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EXPERIMENTAL STUDY AND MODELING OF WATER-ROCK INTERACTION IN XIANGSHAN FOSSIL GEOTHERMAL FIELD, SOUTH-EASTERN CHINA *

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ABSTRACT

Xiangshan fossil hydrothermal system is found in a Mesozoic volcanic basin of south-eastern China. The genesis of the uranium deposits in the fossil hydrothermal system has been disputed for a long time. The experiments have been designed to simulate the water-rock interaction and the evolution of ore-forming hydrothermal fluids in Xiangshan hydrothermal system. The experiments show that oxygen isotope could easily be exchanged between the water and rock in hydrothermal system, resulting in the $\delta^{18}O$ decrease for rocks and $\delta^{18}O$ increase for water, that is, the "oxygen isotope shift". The δD values are relatively stable, but can apparently also vary if the rock contains a large amount of hydrogen-bearing minerals such as biotite. The concentrations of U, Th for the fluids increased greatly, and uranium-enriched geothermal solution was formed after the water-rock interaction. Consequently, the experiments have proven that the ore-forming hydrothermal solution in Xiangshan Uranium Ore-field is mainly derived from the local meteoric water. EQ3/6 geochemical software package has been applied to model the formation and evolution of the hydrothermal solution, and the alteration and the uranium mineralization The project was supported by IAEA Coordinated Research Project (No.CRP-9716). The modeling reveals the content of uranium in the hydrothermal solution increased up to 0.33~0.553 mg/L after water-rock interaction, in accordance with the results of the experimental study. At the end, the F and SiO_2 enriched U-bearing hydrothermal fluids could be generated by means of the water-rock interaction. U in the hydrothermal fluids remains stable in the low Eh environment, as $UO_2F_3^-$, UO2 $(CO_3)_2^{2-}$ and other uranium complexes have very high stability.

1 INTRODUCTION

Isotope exchange, chemistry of geothermal fluids and alteration of rocks are closely related to water-rock interaction. Therefore, experimental study of the interaction between geothermal water and rock will be very helpful to (1) determine the origin of geothermal fluids; (2) explore the mechanism of many complicated geochemical reactions in geothermal system, and (3) provide useful information to the exploitation and utilization geothermal resources.

In 1997, the International Atomic Energy Agency decided to fund the project of research contract entitled " Experimental study of water-rock interaction in geothermal system" as part of the Coordinated Research Project "The use of isotope in investigating acidic fluids in geothermal exploitation".

According to the Research Contract (No. CPR-9716) signed between the IAEA and the East China Geological Institute in September 1997, the program of the research work should be as follows:

- Determination of isotope exchange between fluids and rocks in fossil and active hydrothermal systems by sampling and analyses of fluids and rock samples.
- Geochemical modeling by EQ3/6 codes.
- Interpretation of results, focusing on origin and genesis of fluids.

In order to fulfill the tasks above, Xiangshan fossil hydrothermal field has been selected as the major target of the project. The progress and main results are given below.

2 EXPERIMENTAL STUDY

2.1 Introduction

Xiangshan fossil hydrothermal system is found in a Mesozoic volcanic basin of south-eastern China. The basement rocks of the basin are predominately Precambrian epimetamorphic rocks, such as phyllite and biotite-quartz schist, while the cover rocks are upper Jurassic volcanic rocks, mainly porphyroclasic lava, and some volcanoclastic rocks and normal sedimentary rocks such as tuff and sandstone. By means of tectonic-paleohydrogeological analyses (Zhou & Li, 1995), two fossil hydrothermal systems have been identified in the northern and southern parts of the basin respectively, in which alkai-metasomatic and fluorite-hydromica type uranium mineralization were formed separately.

The genesis of the uranium deposits in fossil hydrothermal system has been disputed for a long time, and many models, such as "Double Mixing" and "Mineralization in Discharge Area of Hydrothermal System", have been put forward by different authors (Chen, 1982, Li, 1986). The focus of the arguments are always on the origin of the hydrothermal fluids in the hydrothermal systems.

