The Discovery of Natural Native Uranium and Its Significance

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Abstract: This study analyzed the composition and uranium valence of pitchblende samples from the hydrothermal Guidong and Zhuguang uranium deposits of the middle Nanling metallogenic belt, Southern China using X-ray photoelectron spectroscopy (XPS). A revolutionary discovery is that the uranium not only exists in the forms of tetravalent and hexavalent uranium oxides, but also occurs in the form of native uranium. This is the first discovery of the existence of native uranium in nature. It greatly helps to reveal the origin of hydrothermal mineralization of uranium, and also has great significance for studying the thermal energy, formation and evolution of the earth.

Key words: pitchblende, uranium deposit, native uranium, first discovery, metallogenic origin

Uranium, widely distributed in various geological bodies on the earth, usually occurs in compounds of multiple valences such as U4+, U6+, U5+ and U6++; among them compounds of U4+ and U6+ are relatively common in nature (Li et al., 2010). U4+ mainly exists in the form of pitchblende (UO2) during magmatic, metamorphic and hydrothermal processes. U6+ often dissolves in the water in the form of uranyl compounds or forms secondary uranium minerals in sulfate, carbonate, vanadates and phosphate in the environments of sedimentation, evaporation and oxidation (Hazen et al., 2009). Till now, no natural native uranium has been discovered prior to this study for its instability and changeable valence of uranium.

This study systematically analyzed the composition and uranium valence of pitchblende from the hydrothermal Guidong and Zhuguang uranium deposits in Southern China, and first discovered the natural native uranium in nature. This discovery not only reveals the origin of hydrothermal mineralization of uranium, but also has great significance for the study of thermal energy, formation and evolution of the earth.

1 The Samples

The pitchblende samples were collected from hydrothermal Guidong No. 330 and Zhuguang No. 302 uranium deposits, both of which are located in the northern part of Guangdong Province, Southern China (Figs. 1a, b and c), belonging to the famous Nanling uranium and polymetallic metallogenic belt (Li, 1999; Li, 2006; Li et al., 2012, Guo et al. 2014).

The Guidong No. 330 uranium deposit occurs in the Guidong multi-stage granitic batholith and mafic dikes (Fig. 1b), which is typical granite-related uranium deposit (Li et al., 2004). The lithology of the granitic batholith is mainly coarse-grained and medium-grained porphyritic biotite granite, medium-fine grained biotite granite, coarse-grained porphyritic hornblende biotite monzonite granite, fine-grained biotite granite and fine-grained garnet muscovite granite, and their ages range from 258 Ma to 121 Ma based on detailed geochronological studies (Li et al., 2010). Mafic dikes of diabase occur in the batholiths, which were formed at 110–90Ma. Dacite and granodiorite bodies were hosted in the northern part of the batholith (Fig. 1b). Pitchblende occurs in black veins controlled by fractures and faults at age of 85 Ma (Figs. 2 and 3) and as kidney-like structure under scan electronic microscope (Fig. 4, Li et al., 2010). Fluid inclusion studies show that the mineralization temperature ranges from 150°C and 300°C. Pyrite is a dominant associated mineral, and others include galena, sphalerite, marcasite, a little coffinite, monazite, greenockite, lillianite and clausthalite. Quartz, calcite and fluorite are the major gangue minerals; and altered minerals are mainly alkali feldspar, illite and clay minerals. The existence of all these minerals indicates that the composition of this hydrothermal ore-forming fluid is complicated and of reducing signature (Li, 1999; Li, 2006; Li et al., 2010; Li et al., 2012).

The Zhuguang No. 302 uranium deposit occurs in the
Zhuguang multi-stage granitic batholiths (Qi et al., 2014, Cai et al., 2015). These granitic batholiths are dominated by coarse-, medium- and fine-grained porphyritic biotite granite or two-mica granite with ages ranging from 388
Ma to 103 Ma (Fig. 1c). Pitchblende occurring in black veins is controlled by fractures and faults formed at age of 90 Ma. Fluid inclusion experiments suggest that the major mineralization temperature lies between 150°C and 350°C. Pyrite is a dominant associated mineral. Other associated minerals include sulfides such as galena, sphalerite, marcasite, and minor coffinite and monazite. Quartz, calcite and fluorite are the major gangue minerals. Altered minerals include alkali feldspar, illite, chlorite and clay minerals. Similarly, the existence of all these minerals indicates that the composition of hydrothermal ore-forming fluid is complicated, and was formed in a reducing environment.

The studied pitchblende samples are listed in Table 1.

