Technetium in Cosmo- and Geochemical Fields

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Since ^{98}Tc and ^{99}Tc decay to ^{98}Ru and ^{99}Ru, respectively, via the β^- transition, the property of Tc in cosmo- and geochemical fields can be deduced from precise isotopic studies of Ru. Through the approaches on isotopic analyses of Ru in cosmo- and geochemical samples, mass spectrometric techniques with thermal ionization mass spectrometry (TIMS), inductively coupled plasma mass spectrometry (ICP-MS) and secondary ion mass spectrometry (SIMS) have been effectively used. I report herewith the following three topics about the Ru isotopic studies related with the behavior of Tc in cosmo- and geochemical fields: (1) Initial abundance of Tc in the solar system deduced from the Ru isotopic compositions in meteoritic samples, (2) geochemical behavior of fissiogenic Tc in natural fission reactor zones at the Oklo uranium deposit, and (3) a possibility of cosmic-ray produced Tc in terrestrial molybdenite ore bodies.

Introduction

Physicochemical behavior of extinct nuclide Tc in natural environments at planetary surface is one of major concerns for geochemists. Although the properties of metallic Tc under reducing conditions and at high temperatures and pressures are poorly constrained, Tc has the potential to escape to the environment owing to volatility ($HTcO_4$ and Tc_2O_7) and aqueous mobility in soil systems (TcO_4^-). Tc has no stable isotopes, but two isotopes, ^{98}Tc and ^{99}Tc, have relatively long half-life, 4.2×10^6 and 2.1×10^5 years, respectively. Since ^{98}Tc and ^{99}Tc decay to ^{98}Ru and ^{99}Ru, respectively, via the β^- transition, the behavior of Tc in cosmo- and geochemical fields can be deduced from precise isotopic studies of Ru. Elemental abundances of Ru in cosmo- and geochemical samples are generally lower than a few ppb, because Ru is a highly siderophile element which is incompatible with silicate materials. Therefore, preconcentration and purification of Ru are required for the mass spectrometric works. Recent development of mass spectrometric instrumentation and technical advance of separation chemistry make it possible to more sensitively and precisely determine Ru isotopic composition than before.

I report herewith current three topics of Ru isotopic studies related with the behavior of Tc in cosmo- and geochemical fields. First, the Ru isotopic measurements in meteoritic samples were performed for the purpose of estimation of the initial Tc abundance in the solar system. The development of ^{98}Tc-^{98}Ru and/or ^{99}Tc-^{99}Ru chronological systems may provide important information on the chemical evolution process of the solar system. Next, the geochemical behavior of Tc was deduced from the isotopic variation of fissiogenic Ru components of natural fission reactors at the Oklo uranium deposits, the Republic of Gabon. Since ^{99}Tc is highly produced by fission reactions and decays to ^{99}Ru, geochemical differentiation between Tc and Ru causes the isotopic variations of ^{99}Ru. The Oklo natural fission reactor at the Republic of Gabon is the best sample to study the long-termed behavior of ^{99}Tc in and around the uraninite ore. The knowledge from the Oklo study is usefully applicable to radioactive waste disposal in geosphere. The third approach to measuring the Ru isotopic compositions in old terrestrial molybdenites is based on the cumulative effects of double beta decay

^{100}Mo-^{100}Ru. Through the detection of double-beta-decay products, a possibility of Tc production by cosmic-ray irradiation on Mo matrices would be discussed from the Ru isotopic data.

