AN OXYGEN ISOTOPE STUDY ON HYDROTHERMAL SOURCES OF GRANITE-TYPE URANIUM DEPOSITS IN SOUTH CHINA*

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INTRODUCTION One of the critical questions in the study of granite-type uranium deposits is the sources of the ore-bearing solutions. This information is essential to understanding the genesis and evolution of uranium metasomatizing hydrothermal systems. Because water is the dominant constituent of ore-forming fluids, a knowledge of its origin is fundamental to any theory of ore formation. The ultimate source of the water can best be deciphered by studying some geochemical parameters based on the water molecules themselves. Oxygen isotope analyses provide just such a parameter, because natural waters of various origins exhibit systematic differences in their $^{18}O/^{16}O$ ratios (cf. Taylor 1979).

Beijing Institute of Uranium Geology and Department of Geology at Nanjing University have intensively studied the granite-type uranium deposits in South China (see also Du Letian et al. 1982), but there are problems involved in the hydrothermal sources. In this paper, according to oxygen isotope determinations of four typical granite-type uranium deposits in South China, along with their geologic-geochemical investigations, the sources of uranium-bearing solutions are discussed and classified. It must be stressed that part of the data presented are the work of others and related references are given in acknowledgement.

Because the oxygen isotope compositions of oxygen-bearing minerals in hydrothermal uranium deposits are different from that of the ore-forming solutions in which these minerals are formed, the method is utilized to determine oxygen isotopic compositions of natural hydrothermal fluids, that is oxygen isotope analyses of hydrothermal minerals, measurement of temperatures of formation utilizing inclusion thermometry and, finally, calculation of oxygen isotope compositions of waters in equilibrium with the assemblages at their temperatures of formation. The oxygen isotope fractionation equations between relative mineral and water are given in references.

CLASSIFICATION OF THE HYDROTHERMAL SOURCES From meteoric water 1. Oxygen isotope compositions of the ore-bearing solution in pre-ore stage are not homogenized and the solution does not exchange oxygen with the wall rocks and $^{18}O$ values of the solution are mainly negative and have larger changes. A typical example is the No. 322 uranium deposit.

2. Oxygen isotope compositions of the ore-bearing fluid in pre-ore stage have been homogenized, and the fluid exchanged oxygen with the wall rock and mixed with meteoric water during the metasomatizing process. So $^{18}O$ values of the fluid have larger changes overall, but relative stability in a certain ore-forming stage. A typical example is the No. 376 uranium deposit.

From mixing solution of magmatic and meteoric waters 1. The hydrothermal solution in pre-ore stage is predominantly derived from magmatic water with $^{18}O$ values over $+6\%$, and in post-ore stage from meteoric water with negative $^{18}O$ values. It is in ore stage that the magmatic water is mixed with the meteoric water and the $^{18}O$ values of the mixing solution are between that of the magmatic water and that of the meteoric water. A typical example is No. 8411 uranium deposit.

2. In pre-ore stage, the mixing between magmatic water and meteoric water has taken place and uranium mineralization is formed in the mixed solution. Hydrothermal solution in post-ore stage is derived from the meteoric water. A typical example is No. 6217 uranium deposit.

From magmatic water Oxygen isotope compositions of the ore-bearing solution have relative stability with $^{18}O$ values of $+6$ to $+9.5\%$, but the lower limits of $^{18}O$ value for reequilibration magmatic water are about $+4.5$ to $+5.0\%$ and that for primitive magmatic water about $+8.5$ to $+11.5\%$ (Zhang Ligang 1982). A few amounts of meteoric water may be drawn into the solution in post-ore stage for the reequilibration one, but the mineralization is still formed in the magmatic fluid and not related to the mixing of both the waters.

CASE STUDIES The results of oxygen isotopic analyses of four typical granite-type uranium deposits in South China are summarized in table 1, and that of their related granites in table 2. Mineral and whole-rock samples are prepared for oxygen isotope analyses using standard techniques: BrF$_3$ for extraction of oxygen from silicates and oxides (Clayton & Maveda 1963) and phosphoric acid for extraction of carbon dioxide from carbonates (McCrea 1950). Oxygen isotope composition of the prepared gas samples are determined using gas ratio spectrometers and reported using the standard $^{18}O$ notation relative to SMOW.