Although a lot of work has been done on the hydrogen and oxygen isotopic compositions of ore minerals, wall rocks and fluid inclusions to solve the problem mentioned above (Zhou & Li, 1989, Zhou, Li & Shi, 1995, Xu, 1985), there still exist big differences in the interpretation of the isotope data. For example, the $\delta^{18}O$ value for the rocks in the hydrothermal system are usually much lower than those of the original rocks, and the data for the hydrothermal fluids lie between the values for the typical local meteoric water and the magmatic water (cf. Figure 1). "Double Mixing Model" is an important evidence for the mixing of meteoric water and magmatic water (Chen, 1982), while the authors believe this is the result of water-rock isotope exchange based on the comprehensive studies of chemistry of fluid inclusion, isotopes and trace and rare-earth elements (Li, 1986, Zhou & Li, 1989). To verify the influence of isotope exchange on the isotopic composition of water and rocks, an experiment of water-rock isotopic

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exchange has been carried out by the authors in the National Key Laboratory on Mineral Deposit Research, Nanjing University. The experimental results will be given and discussed below.

2.2 Experiments

Experimental model

The experiment is designed to simulate the hydrogen and oxygen isotope exchange during the processes of water-rock interaction and the evolution of ore-forming hydrothermal fluids in Xiangshan hydrothermal system.

Porphyroclastic lava, rhyo-dacite, granitic porphyry and biotite-quartz schist from Xiangshan have been selected as the solid phase of the reaction, while the ground water (XS-D) from a borehole in the same area has been used as the liquid phase in the experiment. The Water/Rock ratio (W/R) is determined to be around 2 (Zhou, Li & Shi, 1995). The temperature and pressure were chosen as 350ºC and 50 MPa respectedly, and the duration of the reaction was designed to 120 hours (Table 1).

Equipment

The experiment was carried out in the National Key Laboratory on Mineral Deposit Research, Nanjing University. The reactions took place within the internally-cooled Rapid Quenching Vessel (RQV). The temperature for the reaction was measured thermally and controlled by XTMA-1000 digital regulator with an accuracy of $\pm$1 ºC. The pressure of RQV was adjusted by a hydraulic pressure device with an accuracy of 1MPa.

The reaction tube is made of pure gold, 4.2 mm in diameter and 100 mm long, effective volume being some 1.3 ml after being sealed.

Procedure

First, a certain quantity of rock powder and water sample (XS-D) are added into the reaction tube, then the open end of the tube is sealed by melting. The tube is sealed at the bottom of the high pressure vessel, a steel bar added to reduce the free space, and the vessel then filled with distilled water and closed. The vessel is then heated with tube-like electric stove and kept at predetermined temperature, provided no leakage occurs from the vessel after being pressurized for 2 hours. When the reaction time is up, the vessel is moved out of the stove and quenched. After being cooled down to room temperature, the reaction tube is removed from the vessel under some negative pressure. Then, the tube is examined with respect to leakage by means of surface observation and weighing.

The reaction product is separated into solid and liquid phases using spin separator, and the liquid phase transferred into a small plastic sample bottle with an injector. The sample of solid phase is prepared by leaching, washing and drying. The oxygen and hydrogen isotope composition for the rock and water samples were measured by the Institute of Ore Deposit, Chinese Academy of Geological Sciences, Beijing.

Hydrogen isotope exchange

Compared with the situation for $\delta^{18}O$ variation, the values of δD for water have not changed significantly before and after its reaction with rocks. The original δD value for the water XS-D is -50 ‰ (SMOW), and maintains the same value after its reaction with the porphyroclastic lava. Similarly, the δD values for the water XS-D have been changed in a small degree by its reaction with rhyo-dacite and granitic porphyry, just shifting to -44‰ and -52‰ (SMOW) respectively. Therefore, it has been experimentally proven that the δD values for the hydrothermal solutions are relatively stable due to the lack of hydrogen exchange reaction in most water-rock systems. As an exception, the δD value for the water XS-D have been varied greatly, from -50‰ to -38‰ (SMOW) by the interaction between water XS-D and biotite-quartz schist because the rock contains a large amount of biotite, a hydrogen-bearing mineral, which could exchange hydrogen isotope with the water.