2 Method

2.1 Introduction

The X-ray Photoelectron Spectroscopic (XPS) method utilized x-rays on the surface of the sample in an ultra high vacuum environment to investigate the chemical composition and elemental valence (Wagner et al., 1979; Briggs, 1990; Briggs and Grant, 2003; Wen, 2006). This study used the XPS to solve the following problems:

1) What sorts of elements exist on the surface of the pitchblende, and what are their chemical valences?
2) What are the relative proportions of different valence elements in the pitchblende?
3) Is there native uranium in the pitchblende in nature?

The samples were analyzed by using the instrument of Thermo Electron Corporation VG Multilab 2000 with Al Ka (hν=1486.6eV) at 300W on and at pass energy of 100eV for a better result in quantitative determination. Pass energy of 25eV is set for gaining precise binding energies in qualitative narrow scan analysis, with high vacuum condition less than 3×10⁻⁴ Pa and high resolution of 0.47 eV and 4 nm. Calibration of binding energies is referenced on the adventitious carbon (284.6eV). The XPS spectra are processed by using the software Avantage V4.54.

2.2 Measurement error and reliability

Every element has its own characteristic electron binding energy and shows characteristic XPS spectrum. The chemical valence of target elements can be identified by locating their peaks on the characteristic spectrum (Crist, 2000; Moudler and Stickle, 1992).

The area or intensity of the strongest peak (characteristic peak) is the basis for quantitative calculation and correction of peak intensity by using sensitivity analysis, because the photoelectron intensity of elements is not completely in proportion to their contents. The correction process can be done as follows: the background elimination subjecting to the intersection of tangents between peak edge and background, calculating the peak area size or strength and divided by their corresponding sensitivity factors respectively, and then obtained the relative atomic mole content of the elements (Huang, 2003; Guo, 2007).

The abscissa of XPS curve is binding energy and the ordinate is measurement intensity. The handbook or database for XPS binding energy can be used to identify elements qualitatively (Moudler and Stickle, 1992; Huang, 2003). The quantitative analysis is based on the intensity or size of peak area, which reflects the atomic percentage or relative concentration with precision of 1% to 2%.

The analysis depth of XPS depends on the energy of photoelectron and the properties of analyzed materials. In

Table 1 Pitchblende samples and their locations

<table>
<thead>
<tr>
<th>Number</th>
<th>Sample</th>
<th>Mineral</th>
<th>Location</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>GD-1</td>
<td>Pitchblende</td>
<td>Guidong Deposit No. 330</td>
<td>Pitchblende occurring in black veins are controlled by fractures and faults at age of 85Ma. Associated minerals include pyrite, galena, sphalerite, marcasite, a little coffinite, monazite, greemockite, lilianite and claushtalite.</td>
</tr>
<tr>
<td>2</td>
<td>GD-2</td>
<td>Pitchblende</td>
<td>Guidong Deposit No. 330</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>GD-3</td>
<td>Pitchblende</td>
<td>Guidong Deposit No. 330</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>GD-4</td>
<td>Pitchblende</td>
<td>Guidong Deposit No. 330</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>RE1</td>
<td>Pitchblende</td>
<td>Zhiqiang Deposit No. 302</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>RE2</td>
<td>Pitchblende</td>
<td>Zhiqiang Deposit No. 302</td>
<td></td>
</tr>
</tbody>
</table>
general, the analysis depth of XPS is defined as three times as the length of mean free path of photoelectron (Guo, 2007; Crist, 2000). Usually, the analysis depth is 0.5 nm to 2 nm for metal samples, 1nm to 3nm for inorganic compounds, and 3nm to 10nm for organics. XPS can be used for deeper analysis with the argon ion etching technique.

To guarantee the reliability of analysis result, the analysis was repeated a number of times for each sample. The sample GD-1, for example, was tested twice and presented the same atomic percentage 0.26% of native uranium. Moreover, each sample was subdivided into two parts that were analyzed separately for comparison. The results of qualitative and quantitative analysis are listed in Table 2 and Fig. 6, which show substantial consistency, demonstrating that the analysis is reliable.

3 Results and the Discovery of Natural Native Uranium

3.1 Whole spectrum scanning of the pitchblende

The XPS results of the pitchblende in the uranium deposits indicate that the pitchblende mainly consists of uranium and oxygen with minor calcium, fluorine, thorium and silicon (Figs. 5a, b, c, d and Figs. 6a, b). Fluorine in the pitchblende exists in the form of CaF2/ UO2F2; calcium occurs in the form of Ca3P2(CaF2), and oxygen is in the forms of UO3, UO2 and UO2F2, with a little thorium and silicon as ThO2 and SiO2, respectively. Uranium in the pitchblende exists in the forms of UO3, UO2 and native U.

3.2 Uranium valence of the pitchblende and discovery of native uranium

As chemical shift of inner electrons binding energy reflects the change of charge density on the atoms, the different chemical valence of an element can be determined by examining the chemical shift of inner electrons (Ilton, 2007).