Elemental Abundance of Tc in the Early Solar System

In order to estimate the initial abundance of Tc in the solar system, precise isotopic analyses of Ru in several meteorite samples have been performed.[1–3] Quantitative isotopic treatment of ^{98}Tc-^{98}Ru and ^{99}Tc-^{99}Ru decay systems may provide chronological information on the chemical evolution processes of planetary materials in the early solar system. However, the Ru isotopic compositions of primitive materials in the solar system have been affected probably by extra addition of r- and s-process nucleosynthetic components,[4] and therefore Ru isotopic deviations due to Tc decay have not been clearly found in any meteorite samples yet. The lack of Ru isotopic deviations due to Tc decay in meteorites (iron meteorites and chondritic meteorites) suggests low abundance of Tc (^{98}Tc/^{96}Ru $< 2 \times 10^{-5}$ as upper limit) in the solar system.[3]

Here I focus on the Ru isotopic compositions of metallic grains in carbonaceous chondritic meteorites. Considering the refractory and highly siderophile properties of Tc, metallic fractions in carbonaceous meteorites may have a great advantage to search for isotopic evidence of initial Tc in the early solar system. Four kinds of carbonaceous chondrites, Murchison (type CM2), Isuna (CO3), Maralinga (CK4) and Karoonda (CK5) were used in this study. One gram of each sample was crushed in an agate mortar. Metallic fraction was magnetically removed from the powdered sample. Each sample was divided into two portions for the determination of Ru content by isotope dilution mass spectrometry (IDMS) and for the Ru isotopic measurement. The metallic fraction (0.03–0.10 g) was weighed and dissolved by 5 mL of aqua regia. The Ru in each sample was chemically separated by a distillation method. For IDMS, a ^{99}Ru spike solution was added into each sample solution prior to the distillation process. The isotopic analyses were performed by TIMS. The details of separation procedures and mass spectrometric techniques are described in the previous paper.[5]

Measurements via IDMS resulted in Ru concentrations of 24.31 ppm for Isuna, 14.83 ppm for Maralinga, and 44 ppm for Murchison. The IDMS analysis for Karoonda was failed. It should be noted that the Ru concentrations of individual magnetic fractions are more than 10 times higher than those of the

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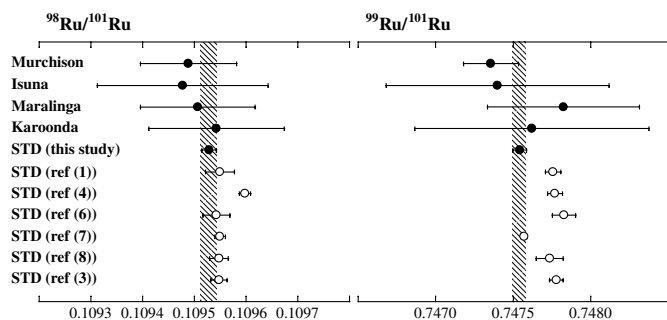
Figure 1. The ^{98}Ru/^{101}Ru and ^{99}Ru/^{101}Ru isotopic data for metallic fractions of individual meteorites and standard materials. Shaded zones in the figure represent standard data from this study: ^{98}Ru/^{101}Ru = 0.109529 ± 0.000014 and ^{98}Ru/^{101}Ru = 0.747552 ± 0.000044. The analytical uncertainties are 2σ of the mean.

carbonaceous bulk components.

The isotopic results are shown in Figure 1. Judging from high sensitivity of TIMS analysis, more precise analytical results were expected. However, the analytical precision in this study was not good enough to make a critical discussion about the presence of isotopic excesses on ^{98}Ru and ^{99}Ru in the individual samples, because the quantities of Ru treated in this study were extremely low. As shown in Figure 1, all of the data from meteorite samples overlap with those of standard materials[1, 3, 4, 6–8] within analytical precisions indicated by 2σ of the mean. Further analysis is required to discuss about the initial abundance of Tc in the early solar system from the Ru isotopic data.