In summary, this experiment indicates that the oxygen isotope exchange between water and rock could be extensive, and the $\delta^{18}O$ decrease in altered rocks and the $\delta^{18}O$ increase in the hydrothermal waters are the results of water-rock oxygen isotope exchange reaction. Consequently, this experiment has provided an evidence for the model that the ore-forming hydrothermal solutions in Xiangshan Uranium Ore-field were mainly derived from the local meteoric water (Li,1986, Zhou & Li, 1989).

2.3 Results and Discussions

The analytical results of hydrogen and oxygen composition for the rock and water before and after the interaction are listed in table 2 and table 3. Discussions will been made below based on the isotopic data.

Oxygen isotope exchange

The values of $\delta^{18}O$ for the ground water sample (XS-D) have increased from -8.2‰ (SMOW), its original value, to 1.3‰, -0.4‰, -2.1‰ and 0.6‰ (SMOW) after its reaction with porphyroclastic lava, rhyo-dacite, granitic porphyry and biotite-quartz schist, respectively, thus exhibiting obvious "oxygen shift" (Figure 1). Simultaneously, the $\delta^{18}O$ values for the rocks have declined from 9.6 ~ 10.2‰ to 6.3 ~ 9.3‰ (SMOW), in accordance with the $\delta^{18}O$ decrease for the rocks in alteration zones in Xiangshan ore-field.

The measured values of $\delta^{18}O$ for the waters from the fluid inclusions in minerals of ore stage for Xiangshan Uranium Ore-field vary from -2.08 to +1.83‰ (SMOW) (Zhou, Li & Shi, 1995) which could be considered as the representative of the ore-forming hydrothermal solution in Xiangshan Ore-field, while the $\delta^{18}O$ values of water XS-D are between -2.1 and +1.3 ‰ (SMOW) after its reaction with rocks, just falling into the $\delta^{18}O$ range for the ore-forming hydrothermal fluids. This fact indicates that $\delta^{18}O$ values of water can apparently be raised up to the level between those for typical meteoric water and magmatic water through water-rock oxygen isotope exchange. Thus, it is not rational to take hydrothermal solutions with $\delta^{18}O$ values around 0 ‰ simply as the mixture of meteoric water and magmatic water.

3 MODELING OF THE FORMATION OF ORE-FORMING HYDROTHERMAL SOLUTION

3.1 Concept of the Modeling

Like the water-rock interaction experiment, the modeling of the formation of ore-forming hydrothermal solution should first select the sample. The local meteoric water of Xiangshan (XS-D) has been used as the water sample for the modeling,

its hydrochemical composition is reported in table 4, while the porphyroclastic lava of Xiangshan has been used as the rock sample for the modeling. The principal rock-forming mineral is alkaline feldspar (sanidine and albite), plagioclase, quartz and biotite, and the minor minerals are fluorite, apatite and magnetite etc. The major uranium mineral is uraninite, and the thorium mineral is thorinite.

The geochemical model for the study is the interaction between meteoric water and porphyroclastic lava.

The computer model uses the EQ3/6 geochemical software package and runs on a SUN Sparc 20 workstation in the East China Geological Institute. The calculation model is the reaction path calculation in a closed system, and the direct result of the modeling are in OUTPUT and TAB data files, and the data of interest were selected and plotted using GRAPHER software package.

3.2 Results and Discussions

The Formation and Evolution of the Hydrothermal Solution

After infiltration into the ground, the local meteoric water circulated deeply along the faults, an is then heated up to 250°C. The original pH of the solution is 6.7, $\sum CO_3$=0.1mol , lgf_{O_2}=-0.7. In the early stage of water-rock interaction (10-1000d), feldspar, quartz, biotite and other minerals in the porphyroclastic lava are under-saturated, and remain in solution. The quartz dissolves strongly in the early stage of the interaction, and the amount of silica in solution reaches its peak in around 1000 days, and then declines 1000 days later, the dissolution of albite surpasses that for quartz and maintains the tendency of increasing, and the uraninite becomes saturated after 10 days.

