkazan and Unuma boundaries. in Gifu Prefecture. These are the sites well known for the exposed P/T boundaries. We note that Chizawa et al (1999) found fullerenes from the P/T boundary layer at Kinkazan.

The picture of Kinkazan site is shown as plate 1. It is part of the Kinkazan park of Gifu city. The layer is fairly thick, but a clay layer similar to the K/T boundary in Gubbio, Italy has not been identified. It is therefore not possible to pinpoint a layer which one can claim as the boundary. This is a situation typical of the P/T boundary. We have collected three samples from the layer.


[plate1.jpg]

Plate1: Gate to the passage of Kinkazan, where the samples were collected.


[plate2.jpg]

Plate2: The rock of the P/T boundary (lower Triassic).

At Unuma, the boundary is exposed as a bed of Kiso river. We have also collected three samples from the site. Stratigraphic chart of Chijiwa et al (1999) shows that Kinkazan is just above the late-Permian, whereas Unuma section belongs to middle Triassic.

3. Method of measurement

In order to measure Ir contained in a geological sample, activation of the sample by neutrons is needed, because Iridium is extremely rare not only in the earth crust, but also in extra-terrestrial bodies.

We have used the nuclear reactor of the Kyoto University Reactor Laboratory. Earlier, we have adopted the neutron activation method to measure Ir content of a Yamato carbonaceous chondrite collected from the Southern Pole (Yabushita et al 1988).

The samples were prepared in the following manner. Each sample of approximately 100 mg was crashed by a plier, and had been heated in an oven to 100 degrees Celsius for three days. After having measued the weight of each sample, they were contained in poly-ethylene bags. As monitors for comparison with the samples, we adopted 2.5μg of Ir, a similar amount of Cr and 25μg of Osmium. Each sample collected from three locations at Kinkazan, altogether three, was further dived into two and for each of them, the measurement has been made by the same procedure.

The samples activated in the reactor have been allowed to cool for 50 days until all of the short-lived radioactivity have decayed. The gamma ray counting has since been carried out using the gamma ray monitors. The actual measurement took place from September 9th to 14th, 2002.

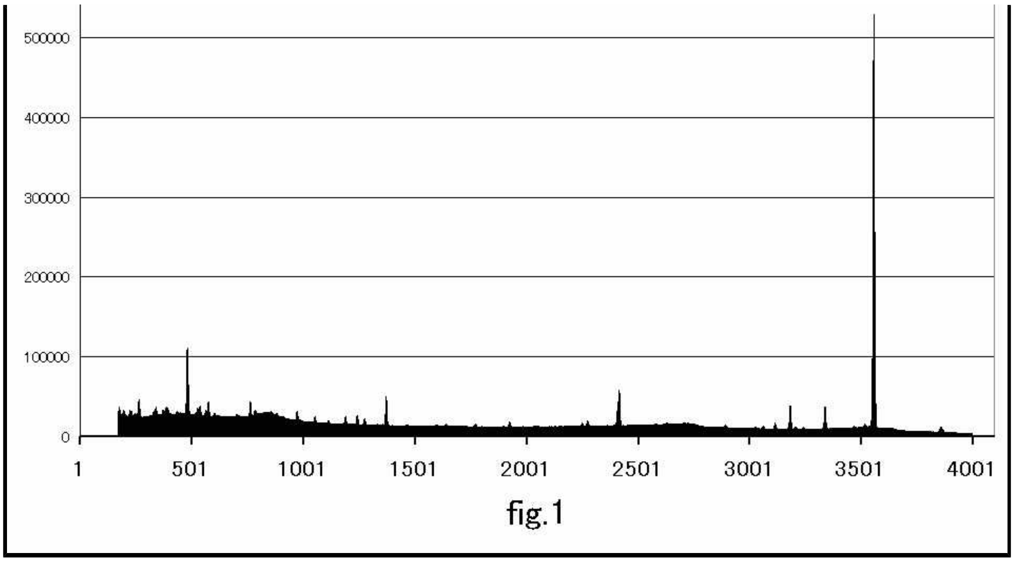
4. Result

Counting of the gamma rays is referred to as monitoring. The monitoring has been made at various energies of the gamma rays and the obtained spectrum is shown as Fig.1. For comparison, we give a similar spectrum for Iridium, which was used as standard in our experiment. The content of Ir was estimated by the gamma ray counting at channel numbers 1857-1882, although in some of the similar experiments, channel numbers 1251-1273 are adopted. The reason for our choice is that for the latter, there is a shoulder of Cr spectrum, which may not allow an accurate estimate of the contribution from Ir. In the Table given below (Table 1), the result of the measurement is presented.