Fissiogenic Tc in the Oklo Natural Reactors

Technetium-99 is highly produced by fission and turned to ^{99}Ru via β$^-$ decay. Kenna and Kuroda found natural ^{99}Tc produced by ^{238}U spontaneous fission in a pitchblende sample.[9] One rare example that Tc behavior can be studied in terrestrial field is natural fission reactors at the Oklo and Bangombe uranium deposits at the Republic of Gabon. Large-scaled fission chain reactions spontaneously occurred, and significant amounts of fissiogenic isotopes were produced in the natural reactors around 2.0 billion years ago.[10] Isotopic studies of the natural reactors provide long-termed behavior of fission products in and out of uranium matrices.[11] All of fissiogenic isotopes produced in the reactors completely decayed to stable isotopes at present. Isotopic analyses of Ru for the Oklo samples have been also carried out in order to study geochemical behavior of fissiogenic Tc.[12–15]

Four of seven Ru stable isotopes, ^{99}Ru, ^{101}Ru, ^{102}Ru and ^{104}Ru, are produced by fission. In the natural reactor samples, only four fissiogenic Ru isotopes and ^{100}Ru produced by neutron-captured ^{99}Ru can be detected because of high fission product yields of Ru and extremely low abundance (in general, less than ppb) of non-fissiogenic Ru in terrestrial crustal samples. The Ru isotopic compositions of natural reactor samples are expected from the fission product yields of ^{99}Ru, ^{101}Ru, ^{102}Ru and ^{104}Ru. However, significant variations of ^{99}Ru isotopic abundances have been often observed in the natural reactor samples.[12–15] In particular, micro-metallic grains consisting mainly of Pb, S, Ru, Rh and As found in the reactor samples show a large excess of ^{99}Ru.[15] This fact suggests the chemical fractionation between Tc and Ru during and after fission reactions. Since ^{99}Ru experienced long-lived ^{99}Tc as a radioactive precursor, differentiation between Tc and Ru can be presently seen as enrichment or depletion of the ^{99}Ru isotopic abundance.

Isotopic excesses of fissiogenic ^{99}Ru is defined as the following parameter Δ^{99}Ru:

$$\Delta^{99}\text{Ru}(\%) = \left[\frac{(^{99}\text{Ru}/^{101}\text{Ru})_{measured}}{(^{99}\text{Ru}/^{101}\text{Ru})_{calculated}} - 1 \right] \times 100,$$

where $(^{99}\text{Ru}/^{101}\text{Ru})_{measured}$ is the ^{99}Ru/^{101}Ru isotopic ratio of each sample, and $(^{99}\text{Ru}/^{101}\text{Ru})_{calculated}$ is the ^{99}Ru/^{101}Ru isotopic ratio calculated from fission product yields of ^{238}U, ^{239}Pu and ^{235}U.

Table 1 shows Δ^{99}Ru values resulted from the Ru isotopic measurements of several kinds of the Oklo samples. The positive Δ^{99}Ru value means the enrichment of Tc relative to Ru in the sample, while the negative one means the depletion. The difference of physico-chemical properties between Tc and Ru finally causes such isotopic variation of ^{99}Ru. It is considered that both Ru and Tc are easily mobile when they form oxide compounds such as RuO$_4$ and Tc$_2$O$_7$. As shown in Table 1, the Δ^{99}Ru values vary in uraninite matrices. Uraninite is generally stable under reducing condition, because U(IV) is much more insoluble than U(VI). Therefore, the uraninite ore body might have kept stable in reducing condition. However, in a rare case, some minerals which form under a strongly oxidizing condition, such as minium (Pb$_3$O$_4$) coexist in uraninite marices.[16] The presence of a minium shows evidence for a local oxidizing condition even in uraninite. As a reason of making the local oxidizing condition in uraninite, radiolysis of water is reasonably considered. The oxygen arising from radiolysis of water was locally accumulated, and played a role in changing the oxidizing conditions in uraninite. In this situation, fissiogenic Tc and Ru might have been locally mobile and have differentiated with each other. The variation of Δ^{99}Ru in several uraninite samples also supports the presence of local oxidizing condition due to water radiolysis in uraninite.

