# CHEMICAL SPECIES OF IRIDIUM AND OTHER TRACE ELEMENTS IN THE CRETACEOUS–TERTIARY BOUNDARY CLAYS AND ITS IMPLICATION*

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## ABSTRACT

The geological samples: Cretaceous– Tertiary (K– T) boundary clays, meteorites, volcanic lava, and ultrabasic rock were separated into carbonate, metal, sulfide, oxide, silicate and acid– resistant residue by a selective chemical dissolution procedure developed in our laboratory. Some conclusions were drawn by analyzing the chemical speciation of anomalous iridium in the above samples and especially by studying the characteristics of mineral components in those residue phases. (1) It is impossible that the anomalous Ir was caused by geochemical enrichment; (2) The iridium enrichment in the K– T boundaries did not necessarily associate with kerogen; (3) The volcano activity has participated in the extinction event at the end of Cretaceous; (4) Extraterrestrial impact was the trigger of K– T event. Then, we proposed a mixed model by which the extant anomalous Ir in K– T boundary clays was interpreted as a combined effect of extraterrestrial impact, volcano eruption and post– depositional redistribution.

**Keywords:** Iridium anomaly Chemical speciation Insoluble residue Spherule Transmission electron microscope

## I .INTRODUCTION

During the latest ten years, much attention has been paid to the sources of the anomalous iridium found globally widespread in Cretaceous– Tertiary boundary[1-4]. Since the first discovery of anomalous Ir in K– T boundary by Alvarez et al.[1] and their proposition of an asteroid impact hypothesis, scientists discovered that volcano eruption[5] and geochemical enrichment[6] could also explain the iridium anomaly. It means that the absolute abundances of anomalous Ir in geological boundaries are not exclusive criteria to judge their sources. Recently, interests have been focused on finding some new clues from special texture components, i.e. sanidine spherules[7], microtektite– like material[8] and shock– metamophic quartz[9]. Even though much succeeding research has been catalyzed, no imperative evidence either for or against any hypotheses has yet been given.

The present research on kerogen extracted from K– T boundary clay seems to shed some new light on this problem. Schmitz et al.[10], reported that the concentrations of Ir in kerogen leached from two K– T boundary clays may reach 1100

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ppb (Stevns Klint, Denmark) and 1500 ppb (Caravaca, Spain). Thus, the imperative problem is to evaluate the role of kerogen and to attempt to find whether the anomalous Ir is originated from biomass extinction, or in another words, organic matter and microbial activity may have played roles for the accumulation of Ir. Wells, et al.[11] reported that typical marine biological materials are low in Ir (range<4- 80 ppt). From such low abundances of Ir, we can deduce that marine organisms themselves can be rejected as a significant contribution of Ir to K- T boundary sediment.

We claim that critical problem to solve the sources of the anomalous Ir is first to find a factor which could indicate the different characters of Ir in its various enrichment mechanisms, including extraterrestrial, volcanogenic, biogenic and geochemical. We believe the chemical species of Ir could act as the finger to indicate its sources. So our research is focused on the chemical species of anomalous Ir in K-.T boundary samples and their difference from those of meteorites and/or volcanic materials. We attempt to draw a conclusion from the different behaviors of Ir to reveal the true enrichment mechanism of the anomalous Ir in K- T boundary.

## II. EXPERIMENTAL

*1) Sample preparation and determination* The geological samples were dissolved step by step by a selective chemical dissolution procedure newly- developed in our laboratory (see Kong and Chai[13]), eventually separated into six components: carbonate, metal, sulfide, oxide, silicate and HCl- HF resistant residue. We determined the contents of Ir and other elements in each component by radiochemical neutron activation analysis (RNAA)[12] and INAA. The detection errors for Ir and other elements are below 10% by NAA.

*2) Light element analysis* Light elements were analyzed by a method based on the principle of adsorption- desorption of gas components produced during combustion process, and the determination of the separated components by heat- conduction detector. The detect limits for C, H, N are <0.3%.

*3) Transmission electron microscope* The separated residues were carried out micro- spherules analysis by transmission electron microscope of model H- 800 made in Japan. By X- ray energy dispersive analysis (EDAX), we can analyze elements with atomic number larger than 8.