The minerals of the surrounding rocks are continuously dissolved, and the content of relevant elements in the solution increases gradually during the process of water-rock interaction. The composition of the solution shows minor variation as the dissolution of minerals is very little at the eraly stage of the reaction, and 1-10 days later, the contents of relevant elements in the solution increase quickly. The contents of Na, K, Al, Si, F and U in the solution have been increased in the process of water-rock interaction, especially the element of U, Si, F, K and Al (Figure 2). After water-rock interaction, the content of uranium in the hydrothermal solution amounts to 0.33—0.553 mg/l, in accordance with the results of the experimental study. At the end, the F and SiO_2-enriched uranium-bearing hydrothermal fluids could be generated by means of the water-rock interaction. The $\log f_{O_2}$ and Eh value in the fluids have decreased by a big margin as the result of oxidation of uranitite in the rock while meteoric water joining the deep circulation. $\log f_{O_2}$ and Eh are separately −0.7 and 0.446V to −27.301 and −0.258V, belonging to the reducing environment. However, the uranium in the hydrothermal fluids maintains high consistency rather than being reduced and precipitated, since $UO_2F_3^-$, $UO_2(CO_3)_2^{2-}$ and other uranium complexes are mobile species of uranium, and have very high stability, showing the migration capability of uranium in the reducing condition.

Some new minerals could be generated with the dissolution of the original rock by the interaction between hydrothermal fluid and surrounding rock. The principal alteration types are carbonatization, hematitization and apatitization. Dynamic equilibrium of dissolution-precipitation could be established rather than the stop of dissolution when the uranium is saturated in the hydrothermal solution. The modeling results suggest that uraninite could be continuously dissolved at a fixed speed as $UO_{2.25}$ is precipitated from the fluid, and reaching a dynamic equilibrium. This fact shows the importance of hydrothermal alteration for the mobilization of uranium. Uraninite with high degree of crystallization has a low solubility. However, when it is changed into $UO_{2.25}$ which has a low crystallization and higher oxygen-bearing coefficient, its solubility improves greatly, and forms the active uranium.

Major factors affecting the formation of the uranium-bearing hydrothermal solution

The results of modeling calculation show the relation between uranium content and pH, $\sum CO_3$ and temperature as indicated in figure 3 through figure 5.

pH value

The influence of pH on the uranium migration is reported in figure 3. It suggests that uranium has a strong migration capability under acid and alkaline condition, but neutral condition does not favour its migration. The result is in accordance with the experiment at elevated temperature and pressure.

Ligand concentration

CO_3^{2-} and F^- are the major ligands of the uranyl complex in fluorite-hydromica type of uranium deposit found in western Xiangshan uranium ore-field. Uranium content of hydrothermal solution is increased along with the $\sum CO_3^{2-}$, especially at the low concentration stage (cf. figure 4).

The migration capability becomes weaker against the increase of F- when the content of F^- is less than 0.005mol/L due to the fluorite precipitation. If F^- content increases continuously following the declining of calcium ion content, the water type could be changed into NaF type, and the content of effective F^- is increased, then forming stable $UO_2F_3^-$ which is favorable to the migrate of uranium.

Temperature

Temperature has a great influence on the migration of uranium. Uranium content increases linearly in the hydrothermal solution with the increase in temperature (cf. figure 5). The uranium content is increased from 0.0744mg/l, to 0.221, and to 0.549 mg/l in solution while the temperature is increased from 25 °C to 100 °C and then to 250 °C.

CONCLUSIONS

- The water-rock isotope exchange experiment showed that oxygen isotope could convincingly be exchanged between the water and rock in a hydrothermal system, resulting in $\delta^{18}O$ decrease for rocks and $\delta^{18}O$ increase for water, that is, causing an "oxygen shift". The δD values are relatively stable, but can apparently also vary if the rock contains a large amount of hydrogen-bearing minerals such as biotite. Consequently, the experiment has proven that the ore-forming hydrothermal solution in Xiangshan Uranium Ore-field is mainly derived from the local meteoric water.
- The modeling reveals that the content of uranium in the hydrothermal solution increased up to 0.33~0.553 mg/l after the water-rock interaction, in accordance with the results of the experimental study. At the end, the F and SiO_2 enriched U-bearing hydrothermal fluids could be generated by means of the water-rock interaction.
- Uranium in the hydrothermal fluids remains stable in the low Eh environment, since $UO_2F_3^-$, UO2 $(CO_3)_2^{2-}$ and other

uranium complexes have a very high stability.