TABLE 1: Δ^{99}Ru Values of Various Kinds of the Oklo Samples

| Sample	Δ^{99}Ru
Whole rock	
GL13-3477	−15.3
GL13-3492	+4.7
GL13-3522	+103.6
GL13-3535	−41.2
SF84-1469	+4.41
SF84-1480	+2.82
SF84-1485	−5.15
SF84-1492	−1.21
SD37-S2	+11.6
Metallic aggregate	
SD37-S2/CD.2	+85.9
SD37-S2/CD.3	+49.9
SD37-S2/CD.5	+118

Data are from Hidaka et al.[14, 15]

Figure 2 illustrates the comparison of Ru isotopic abundance patterns between metallic aggregates and the whole rock taken from one of the Oklo reactor zones. The Ru isotopic compositions of all of the metallic aggregates show positive Δ^{99}Ru (+49.9 to +118) much larger than that of the whole rock (+11.6). This is caused by the enrichment of ^{99}Tc in the metallic aggregate because of differentiation between Ru and Tc, suggesting that Tc has a stronger chalcophile property (chemical affinity with sulfur) than Ru.

Cosmic-ray-induced Tc from Mo in Old Terrestrial Molybdenite (MoS$_2$)

Double beta decay is known as the rarest nuclear phenomenon having extremely long half-life over 10^{18} years. Geochemical analysis of isotopic excesses in geological materials caused by accumulation of the decay daughter isotope is a useful method for detection of the double beta decay products.
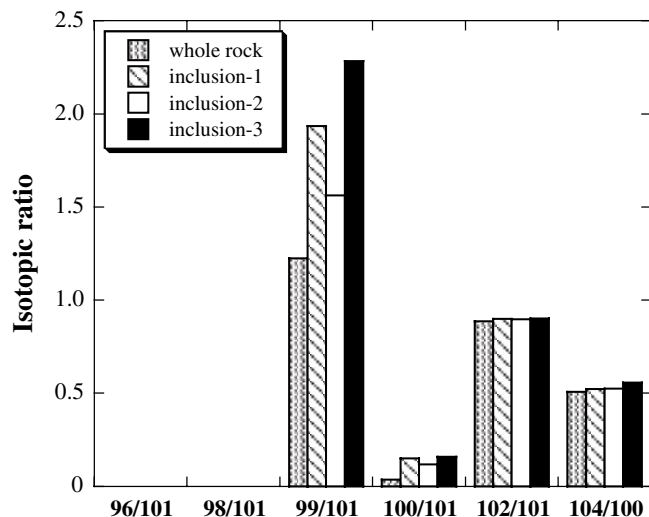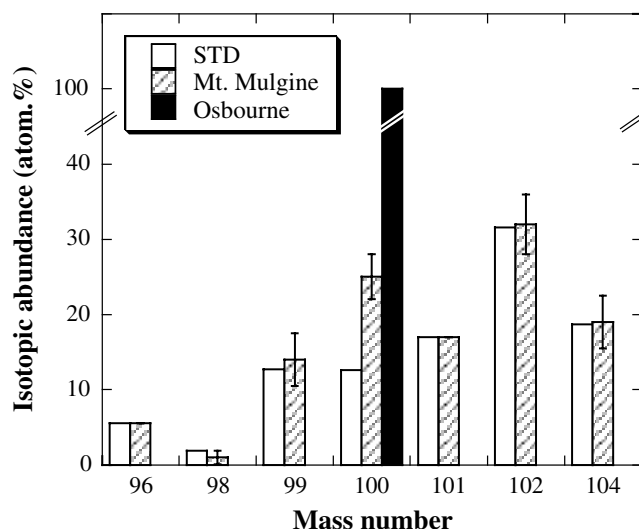
Figure 2. The Ru isotopic patterns of metallic aggregates and whole rock samples taken from the Oklo reactor zone 13 SD37-S2.

The half-life of ^{100}Mo-^{100}Ru double beta decay has recently been determined from a ^{100}Ru isotopic excess in geologically old molybdenum minerals.[17] However, the half life of ^{100}Mo estimated from the present geochemical analysis, 2.1×10^{18} years, is a factor of 4 lower than that from direct counting measurements.