## III. RESULTS AND DISCUSSION

### 1. Chemical species of Ir in geological sample

In impact event, extraterrestrial materials could form a micrometersized nuggets composed almost entirely of platinum group elements during their atmospheric entry according to the large differentiation of mineral density[14]. In volcanic eruption, Zoller[15] discovered from the correlation of Ir and halogen in volcano ash from Kilauea, Hawaii, that the Ir enrichment in the plume from Kilauea is linked to the high fluorine content, may be present as $IrF_6$. In geochemical enrichment, Ir was concentrated in sulfides and metalorganic compounds as a results of the production of $H_2S$ along with the mass extinction[6]. Because of the difference of the chemical speciation of anomalous Ir in the above hypotheses, it is possible that the distribution patterns of Ir in different chemical components can play an indicative role to decipher the origin of Ir anomaly.

Thus, the geological samples were separated and determined for this purpose. The results were listed in Tables 1- 4.

**Table 1**

**Phase distribution patterns of geological samples (unit in %)**

| Sample | Carbonate | Metal | Sulfide | Oxide | Silicate | Residue |
|---|---|---|---|---|---|---|
| Baoxian meteorite LL4 | 7.9 | 38.9 | 10.0 | 10.5 | 28.1 | 4.6 |
| Ningqiang meteorite CV3 | 8.6 | 24.2 | 7.5 | 26.2 | 27.8 | 5.7 |
| K- T boundary, Morgan Creek, Canada | 9.5 | 11.1 | 8.5 | 6.8 | 53.1 | 11.0 |
| K- T boundary, Montana, USA | 0.8 | 3.2 | 10.3 | 12.9 | 72.2 | 0.2 |
| K- T boundary, Stevns Klint, Denmark, Fish Clay L3S1 | 24.7 | 9.4 | 22.0 | 14.2 | 25.1 | 4.6 |
| lava, Kilauea, Hawaii | 1.6 | 1.7 | 18.1 | 19.1 | 59.1 | 0.4 |
| Ultrabasic rock, SRTH, Xinjiang | 19.3 | 13.8 | 15.4 | 36.2 | 14.9 | 0.4 |

**Table 2**

**Distributions of Ir in geological samples (unit in %)**

| Sample | Carbonate | Metal | Sulfide | Oxide | Silicate | Residue |
|---|---|---|---|---|---|---|
| Baoxian meteorite LL4 | 6.1 | 43.4 | 33.8 | 11.8 | 4.9 | - |
| Ningqiang meteorite CV3 | 6.6 | 27.8 | 18.0 | 11.5 | 8.6 | 27.6 |
| K- T boundary, Morgan Creek, Canada | 17.0 | 16.0 | 9.7 | 7.3 | - | 49.9 |
| K- T boundary, Montana, USA | 32.1 | - | - | - | 24.1 | 43.8 |
| K- T boundary, Stevns Klint, Denmark, Fish Clay L3S1 | 4.0 | 21.5 | - | 9.4 | 12.0 | 54.5 |
| lava, Kilauea, Hawaii | 3.0 | 5.0 | 2.4 | 38.7 | 35.7 | 15.7 |
| Ultrabasic rock, SRTH, Xinjiang | - | 26.0 | 49.7 | 4.2 | 20.1 | - |

Following conclusions can be drawn from data in Tables 1- 4:

*1) Distributions of Ir* In the K- T boundary clays we analyzed, about 50% of Ir existed in each residue phase, but little in sulfide phase, regardless of their formation circumstance, either marine for sample Fish Clay L3S1, in Stevns Klint, or continental for samples in Montana, USA and Morgan Creek, Canada. This result objects to the hypothesis of geochemical enrichment of Ir proposed by Keith[6] who believed the Ir should be concentrated in sulfides and metal- organic compounds. That means, most probably, that the anomalous Ir was not mainly caused by the geochemical enrichment.