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Table 1. Parameters for the experiments

No.	Rock	Fluid	W/R	T (ºC)	P (MPa)	Duration (hours)
XS-07	Porphyroclastic lava	XS-D	2.29	350	50	120
XS-08	Rhyo-dacite	XS-D	2.29	350	50	120
XS-09	Granitic porphyry	XS-D	2.29	350	50	48*
XS-10	Biotite-quartz schist	XS-D	2.29	350	50	120

*Halted due to equipment problem

Table 2. $\delta^{18}O$ values for rock before and after the water-rock interaction*

No.	Rock	$\delta^{18}O_i$ (‰) (SMOW)	$\delta^{18}O_f$ (‰) (SMOW)
XS-07	Porphyroclastic lava	9.6	9.3
XS-08	Rhyo-dacite	9.8	6.3
XS-09	Granitic porphyry	10.2	8.7
XS-10	Biotite-quartz schist	9.9	7.9

*Measured by the Institute of Ore Deposit, Chinese Academy of Geological Sciences, Beijing.

Table 3. The evolution of $\delta^{18}O$ and δD of Xiangshan ground water (XS-D) after water-rock interaction**

No.	Reacted with	$\delta^{18}O$ (‰) (SMOW)	δD (‰) (SMOW)
XS-D		-8.2	-50
XS-07	Porphyroclastic lava	1.3	-50
XS-08	Rhyo-dacite	-0.4	-44
XS-09	Granitic porphyry	-2.1	-52
XS-10	Biotite-quartz schist	0.6	-38

** Measured by the Institute of Ore Deposit, Chinese Academy of Geological Sciences, Beijing.

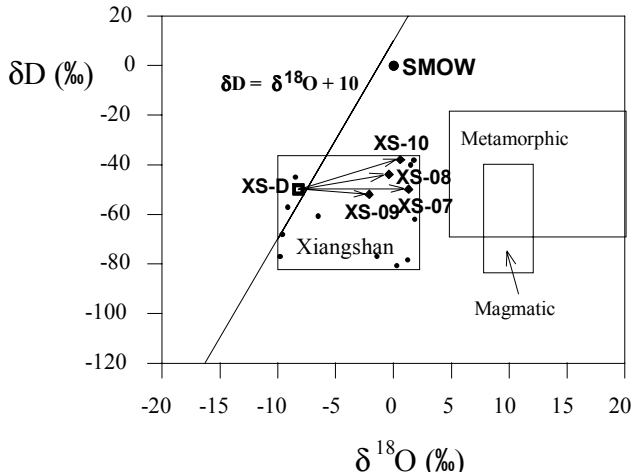

Figure 1. The evolution of isotope composition of water during water-rock interaction

Table 4 Hydrochemical composition of the water sample (XS-D) for modeling

Items	(mol/l)	(mg/l)	Items	(mol/l)	(mg/l)
Cl	3.13×10^{-5}	1.1	K	2.392×10^{-5}	0.9352
SO_4^{2-}	7.5×10^{-6}	0.72	Na	1.195×10^{-3}	27.48
HCO_3^-	3.358×10^{-3}	204.83	Cu	7.868×10^{-9}	0.0005
NO_3^-	/	0.31	Pb	1.448×10^{-8}	0.003
$SiO_{2(aq)}$	2.95×10^{-4}	17.72	Zn	6.118×10^{-8}	0.004
Al	1.81×10^{-6}	0.0488	F	9.578×10^{-5}	1.82
Ca	9.823×10^{-4}	39.37	U	3.074×10^{-8}	0.0083
Mg	3.168×10^{-5}	0.7699	$\log f_{O2}$	-0.7	
Fe	9.215×10^{-8}	0.0051			