No. 322 Uranium Deposit This ore deposit is located in contact zone of Early Mesozoic Z granitic batholith and Lower Paleozoic metasedimentary rocks, over these rocks Late Cretaceous red basin is developed. Hydrothermal uranium metasomatization occurs mainly in faulted structures of the granites and metasedimentary rocks on the border of the red basin. The timing of the mineralization is between Late Cretaceous and Early Tertiary. There are three mineralizing patterns: uranium-hematite (chlorite), uranium-chalcedony, and uranium-fluorite. The industrial uranium mineral is pitchblende. The wall rock alteration are alkaline replacement (K-feldsparization is mainly developed in shallow and albitization in deeper), silification, hydrocrazation, hematitization, chloritization, pyritization, fluoritization, carbonatization, and kaolinitization. The mineralization is related to silification, chloritization, and hematitization and usually coexists with sulfides.

Two feldspar, five quartz, two chalcedony, and six calcite samples are analyzed for their oxygen isotope compositions and the inclusion temperatures for use in calculation of the $^{18}O_{H_2O}$ values (Table 1). The $^{18}O_{H_2O}$ values obtained have larger changes with most of negative values wheter pre-ore, post-ore stages or ore stage, and they are clearly different from that of magmatic water in equilibrium with the Z granite (Table 2). As there is larger interval time between
formation of the mineralization and that of the granite (over 130 Ma), it is evident that the ore-forming solution is derived from meteoric water and not homogenized in pre-ore stage.

The hydrothermal solution $^{818}$O values in pre-ore stage range from $-15.70_{\%}$ to $+5.62_{\%}$, and in ore stage from $-4.19_{\%}$ to $0.24_{\%}$ and post-ore stage from $9.06_{\%}$ to $+3.74_{\%}$. As the mineralization goes, the $^{818}$O values of the solution become higher and its range reduces smaller, which may be related to oxygen isotope exchange of the hydrothermal fluid with the wall rocks. Combination of the above mentioned study with other geologic investigation shows a mineralizing process as follows: L. Cretaceous red basin (ref. 6), and uranium in the Z granite is leached out by meteoric water and migrated into fracture zones of the basement rocks on the border of the basin, and ore-bearing fluid is heated during its deep circulation (anomalous geothermal gradient in the vicinity of the ore field is about $10^7$C/km), then the fluid uplifts when the tectonic movement takes place and, finally, the mineralization is formed in the relative closed second structures on both sides of the control-basin and control-ore structures.

No. 376 Uranium deposit

This ore deposit is located at the endo- and exo-contact zones on the southwestern border of the M granite batholith of Xuefeng age and related to Late Caledonian metamorphism, and belongs to the meso- to epic-thermal uranium deposit. The ore bodies occur both endo-zone of medium- to fine-grained granite and exo-zone of upper Proterozoic Sibao Formation being epizonal metamorphic sandstone. The mineralization is controlled by fracture structures. The ore pattern is simple and belongs to mono-granite type. The ore mineral is pitchblende, secondary minerals of uranium are autunite, torbernite, uranophane, and guano. Accompanying metallic minerals are mostly pyrite and small amounts of chalcopyrite, bornite, galena, sphalerite, pyrrhotite, chalcocite, and covellite. The gangue minerals are quartz, chlorite, fluorite, calcite, and hydromica.

Two chlorite, six quartz, and two calcite samples belonged to different mineralizing stages are analyzed for their oxygen isotope compositions and the inclusion temperatures for use in calculation of the $^{818}$O$_{H_2O}$ values (Table 1). The whole-rock $^{818}$O value of the M granite is $10.7_{\%}$ and temperature of formation is about $450^\circ$C using inclusion geothermometry with calibration of pressure and salty degree. According to the petrochemical data and O’Neil et al. (1967) fractionation equation of silicate-water, it is calculated that $^{818}$O value of the magmatic water in equilibrium with the M granite is about $7.9_{\%}$, which is higher than $^{818}$O values of the ore-bearing solution. Besides, whole-rock RB-Sr isochron age of the M granite is about 723 Ma, but pitchblende U-Pb isochron age of the No. 376 uranium deposit is about 330 Ma. The interval time between formation of the mineralization and that of the granite is so large (over 400 Ma) that the hydrothermal solution can not be derived from the magmatic water. Because the mineralizing time is consistent with the time when Late Caledonian tectonic movement takes place in this region, the water accumulated by meteoric water is heated during Late Caledonian metamorphism and leaches out uranium from the M granite and exchanges oxygen isotope with the wall rock, which results in increasing in $^{818}$O values of the ore-bearing solution. According to water-rock exchange equation (Taylor 1979):

$$W^{818}O_{\text{water}} + R^{818}O_{\text{rock}} = W^{818}O_{\text{water}} + R^{818}O_{\text{rock}}$$

assume that $^{818}$O$_{\text{water}} = -5_{\%}$, $^{818}$O$_{\text{rock}} = 11.5_{\%}$, when the temperature of oxygen isotope exchange is about 350$^\circ$C and the water/rock ratio is about 0.3, it is calculate
Table 2 – Oxygen isotope compositions of some granite and magmatic water in equilibrium with the granitic magma in South China