2) *Difference of ultrabasic rock and volcanic lava* The ultrabasic rock, dunite, and the volcanic lava from Kilauea, Hawaii, were believed all to be products from the upper mantle. Even though the samples come from the same parent materials, the Ir distributions showed obvious difference. The reason of the difference is that the ultrabasic rock and the lava from Kilauea have experienced different magmatic action. The analyzed ultrabasic rock is an intrusive rock on the basis of its geological structure, and was slowly condensed compared to the lava of Kilauea. The Kilauea lava possessed vesicle texture resulted from volcanic action and belonged to an extrusive rock. Because the geological circumstance and physico- chemical condition in which the extrutive rock formed are of high temperature and low pressure[16], the lava we analyzed then cooled promptly after the volcano eruption. In gradually condensed process from high temperature, the elements in minerals will be redistributed along with the separation of minerals of different densities and Ir will be diffused as allomerism in any minerals. While in a rapid cooling process, because it has not sufficient time for Ir to be carried in rock- forming minerals, the Ir tends to be present in its own minerals. Since noble minerals are insoluble in any acidic reagents, the content of Ir in the residue phase of the Kilauea lava is then more than that of the ultrabasic rock. We can suppose that the faster the cooling speed is, the more the Ir is in residue.

**Table 3**

**Element distributions of sample L3S1 in Stevns Klint, Denmark (unit in %)**

| Element | Carbonate | Metal | Sulfide | Oxide | Silicate | Residue |
|---|---|---|---|---|---|---|
| Ir | 4.0 | 21.5 | - | 9.4 | 12.0 | 54.5 |
| Co | 28.2 | 61.8 | 7.1 | 2.7 | 0.1 | - |
| Ni | 28.0 | 59.4 | 9.4 | 1.5 | 1.7 | - |
| Fe | - | 51.8 | - | 10.8 | 15.8 | 21.6 |
| Sb | 5.5 | 76.1 | 10.0 | 4.1 | 0.3 | 4.1 |
| Sc | 33.8 | 7.8 | 5.8 | 40.0 | 7.9 | 4.7 |
| Th | 73.3 | 23.1 | 0.6 | 2.0 | 1.0 | - |
| Cr | 24.2 | 4.6 | 10.2 | 48.4 | 12.6 | - |

3) *High temperature process* Considering such high contents of Ir in the residue, that is, about 50% of Ir are present in the residue phases constituting less than 5% (weight ratio) of bulk samples, about 11 (for Stevns Klint) and 39 times (for Montana) more than their bulk samples, respectively, having nothing in common with that of meteorite or volcano sample, we believed that the Ir has been redistributed at the end of the Cretaceous, taking further inference, a high temperature process at that time has taken place. It is difficult to judge which source of anomalous iridium is

plausible as both of the meteorite impact and volcano eruption could cause a fast cooling process. However, we could hardly imagine that such a high temperature process was led by geochemical function. Thus, the hypothesis of geochemical enrichment of anomalous iridium is not valid in this aspect.

4) *Correlation of Ir and other elements* There is no correlation between Ir and other elements including siderophile, chalcophile or lithophile (see Table 3). This result also disfavors the mechanism of geochemical enrichment of Ir.

5) *Ratio of Ir to Au* The results in Table 4 showed that the distribution of Au are nothing in common with those of Ir, while in our knowledge available, the behavors of Ir and Au should be the same even if redistribution have been occured. In our results, most of Au exist in sulfides and other easily- soluble phases not only in samples of meteorite and lava, but also in K- T boundary samples, and that demonstrated the sedimentation and weathering functions of Au are much easier than those of Ir, which lead to the transformation of Au distribution patterns. Considering the loss of Au in long geological history, we proposed that the ratio of Ir/Au used as the indicator of extraterrestrial or terrestrial materials is somewhat lack of accurate meaning. The ratio of Ir/Au can only partly reflect the characteristics of original material.

**Table 4**

**Distributions of Au in geological samples (unit in %)**

| Sample | Carbonate | Metal | Sulfide | Oxide | Silicate | Residue |
|---|---|---|---|---|---|---|
| Ningqiang meteorite CV3 | 27.9 | 16.4 | 38.9 | 3.3 | 13.5 | - |
| K- T boundary, Stevns Klint Denmark, Fish Clay L3S1 | 9.5 | - | 78.6 | 7.9 | 3.9 | - |
| lava, Kilauea, Hawaii | 6.3 | - | 54.1 | 23.8 | 5.6 | - |
| K- T boundary, Morgan Creek Canada | - | 7.0 | 63.9 | 15.0 | 14.0 | - |

In the above discussion, we did not consider the possibility of Ir remigration which had taken place after enriched by the geochemical mechanism. We will give an impossible explanation to this possibility in the following paragraphs.

## 2. Light elements in residue phase

Since about 50% of Ir exist in less than 5% of the residue phase of K- T boundary samples, we should know the components of residue phase, the speciation of Ir in residue phase and its relationship with kerogen. So we analyzed the composition of some light elements in the residue phase in the preceding samples as showed in Table 5.