By repeatedly scanning the narrow zones of the pitchblende, we found that there exist three chemical valences of uranium, i.e., U⁶⁺ (native uranium, see Table 3), U⁷⁺, and U⁶⁻ (Figs. 7 and 8). It should be noted that this is the first discovery of native uranium in natural uranium minerals worldwide.

Table 2 Comparison of duplicate measurement results from one sample

<table>
<thead>
<tr>
<th>Number</th>
<th>Sample</th>
<th>Mineral</th>
<th>O %</th>
<th>U %</th>
<th>F %</th>
<th>Ca %</th>
<th>Position</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>RE1</td>
<td>Pitchblende</td>
<td>91.11</td>
<td>1.7</td>
<td>4.21</td>
<td>2.99</td>
<td>Zhuguang uranium deposit No.302</td>
</tr>
<tr>
<td>2</td>
<td>RE2</td>
<td>Pitchblende</td>
<td>93.38</td>
<td>1.59</td>
<td>2.1</td>
<td>3.96</td>
<td>Zhuguang uranium deposit No.302</td>
</tr>
</tbody>
</table>

* Atom numbers of absorbed oxygen are included.

Fig. 5. Whole spectrum scanning results of the pitchblende in the Guidong uranium deposit. a, Sample GD-1; b, Sample GD-2; c, Sample GD-3; d, Sample GD-4.
3.3 Quantitative analysis

The key of XPS quantitative analysis is to convert element signal strength to element content, i.e., converting the peak area size into chemical content, and thus to obtain atomic percentage (At.%). The atomic percentage (At.%) of native uranium for six samples from both the above-mentioned uranium deposits are shown in Table 3. The percentages are generally low and variable, which indicate pitchblende are not homogeneous in natural ores under complicated geological conditions. In addition, the pitchblende is easily oxidized in the exposed condition.

As one element usually has different chemical valences and the peaks of different chemical valences may overlap each other, the Gauss-Lorentz function is used to fit the overlapped peak. The peak fitting curves of the different uranium chemical valences are shown in Fig. 7 and Fig. 8.

4 Conclusions

Under different geological conditions, uranium usually exists in different valences or compound forms, and its different valences or forms generally indicate different formation conditions. Therefore, the discovery of natural native uranium has great significance for revealing the formation of hydrothermal uranium deposits, and is also critical for understanding the evolution of the Earth.

(1) To date, it has been known that uranium exists in minerals of uranium deposits only with valences of four and six. However, the discovery of natural native uranium indicates that the uranium of hydrothermal deposits derives from the depths of the earth. Uranium occurs as native state or lower valences inside the earth because of the strong reduction environments. When uranium-bearing fluids migrate from the depths to the near surface of the earth, uranium is mostly oxidized into \( U^{4+} \) or \( U^{6+} \) due to the increasing oxygen fugacity, and only part of uranium is remained to exist as native state, resulted in the different uranium valences coexisting in deposits. It is concluded that the proportions among \( U^6 \) (native uranium), \( U^{4+} \) and \( U^{6+} \) in hydrothermal uranium deposits can be used to reveal the oxidation condition and metallogenic depth of uranium mineralization, i.e., the more \( U^6 \) the mineral contains, the deeper it forms. Moreover, this new discovery demonstrates that hydrothermal uranium mineralization does not form through oxidation-reduction processes, and that uranium can not be transported as uranyl carbonate in the deep part of the earth and reduced to form pitchblende under high oxygen fugacity in shallow part of the earth.

(2) The discovery of natural native uranium may provide evidence for the existence of native uranium in the earth centrosphere. Herndon (1993, 2003, 2006), an American geophysicist, considered that U-fission reactor could exist inside the earth, which was evident by discovering \(^4\text{He}\) in volcano ejectas. He also suggested that 64% of the uranium is assembled in the centrosphere. This theory can explain the periodic change of earth magnetic field. The results of modern geophysical and geological researches show that core-mantle materials could reach the surface through the mantle plume tectonics (Morgan, 1971), particularly during the early history of the earth. This point view can also well explain the inhomogeneous and concentrated distribution of uranium deposits in the world, particularly the obvious relationship between deep uranium sources and the formation of rich, great uranium deposits in Proterozoic, such as unconformity uranium deposits in Athabasca Basin/Canada and Olympic Dam uranium poly-metallic deposit in Australia. The radiogenic heat from uranium fission should be the source of energy within the earth. In fact, the natural nuclear reactor does exist in nature. In 1972, A French scientist founds a nuclear
reactor in oklo uranium deposits, Gabon (Pchelkin, 1976; Kuroda, 1983; Hidaka, 1999; Bentrudi et al., 2011), which took place 1.8 billion years ago and might last millions of years (Kikuchi and Hidaka, 2009), producing tremendous power and driving the geotectonic evolution.

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References


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