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Sample Type</th>
<th>δ18O (‰)</th>
<th>Temp. (°C)</th>
<th>r*</th>
<th>δ18Ow (‰)</th>
</tr>
</thead>
<tbody>
<tr>
<td>79507</td>
<td>quartz</td>
<td>13.30</td>
<td>680</td>
<td>12.18</td>
<td></td>
</tr>
<tr>
<td>79508</td>
<td>quartz</td>
<td>12.55</td>
<td>680</td>
<td>11.43</td>
<td></td>
</tr>
<tr>
<td>79509</td>
<td>quartz</td>
<td>13.78</td>
<td>680</td>
<td>12.66</td>
<td></td>
</tr>
<tr>
<td>M01</td>
<td>whole-rock</td>
<td>10.7</td>
<td>450</td>
<td>7.9</td>
<td></td>
</tr>
<tr>
<td>1068</td>
<td>whole-rock</td>
<td>7.8</td>
<td>870</td>
<td>9.0</td>
<td></td>
</tr>
<tr>
<td>2078</td>
<td>whole-rock</td>
<td>8.0</td>
<td>865</td>
<td>9.1</td>
<td></td>
</tr>
<tr>
<td>1215-1</td>
<td>whole-rock</td>
<td>9.3</td>
<td>855</td>
<td>10.1</td>
<td></td>
</tr>
<tr>
<td>3126</td>
<td>whole-rock</td>
<td>10.5</td>
<td>835</td>
<td>11.3</td>
<td></td>
</tr>
<tr>
<td>5081</td>
<td>whole-rock</td>
<td>10.3</td>
<td>720</td>
<td>10.3</td>
<td></td>
</tr>
<tr>
<td>T057C</td>
<td>whole-rock</td>
<td>8.14</td>
<td>695</td>
<td>7.98</td>
<td></td>
</tr>
<tr>
<td>T201</td>
<td>whole-rock</td>
<td>11.54</td>
<td>755</td>
<td>11.82</td>
<td></td>
</tr>
<tr>
<td>T225</td>
<td>whole-rock</td>
<td>4.50</td>
<td>735</td>
<td>4.88</td>
<td></td>
</tr>
<tr>
<td>T074-2</td>
<td>K-feldspar</td>
<td>9.03</td>
<td>650</td>
<td>8.32</td>
<td></td>
</tr>
</tbody>
</table>

* r = (δ818O + A) (atomic member ratio)

The δ18O values are calculated with the fractionation equations from: silicate-water (O’Neil et al., 1967), quartz-water and alkaline feldspar-water in 500-800°C (Matsuhashi et al., 1979)

that δ18Owater = 5.1‰. The exhalation has been demonstrated by development of alkali replacement in the mineralizing wall rock. Accordingly, No. 376 uranium deposit belongs to the tectonic hydrothermal mineralization, and during the mineralizing process the meteoric water enters the ore-bearing fluid yet, which results in regularly decreasing in average δ18O values of the hydrothermal solutions from 4.16‰ in pre-ore stage to 1.65‰ in ore stage to -5.42‰ in post-ore stage.

No. 8411 Uranium deposit

This uranium deposit is located at contact zone of Late Yanshanian H quartz-syenite body belonged to the crust-mantle mixing-type granitoids with Jurassic Xiangshan Formation being feldspar-quartz sandstone. Distribution of the ore bodies is controlled by faulted structures. Mineral composition of the ore is relatively complicated. The main uranium minerals include pitchblende and small amounts of uranium black, metavarobernite, and autunite. The metallic minerals are dominantly pyrite and trace amounts of sphalerite, galena, molybdenite, chalcopyrite, marcasite, magnetite, hematite, niccolite, and millerite. The gangue minerals are mostly chalcedony, dolomite, calcite and fluorite. The wall rock alterations are pyritization, carbonatization, albitionization, silification, hydromicaization, and hematitization (this is generally called the redization).

Two magnetite, five chalcedony, and two dolomite samples are analyzed for their oxygen isotope composition and the inclusion temperatures for use in calculation of the δ18Ow values (Table 1). Besides, five the whole-rock samples from H body are analyzed for their oxygen isotopic and petrochemical compositions as well as inclusions temperatures for use in calculation of the δ18Ow values of magmatic water in equilibrium with the H granite (Table 2).