We can see from Table 5 that the main component of Fish Clay L1S1, Stevns Klint, Denmark is kerogen, whereas there is no kerogen in the residue of continental K- T sample, Montana, USA and this result was also proved by microscopic observation. The results we obtained in the different circumstances where the anomalous Ir formed showed that the Ir enrichment in boundary samples did not necessarily associate with kerogen, that is, the Ir enrichment is due to primitive sources and not particularly due to the existance of kerogen. We proposed that the high content of Ir found in kerogen resulted from the primitively anomalous Ir remigration by kerogen physical adsorption. Whether the kerogen exists or not is related to the geological circumstances.

**Table 5**

**Concentrations of light elements in residue phase**

| Sample | | C(%) | H(%) | N(%) |
|---|---|---|---|---|
| Fish Clay L1S1 | 1. | 34.98 | 2.56 | 3.78 |
| | 2. | 35.56 | 2.35 | 3.83 |
| Montana, USA | 1. | 3.34 | 1.96 | <0.3 |
| | 2. | 4.96 | 1.97 | <0.3 |
| Ningqiang meteorite CV3 | 1. | 2.61 | 0.85 | 0 |
| | 2. | 3.65 | 1.06 | 0 |
| Baoxian meteorite LL4 | 1. | <0.3 | 0.35 | 0 |
| | 2. | <0.3 | 0.51 | 0 |
| Ultrabasic rock, SRTH, | 1. | <0.3 | 0 | 0 |
| Xinjiang | 2. | <0.3 | 0 | 0 |
| Lava, Kilauea, Hawaii | | 3.82 | 0.31 | 0 |
| Morgan Creek, Canada | 1. | 33.71 | 2.79 | 1.24 |
| | 2. | 31.50 | 2.72 | 1.27 |

Schmitz[10] once treated kerogen by concd. $HNO_3$ and found that along with the decomposition of kerogen, the anomalous Ir was also dissolved. Based on the above experiment, he pointed out that the anomalous Ir is closely related to the existence of kerogen and microbial activity. We treated the HCl and HF- resistant residue of two K- T boundary samples we analyzed with sufficient amount in the same way. The results are listed in Table 6.

**Table 6**

**Insoluble residue treated by concd. $HNO_3$***

| Sample | Component | Relative component content (%) | Ir content (ppb) |
|---|---|---|---|
| Morgan Creek, | Kerogen | 94.8 | 15.7 |
| Canada | No kerogen residue | 5.2 | 52.1 |
| Colorado | Kerogen | 88.9 | 8.09 |
| USA | No kerogen residue | 11.1 | 92.9 |

* The insoluble residues we obtained after treated by the phase separation procedure were continuely carried out disposal by concd. $HNO_3$ Hundreds of mg of each insoluble residue was taken out, and was gently boiled in concd. $HNO_3$ solution about 10 minutes, then, centrifuged and washed several times. By this series, the kerogen was decomposed and the remained residue were kerogen- free.

Our results demonstrated that Ir in the residue is even more enriched after the kerogen having been removed. That means Ir is not combined with kerogen, that is, it is impossible that the anomalous Ir was originated from organism themselves. This result is in keeping with our preceding deduction. The discovery of a noble nugget in K- T boundary sample, Morgan Creek, Canada, recounted below, also supports our inference, that is, the anomalous Ir is indeed due to primitive sources and has no necessary association with kerogen. The fact that most of Ir are present in residue of boundary samples regardless of the existence of the kerogen also refuts the possibility of post- depositional of the anomalous Ir enriched in geochemical mechanism.

### 3. Transmission electron microscope analysis of residue phase

In order to know the components of residue phase, we analyzed the basic mineral components by using transmission electron microscope (TEM). The results are listed in Table 7.