Table 1:

	Iridium (ppb)	Cr (ppm)	Monitoring time
Unuma 1 capsule 1	5.8±3.6	41.6±5.3	5h
Unuma 1 capsule 2	4.2±2.4	35.4±2.1	10h
Unuma 2 capsule 1	l.t. 5.3	92.6±10.9	5h
Unuma 2 capsule 2	7.6±3.8	95.4±4.0	10h
Unuma 3 capsule 1	l.t. 4.8	127.3±14.5	5h
Unuma 3 capsule 2	l.t. 5.4	124.3±5.3	10h
Kinkazan 1 capsule 1	l.t. 3.8	57.0±6.9	5h
Kinkazan 1 capsule 2	l.t. 2.9	55.9±2.8	10h
Kinkazan 2 capsule 1	l.t. 5.0	46.7±5.7	5h
Kinkazan 2 capsule 2	l.t. 2.7	46.9±2.1	10h
Kinkazan 3 capsule 1	l.t. 3.3	45.5±5.6	5h
Kinkazan 3 capsule 2	3.9±3.1	46.3±2.7	5h

As mentioned, the sample collected from one site had been divided into two, so capsules 1 and 2 correspond to the same original sample. The result of the measurement is shown in ppm (parts per million) and in ppb (parts per billion), for Cr and Ir, respectively. The figure after the ± sign denotes one standard deviation associated with the measurement. 'l.t.' in the Table indicates 'less than', or the upper limit of the measurement.



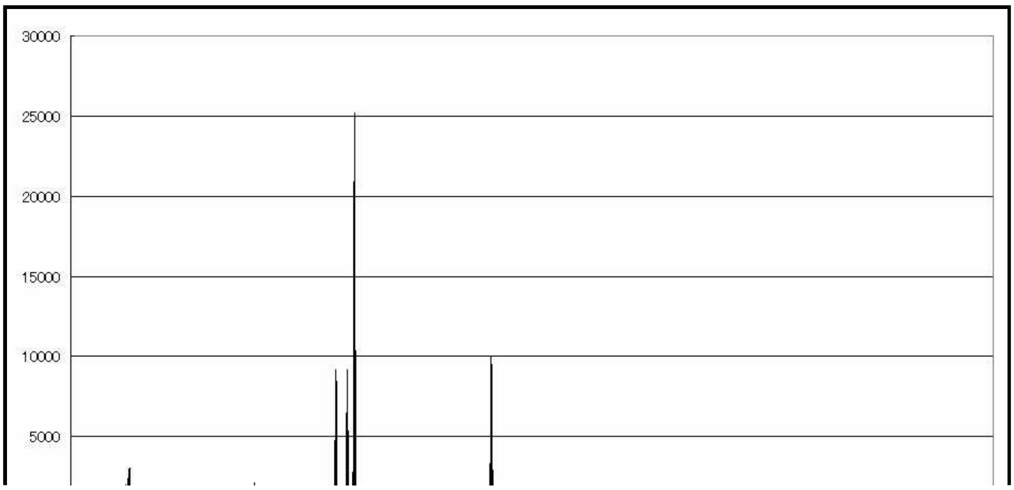
[fig1.gif]

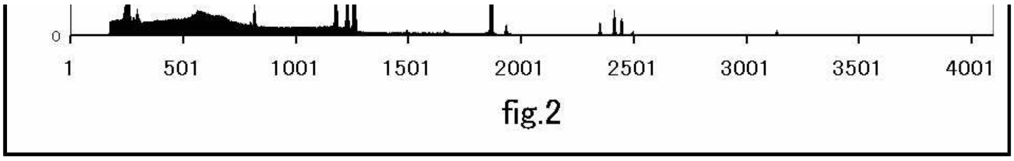
Figure1: Gamma ray energy spectrum of P/T boundary sample (Unuma 2, capsule 2) after neutron activation. Number count is plotted against channel number. Energy (in KeV) is calculated by the relation, $E(keV)=2.204+0.24890X+1.358*10^{-7}X^2$, where X stands for the channel number.

One can see that for Iridium, all of the mean values of the measurement are less than 2 standard errors. This shows that it is not possible to regard the measurement establishing the presence of Iridium at a level indicated by the mean values.

The standard error depends upon the monitoring time, and tends to decrease as longer monitoring time is adopted. Unuma 2 capsule no. 2 seemed most promising regarding the detection of Iridium. We therefore decided to carry out a similar monitoring for a much longer time. It is the usual procedure to increase the time by a factor of 10 to reduce the standard error, and so the gamma ray counting was done for 232042 seconds (64 hours). The result obtained is 1.80±1.48 ppb. It is seen that although the standard error has decreased, so has the mean value. This result indicates that the obtained mean value should not be taken to show the presence of Iridium at the nominal level.