Geologically old molybdenite is a suitable mineral for this study. The samples were collected from the molybdenite ores at Mt. Mulgine (Western Australia) and Osbourne (Queensland, Australia). The crystallization ages of the two minerals dated by ^{187}Re-^{187}Os method were $(2.903 \pm 0.004) \times 10^9$ years for Mt. Mulgine and $(1.051 \pm 0.001) \times 10^9$ years for Osbourne. In addition, an extremely low abundance of primordial Ru content in the molybdenite (50 ppt for Mt. Mulgine, 22 ppt for Osbourne) is a great advantage for isotopic detection of ^{100}Ru produced by the double beta decay.

There are some possible sub-reactions to provide Ru isotopic anomalies in Mo matrices through the Tc production by muon-induced and proton-capture reactions of Mo and spontaneous fission of ^{238}U. Fissiogenic Tc from spontaneous ^{238}U can be estimated to be negligible because of low U contents (< 10 ppm) in the molybdenites. In previous work by Cowan and Haxton[18], the amount of muon-induced Tc in a molybdenite ore was estimated. On the basis of their concept, the amount of muon-induced ^{100}Tc, and therefore ^{100}Ru, is simply calculated to be less than 90 pg for a 3 billion-years old sample with 6.7 m^3 volume. This result shows that the amount of muon-induced products is not enough to produce the isotopic excess of ^{100}Ru. Of more concern are the proton capture of ^{100}Mo(p,n)^{100}Tc and the subsequent decay of ^{100}Tc to ^{100}Ru. It should be noted that proton capture reactions on Mo would also involve the ^{98}Mo isotope and produce ^{98}Tc by ^{98}Mo(p,n)^{98}Tc. The production rates can be defined by $\psi \sigma N$; where ψ is the proton fluence from cosmic rays, σ is the cross section for proton capture reaction, N is the number of target isotopes. Considering the proton capture cross sections[19] and isotopic abundances for ^{98}Mo and ^{100}Mo, the production rate of ^{98}Tc is estimated to be 2.8 times higher than that of ^{100}Tc. However, the Ru isotopic compositions of two terrestrial molybdenites show significant isotopic excesses only in ^{100}Ru. Figure 3 shows the Ru isotopic abundance patterns of two molybdenite, Mt. Mulgine and Osbourne, used in this study. If the differentiation between Tc and Ru occurred in the molybdenite ore bodies, it may be possible to produce an isotopic excess of only ^{100}Ru. The half-life of ^{98}Tc (4.2×10^6 years) is much longer than that of ^{100}Tc (15.8 s). The half-life of ^{98}Tc is long enough for occurrence of chemical differentiation between Tc and Ru by geological processes. However, the molybdenite samples used in this study do not show visible evidence for

Figure 3. The Ru isotopic patterns of two molybidenite, Mt. Mulgine and Osbourne. Error bars in the figure are 2σ of means. The data are normalized at ^{96}Ru and ^{101}Ru for correction of instrumental mass fractionation.

alteration and weathering. In conclusion, it is implausible to produce isotopic excess of only ^{100}Ru by interaction of cosmic-ray with molybdenite. Therefore, the production rates of Tc in Mo matrices under natural circumstances are too small to detect by isotopic measurements.

Summary

Isotopic measurements of Ru by mass spectrometric approaches were made to understand the long-termed behavior of Tc in cosmo- and geochemical fields. In particular, the samples containing enough amount of Tc, like natural reactors, showed significant isotopic variations of Ru due to Tc-Ru differentiation in association with geological activities. The existence of micro-metallic inclusion containing a large amount of fissiogenic Ru and significantly positive Δ^{99}Ru reveals that siderophile property of Tc is higher than that of Ru. More precise analysis is required for determination of the initial Tc abundance in the solar system, because current isotopic data from meteorite samples provide no information of initial Tc abundance in the solar system. Tc-Ru chronological system may put a temporal constraint on evolution processes of early planetary bodies such as condensation and evaporation of dust grains, metal-silicate segregation, core crystallization, and aqueous alteration. Ruthenium isotopic data from old molybdenite ores showed isotopic excesses of ^{100}Ru due to double beta decay ^{100}Mo-^{100}Ru. There is no evidence for cosmogenic Tc in the samples.

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