**Table 7**

**Mineral components of residue**

| Sample | Component |
|---|---|
| Fish Clay L3S1 | Pyrite, spinel |
| Fish Clay L1S1 | Kerogen |
| Montana, USA | Spinel |
| lava, Kilauea | Corundum |
| Ningqiang meteorite | Magnesium oxide |

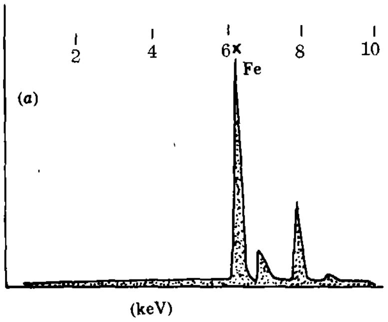
**Table 8**

**Particles in residue phase**

| Sample | | | Component of | | particle | |
|---|---|---|---|---|---|---|
| Fish Clay L3S1 | Bi | S | Fe | | | |
| Fish Clay L1S1 | Bi | | | | Pb | |
| Montana, USA | Bi | S | | | | |
| Morgan Creek, Canada | Bi | S | Fe | Zn | Pb | noble nugget |
| Lava, Kilauea | Bi | | | | | |
| Particle diameter ($\mu$ m) | 0.1- 0.5 | 0.2 | 0.2- 0.6 | 0.1 | 0.04- 0.1 | 0.1 |

The data in Table 7 indicate that there is no peculiar mineral components among different residue phases of boundary samples. Therefore, one question is in what speciation the anomalous Ir existed in the residue, and whether it existed in its own aggregative state? For this purpose, we carried out micro- spherules analysis of the above residues by TEM. The results are as follows:

*1) High temperature process occurred at the end Cretaceous* Some particles composed of iron were found in the residue phase of K- T boundary samples, Fish Clay L3S1 and Morgan Creek, Canada. In principle, these iron particles should be dissolved in the preceding phase separation process. So these particles must have experienced a particular process, as they can survive the attack of concd. HCl and HF. As we know, metal or its oxide would become insoluble after being treated at high temperature, so we believe the Fe particles found in the residue must experience a high temperature and even high pressure process, that is, one special event accompanied with high temperature or even high pressure in the boundary ages must have occurred.



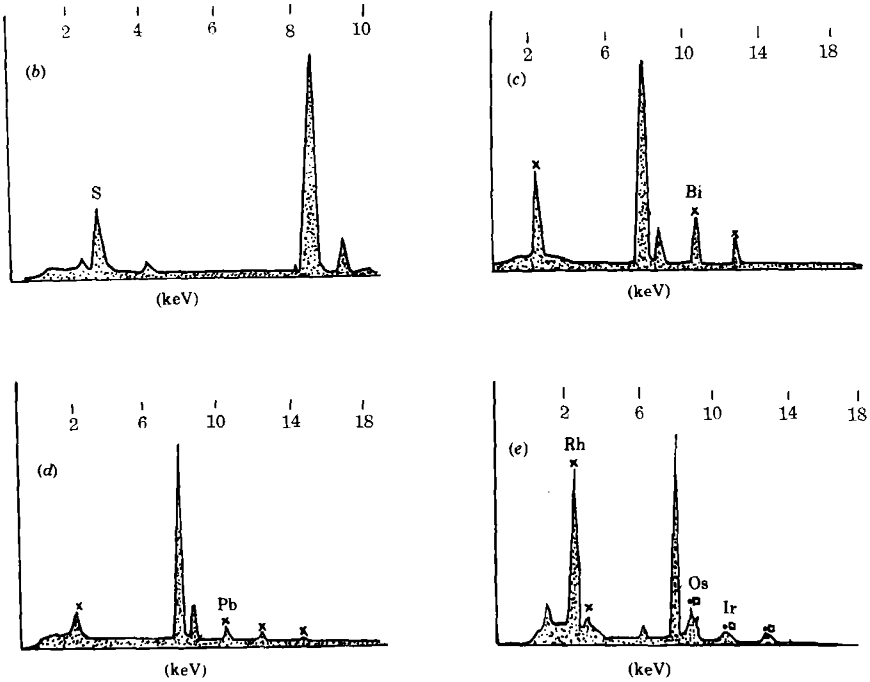


**Fig.1 Particle graphs by EDAX**

(*a*) Fe particle in fish Clay and Morgan Creek, Canada (*b*) S particle in fish clay and Montana, USA (*c*) In lava of kilauea almost all circular particles are composed of Bi, while we found Bi particles in all K- T boundary samples we analyzed too (*d*) (*e*) Pb particle and noble nugget found in Morgan Creek, Canada.