Note: pH=6.7, t=25 °C

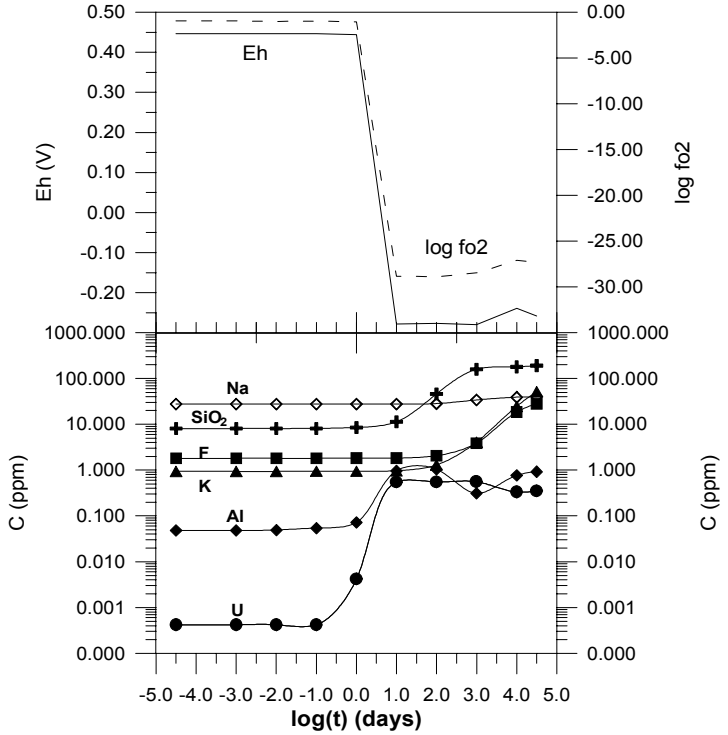

Figure 2. Evolution of composition and Eh for the hydrothermal solution

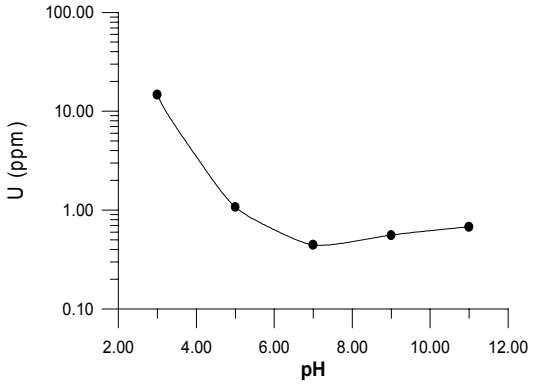

Figure 3. Diagram showing the relation between uranium content and pH of hydrothermal solution

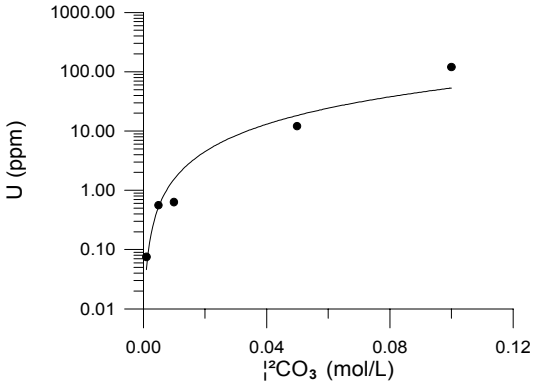

Figure 4. Diagram showing the relation between uranium content and δCO_3^{2-} of hydrothermal solution

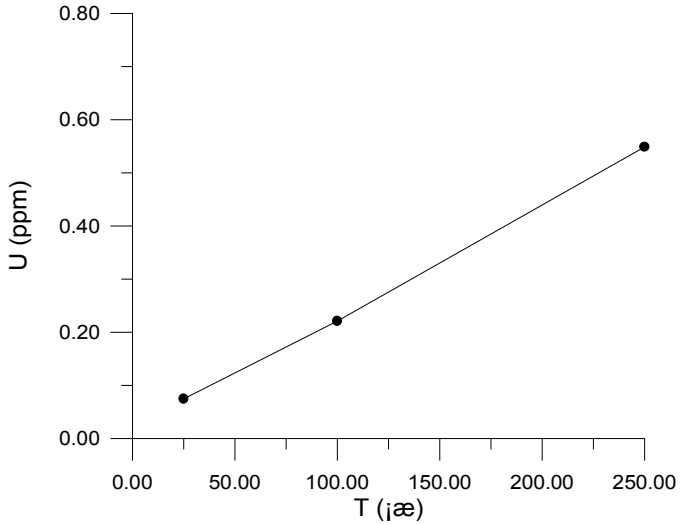

Figure 5. The Influence of temperature on the uranium content in hydrothermal solution