The ore-bearing solution in pre-ore stage has δ18O values of 6.8-9.7‰. As whole-rock Rb-Sr isochron age of the H body is 133.1 Ma and pitchblende U-Pb isochron age of the No. 8411 uranium deposit is 108.7 Ma, together with the results of the table 2, it is evident that the ore-forming fluid in pre-ore stage is derived from magmatic water. The solution in post-ore stage has δ18O values of -8.38 to -8.41‰. As compared with δ18Owater values of -5.30 to -8.88‰ of meteoric water in this region (Liu Yuqing 1982), it is showed that the solution in post-ore stage is dominantly derived from the meteoric water.

The ore-forming solution in ore stage has δ18O values of 5.46-1.75‰, which differs from that of the magmatic water in equilibrium with the H body and that of the meteoric water, and it is a kind of mixing solution of the magmatic water and the meteoric water in differing proportions. With migration of the ore-forming fluid, the deep-seated magmatic water is mixed with the meteoric water, which results in systematic changes of δ18O values of the solutions in different ore-forming stages. Because there are some differences in pH, T, and Eh between the two waters, their mixing must result in changes of physico-chemical conditions in the ore-bearing fluid. Degree of the changes depends on amounts of the mixed meteoric water. It is the mixing that changes the physico-chemical conditions of the fluid and results in disjunction of uranyle complexes in the ore-forming fluid and then forms pitchblende. It is demonstrated that δ18O values of the solution in the ore stage, i.e. during precipitation of pitchblende, are between that of the magmatic water and that of the meteoric water. It has been reported in other ore deposits such as porphyry-copper deposits that the mixing of waters of different sources results in the mineralization (cf. Taylor 1979).

No. 6217 Uranium deposit

This ore deposit is located in contact zone of Triassic D biotite to dimica granitic body belonged to the continental crust transformation type with Late Jurassic L biotite monzonitic granite body belonged to the crust-mantle mixing type, and a meso- to epi-thermal uranium deposit. The wall rock alteration varies from alkalic feldspar-pyroxene porphyry to quartz-pyroxene and feldspar-pyroxene-pyrite porphyry. The pitchblende U-Pb isochron age is about 60 Ma, which shows that the mineralization is probably contemporaneous during the Uppermost Cretaceous to Lowermost Tertiary.

One K-feldspar, five quartz and six calcite samples are analyzed for their oxygen isotope compositions and the inclusion temperatures for use in calculation of the δ18OH2O values (Table 1). Besides, three whole-rock and one K-feldspar samples from the L body are analyzed for their oxygen isotopic compositions and petrochemical compositions and the inclusion temperatures for use in calculation of the δ18O values of magmatic water in equilibrium with the L granite (Table 2).

The δ18O values of the solution in pre-ore stage range from 1.02‰ to 9.80‰ and in ore stage from 4.07‰ to 8.49‰. These values are partly lower than that of the magmatic water in table 2 but clearly higher than that of meteoric water and gallery water in this mining district (~5.92 to ~6.55‰). Which denotes probable derivation of the ore-bearing solution from mixture of the post-magmatic fluid and the deep-cycle subsurface water. This inference is consistent with geologic-geochemical investigation and lead isotope analysis in the No. 6217 uranium deposit. In post-ore stage hydrothermal solution is derived from the meteoric water as it has the δ18O values of -4.92 to -7.88‰.
On the basis of related geologic-geochemical investigation and analysis of lead isotope compositions for the pyrite and ore as well as the wall rock, together with comparison of some metallogenic models postulated by other authors, a new genetic model "mixing solution and composite uranium derivation" genetic model is suggested. This model believes that the ore-forming fluid is derived from both the magmatic water and the meteoric water, and the mineralizing uranium derivation from both the post-magmatic fluid formed by anatexis of palaeocontinental crust and the D granite from which the uranium is leached out, and the mineralization is in close relationship with such the crust-mantle mixing type granitoids as the L granite.

**SUMMARY AND CONCLUSIONS** The usefulness of oxygen isotope measurements in solving problems of hydrothermal sources has been demonstrated in a number of detailed studies of the granite-type uranium deposits in this paper. Remarkably, the granite-type uranium deposits in South China have been shown to have formed from magmatic water, meteoric water, of mixtures of both the above, and origin of waters in the ore-forming fluid may be different for differing uranium deposits or differing stages of the mineralization.

Consequences obtained in this study for four typical uranium deposits of different age and geologic setting agree well with that obtained by other geologic-geochemical investigation. Furthermore, not only meteoric water is of importance to origin and evolution of the ore-forming fluid, but also mixing of waters from different sources is considered to be one of the most characteristic features of many hydrothermal uranium deposits related to granitoids or volcanics (for later case, see also Chen Zhaobo 1985).

**REFERENCES**


...Basta começarmos a perguntar "como" em geologia que a lista cresce como ervas daninhas após uma chuva morna.