2) *Volcano activity in the K–T extinction event* Almost all spherules found in the volcano lava from Kilauea were composed of bismuth, which was believed to be associated with gaseous-composed mineral from volcanic eruption, while in all K- T boundary samples we analyzed, the bismuth spherules were also found. Other particles such as Pb, Zn and S exist in K- T boundary samples too as shown in Table 8. It has great possibility that these particles composed of Bi, Pb, Zn and S, respectively, came from condensation

process of volcanic eruption and, in fact, these particles had all been found in volatile components of volcano. It is hardly believed that these particles could also be caused by single extraterrestrial impact. The graphs of the preceding spherules by transmission electron microscope were shown in Fig.1

*3) A noble nugget in K– T boundary sample at Morgan Creek, Canada* We found a spherule with 0.1$\mu$ m diameter whose main components were Rh (90%), Os (5%) and Ir (5%) in K- T boundary sample at Morgan Creek, Canada by the method of transmission electron microscope and EDAX. Based on the model of the event formation sequence producing noble nugget proposed by Brownlee et al[12], we propose that this spherule of noble nugget was formed in the process of impact material molting at the moment of contacting with target materials followed by recondensed mechanism after erupted to the atmosphere. We believe that this spherule of noble nugget could indicate the leading role of K- T event, that is, the trigger which caused the extinction was extraterrestrial material.

Now, let us discuss the possibility of finding a noble nugget. As we found the diameter of the noble nugget is 0.1$\mu$ m and we suppose the Ir content in noble nugget is about 5% for detection limit needed, we could get the weight of Ir in a noble nugget

$$W=\pi\ DR^3N=3.14\times 22.4\times(0.05\times 10^{-4})^3\times 0.05=4\times 10^{-16}g$$

Among them $D$ stands for Ir density, $R$ stands for radius of a noble nugget and $N$ stands for the proportion of Ir in the nugget.

Considering the content of Ir in residue after leaching kerogen and any data we obtained before, we suppose the Ir content in residues of K- T boundary samples are 500 ppb, then, we should need sample of weight 4×10 exp (– 16)/500×10 exp (– 9) = 0.8 × 10 exp (– 9) g with a noble nugget in it. Here we suppose the sample besides the noble nugget has no Ir at all. If a normal particle has the same size as the nobel nugget and with average density 2.2g/cm$^3$, thus the particle should weigh $2.2\times 3.14\times(0.05\times 10^{-4})^3=8\times 10^{-16}$g. Then, we should have 0.8× 10 exp (– 9)/8× 10 exp (– 16) = 1× $10^{16}$ particles with only one noble nugget in it which could account for the Ir content in residue. Even if thousands of these particles connected together, we should determine one thousand times in order to find a noble nugget. This is the reason why we have found only one noble nugget with taking about 40 hours working in EDAX.

## IV. CONCLUSION

On the basis of the above analyses, we propose: (1) It is impossible that the anomalous Ir was caused by geochemical enrichment; (2) The Ir enrichment in boundary did not necessarily associate with kerogen; (3) The volcano activity must have participated in the extinction event at the end of Cretaceous; (4) Extraterrestrial impact was the trigger of K- T event.

Connecting all the facts we listed above, we summary a sequence which could perfectly explain the K- T extinction and its Ir anomaly.

First, extraterrestrial material impacted the earth at the end of Cretaceous. Because of the gigantic shockwave, the world widespread volcano eruptions on a massive scale were breaked out. The violent eruptions are capable of injecting large amount of sulfate aerosols into the lower stratosphere, with potentially devastating atmospheric consequences, then, causing a massive catastrophe of biological history, ended the reign of dinosaurs with 95% organisms extinction. Along with the mass extinction and geological enrichment, the species of anomalous Ir from the extraterrestrial impact and volcano eruption were redistributed. Some were adsorpted by kerogen. That is why the Ir content was so high in kerogen leaching from some boundary samples. Thus, the species of Ir we found today were the mixing results of all the processes.

Although we have gotten some new data, the problem of the anomalous Ir is far to be solved, such as, what are the sources of the anomalous Ir about half being present in soluble phases, either geochemical enrichment, volcano eruption extraterrestrial impact or their mixing effect if due to mixing effect, what is the proportion of each reason? In Zoller's view[13], the Ir may exist as $IrF_6$ in volcano eruption. Thus, whether the soluble Ir exists as $IrF_6$? Unfortunately, we lack of any data about the solubility of micro- amount of Ir in its compounds. These need us further researchment.

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