We have thus to conclude that our measurement of the samples of the P/T boundary in Gifu prefecture failed to detect Iridium, comparable with the K/T boundary. We also give in Fig.2 the gamma ray spectrum of the measurement, together with a spectrum of Iridium adopted as the standard. Comparison of Fig.1 with Fig.2 clearly shows that the conclusion we have arrived at is well substantiated.





[fig2.gif]

Figure2: Gamma ray spectrum of Iridium (2.5μg) that was used as the standard. Total number count is plotted against the channel number. Note the difference between Fig.1 and Fig.2. There is no peak in Fig.1 which corresponds to Iridium.

5. Discussion

We now discuss the significance of the result obtained in the present paper in relation to earlier investigations.

As referred to in the introduction, Yi et al (1985) claimed to have found iridium in the P/T boundary layer of southern China. The experimental procedure of their measurement is not given in detail, except that the samples were first activated by neutrons in a nuclear reactor. They reported to have found a significant amount of Ir (2.48 ppb) from one of 10 samples, because they estimated that the minimum detectable Ir concentration is 0.5-0.6 ppb. It is not clear however, how they estimated the minimum level of detectable Ir concentration. At first glace, their result appears very similar to ours given in Table 1 in the sense that for some of the samples, the mean value is greater than the standard error associated with it. However, as shown by a result obtained with a longer monitoring time (62 hours in our case), the mean value itself decreased with the longer monitoring time, which shows that the first measurement should not be taken to show the presence of Ir at a nominal level indicated by the mean value.

Later, Clark et al (1986) measured abundances of chemical elements including Ir of the clay layer of the P/T boundary in Changxing, China and obtained the value 0.002 ppb for Iridium. This is certainly far less than either the K/T boundary value or the P/T value of 2.48 ppb obtained by Yi et al (1985). Thus Clark et al (1986) concluded that there is no indication of Iridium deposit over the boundary. Although our experimental procedure cannot yield a reliable value as small as Clark et al's, our result is more in accord with Clark et al's than Yi et al's (1985).

There is another report of geological evidence arguing for extra-terrestrial event ay the P/T boundary. We refer to the report of Becker et al (2001). Samples have been collected from alleged P/T boundary in Sasayama, Tanba from southwest Japan and it is reported that extra-terrestrial helium encapsuled in fullerenes were detected, indicating an impact of a large extra-terrestrial body. Isozaki (2002) on the other hand questioned the experimental procedure adopted by Becker et al (2001) and pointed out a possibility that the fullerenes were formed during the measurement process. Again, he even pointed out that the site of the sample collection may not match the exact P/T boundary.

Thus, when these results are taken as a whole, one is led to conclude that the evidence for extra-terrestrial impact at the P/T boundary is not convincing, to say the least, and perhaps it will be more reasonable to search the cause of the boundary event in terms of the terrestrial phenomena, such as massive volcanism in Siberia.

As by-product of our measurement, a considerable amount of Cr has been confirmed, as may be seen in Table 1. Clark et al's (1986) measurement has yielded the presence of Cr at abundances from l.t.2.7 to 66.6 ppm depending on the boundary sections. Our result shows that the abundance of Cr in our geological samples are significantly greater. A similar experiment carried out for the Sasayama, Tanba geological samples (Yabushita et al 2001) referred to above have also yielded values ranging from 25 to 150 ppm. It seems that the abundance of Cr varies significantly depending not only on locations, but on slight changes in the layers.

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References

- Alvarez, A. L., Alvarez, W., Asaro, H. V. & Michel, H. V., 1980, Science, 208, 1095.
- Becker, L., Poreda, R. J., Hunt, A. G., Bunch, T. E. & Rampino, M., 2001, Science, 291, 1530.
- Chijiwa, T., Arai, T., Sugai, T., Shinohara, H., Kumazawa, M., Takano, M., and Kawakami, S., 1999, Geophysical Res. lett. 26, 767.
- Clark, D. L., Cheng-Yuan, W., Orth, C. J. and Gilmore, J. S., 1986, Science. 233, 984.
- Isozaki, Y., 2002, Planetary People (in Japanese), 11, 29.
- Kyte, F. T. & Wasson, J. T., 1986, Science, 232, 1225.
- Sepkoski, Jr, J. J., 1996, in Global Events and Event Stratigrahyed ed. Walliser, O. H., Springer, Berlin.
- Yabushita, S., Wada, K., Moriyama, H. & Takeuchi, K., 1988, Earth, Moon, and Planets, 42, 301.
- Yabushita, S., Wada, K., H. Moriyama & Fujii, K., 2001, Unpublished.
- Yi, X. D., Lan, M. S., Fang, C. Z., Ying, M. X., Ying, S. Y., Wen, Z. Q. & Zhong, Y. Z., 1985, Nature, 314, 154.
- Zahnle, K. & Greenspoon, D., 1990, Nature, 348, 157.

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