

# Stable isotopes, minor elements and diagenetic alteration associated with Tono sandstone-type uranium deposits in Japan

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## Introduction

Sandstone-type uranium deposits are the most important uranium producers among various types of uranium deposits. Geologic setting and diagenetic alteration mineralogy of this type of deposits have been well documented. The genesis of sandstone-type uranium deposits have been argued based on geologic and mineralogic studies (Nash *et al.*, 1981). However, it is essentially important to estimate chemical features (Eh, pH) and isotopic compositions of fluids responsible for uranium mineralization and associated diagenetic alteration in order to elucidate genesis of the uranium deposits and diagenetic alteration mechanism. A few such geochemical studies on the sandstone-type deposits have been carried out.

In this study, the geochemical features of the diagenetic alteration in the Tono mine area are used to provide constraints on the relationship between uranium mineralization and diagenetic alteration process and the estimation of chemical environments responsible for uranium mineralization.

## Mineralogical and isotopic features of diagenetic alteration

Tono uranium deposits are primarily hosted by lower Miocene sedimentary rocks which are fluvial lacustrine deposits and are composed of arkose sandstone and conglomerate containing lignite of detrital plant origin. Dominant alteration minerals in these formations are pyrite and calcite. Miocene sedimentary rocks conformably overly late-Cretaceous granitic rocks. Upper Miocene sedimentary rocks (Akeyo and Oidawara formations) are generally unmineralized and are composed of marine facies of tuffaceous sandstone and mudstone interbedded with conglomerate. Between the upper unmineralized horizon and the lower mineralized is characterized by abundant smectite-rich horizon which is inferred to have been produced from volcanic glass. Small amounts of framboidal pyrite occurs in the upper horizon,

while abundant pyrite in lower horizon and is euhedral to subhedral in form. This type of pyrite formed later than framboidal pyrite.  $\delta^{34}\text{S}/^{32}\text{S}$  of framboidal pyrite is low, while that of euhedral to subhedral pyrite in the lower part of the Toki formation is high.

$^{13}\text{C}/^{12}\text{C}$  of calcite in lower horizon is low, implying a significant contribution of carbonaceous material in sedimentary rocks.  $^{13}\text{C}/^{12}\text{C}$  of calcite decreases towards upper horizon where marine fossils occur. This tendency indicates that a contribution of marine carbonates is larger in upper marine sedimentary rocks than in lower fluvial-lacustrine sedimentary rocks.

$^{13}\text{C}/^{12}\text{C}$  and  $^{18}\text{O}/^{16}\text{O}$  of calcite can be interpreted by the mixing of the fluid with marine carbon and seawater oxygen and the fluid with  $^{13}\text{C}/^{12}\text{C}$  and  $^{18}\text{O}/^{16}\text{O}$  values which are same to those of modern groundwater in the Toki formation. It is likely that dissolution and reprecipitation of carbonates in the sedimentary rocks have occurred since 15 Ma which corresponds to the age just after the deposition of the Oidawara upper formation.

Negative correlation of  $^{13}\text{C}/^{12}\text{C}$  and  $^{34}\text{S}/^{32}\text{S}$  suggests that marine sulphate was reduced to  $\text{H}_2\text{S}$  by carbonaceous materials.

The  $^{34}\text{S}/^{32}\text{S}$  and  $^{13}\text{C}/^{12}\text{C}$  data which deviate from the negative correlation line indicate that hydrolysis reaction of carbonaceous material producing methane and  $\text{CO}_2$  occurred.

Pyrite can be divided into framboidal-type (Type A) and euhedral to subhedral type (Type B). EPMA analyses indicate that pyrite of Type A sometimes contains Ni and Co more than 0.5 wt.% and pyrite of Type B Mn more than 1 wt.%. Type A formed at earlier and shallower part from the sea-floor contains minor elements (Ni, Co, Mn) less than the detection limit by EPMA. Type A formed later than this type of pyrite contains Ni and Co. Pyrite formed at the latest stage in deeper horizon contains appreciable amounts of Mn (up to 2 wt.%). Rough positive correlation between Mn content and  $^{34}\text{S}/^{32}\text{S}$  of pyrite is obtained. EPMA analyses, and microscopic observation,

combined with the studies of mineral paragenesis, demonstrate that Type A pyrite formed at  $\text{SO}_4^{2-}$  dominant region, while Type B in  $\text{H}_2\text{S}$  dominant region.

Uranium mineralization occurred at the margin of Type B pyrite grain at *c.* 11 Ma, which is close to the formation of Type B pyrite.

#### **Environment of diagenetic alteration and uranium mineralization**

Stable isotope data (S, C, O), sequence of diagenetic alteration, alteration minerals and chemical compositions of pyrite indicate that at early stage small amounts of framboidal pyrite formed at oxidizing condition where  $\text{SO}_4^{2-}$  is dominant compared with  $\text{H}_2\text{S}$  and at late stage large amounts of euhedral to subhedral pyrite and calcite formed in microcavities in smectite accompanied by sulphate reduction by carbonaceous material and ferric minerals and by hydrolysis reaction of organic matter.

Late stage calcite occurring in ore horizon has been formed influenced by downgoing groundwater after uplift of the region (15 Ma). Uranium

enrichment exists adjacent to pyrite, ilmenite and in cleavages in biotite.

Thus, reduction of  $\text{U}^{6+}$  to  $\text{U}^{4+}$  probably as coffinite and uraninite by ferric minerals and organic matter at the stage of groundwater penetration caused uranium mineralization.

Eh-pH conditions for the early stage framboidal to subhedral pyrite were estimated based on stable isotope (S,C,O) data and paragenesis of diagenetic alteration minerals. The Eh-pH range for pyrite and calcite precipitations and uranium mineralization characterized by nearly equal abundances of  $\text{CH}_4$  and  $\text{CO}_2$  and predominance of  $\text{H}_2\text{S}$  over  $\text{SO}_4^{2-}$  which is characterized by nearly equal abundances of  $\text{CH}_4$  and  $\text{CO}_2$  and predominance of  $\text{H}_2\text{S}$  over  $\text{SO}_4^{2-}$  occurred at the margin of pyrite grain is nearly same to that of modern groundwater in the Toki formation. This implies that the Eh-pH condition has been maintained since more than 10 million years ago and considerable amounts of uranium did not remove from the site of ore deposits and have been preserved in such reducing environment, hosted by the rocks with intrinsic reductant as such as ferric minerals and organic matter