Experimental simulation of element mass transfer and primary halo zone on water-rock interaction

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A B S T R A C T

Primary halo zone is an important theory for prospecting the deep blind ore body and predicting resource potential. The common description of primary halo zone of multiple elements is based on their behaviors during hydrothermal alteration or mineralization. A geofluid with multiple elements, which are Bi, Cu, Pb, Zn, Cd, Ag, and As (bearing Ni and Mo), is prepared to simulate the dispersive transfer of elements in a hydrothermal fluid−granite reaction at 15 MPa, 100 °C using a new-constructed core flow-through pressure vessel reactor. Core granite samples with 5 cm long after water-rock reaction are cut into ten sections to analyze their major oxides and trace elements. According to experiment results and the method of immobile plateau, we determine that Al and Ti are immobile elements during the water-rock reaction and the hydrothermal alteration of granite is a mass gained process. The mobility index (MI) of each of experimental elements is calculated based on the immobile component Al_2O_3. The sequence of experimental elements is from As to Ag, Pb, Zn, Cu, Bi, Ni, Cd, and Mo, which are sorted on their values of MI in these reacted granite cores from near to far end respecting to the reaction fluid. This result is consistent with the empirical sequence of zonation of primary halo elements which is derived from the statistical results from 58 gold deposits in China. The denudation coefficient of primary halo zone (Zf or Zfe) is proposed to assess the degree of approaching to ore body on these experiments, which is the averaged MI ratio of front halo elements to ore-body halo elements. The denudation coefficient of primary halo zone is applied on the cross section of gold ore-body hosted in the granite of the Linglong gold deposit located in the Jiaodong peninsula of eastern China. The degree of approaching to the gold ore body is clearly illustrated by the denudation coefficient of primary halo zone.

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1. Introduction

Primary halo zone is an important theory for prospecting the deep blind ore body and predicting resource potential (Li et al., 1995; Shao, 1997; Eilu et al., 2001; Harraz, 1995; Harraz and Hamdy, 2015). It can be used to speculate the existence of blind ore body and to assess the degree of approaching to ore body (Chen and Zhao, 1998; Chen et al., 2008, 2016; Hosseini-Dinani and Aftabi, 2016). Researches on the primary halo zone originated in the 1950s. As one of the most important features of primary halo, the zonation of primary halo has always been the hot topic. In the 1970s, Grigoryan, a geochemist from the former Soviet Union, proposed an index to calculate the element zonation of primary halo and derived an experience zonation of elements of primary halo in hydrothermal deposits (Shao, 1997). In China, Shao also proposed a zonation pattern of primary halo based on lots of case data from ore deposits and discussed its applications on resource prospecting in 1974 (Shao, 1997). With respect to gold deposits, Li et al. (1999) derived an empirical zonation of elements of primary halo based on 58 typical gold deposits in China. The zonation sequence of elements from the top to the bottom of ore body is B-As-Hg-F-Sb-Ba which represents the assemblage of front halo elements, to Pb-Ag-Au-Zn-Cu which is the assemblage of ore body elements, then to W-Bi-Mo-Mn-Ni-Cd-Co-V-Ti, which represents the assemblage of tail halo elements. Although these experience zonation sequences are derived from lots of case studies, no experimental simulation exists on water-rock reaction in hydrothermal mineralization or alteration systems to test the results. In this paper, we designed a simulation experiment on water-rock interaction to investigate the behaviors of elements in the primary halo during hydrothermal alteration or mineralization.

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The common chemical indices for describing the process of alteration are divided into two types. One type is constructed on the major oxides of samples to indicate the degree of alteration, such as Alteration Index (AI; Ishikawa et al., 1976; Date et al., 1983), Chemical Index of Alteration (CIA; Nesbitt and Young, 1982) and Chlorite-Carbonate-Pyrite Index (CCPI; Large et al., 2001). In addition, some weathering index, such as Weathering Index of Parker (WIP; Parker, 1970), Weathering Index of Colman (WIC; Colman, 1982) and Weathering Index of Granite (WIG; Gong et al., 2013) can also be applied for describing the alteration or mineralization process, which can be classified into this type. The other type is presented on element contents of samples to assess elements' quantity of mass transfer, such as Mobility Index (MI; Ng et al., 2001), the percentage of gain or loss (X_{gp}; Ng et al., 2001) and the τ value (Brantley et al., 2007; Brantley and White, 2009; Ma et al., 2011). These indices are calculated on the basis of the immobile elements during hydrothermal alteration. Here, we adopt both two types of index to calculate the degree of alteration of samples and the quantity of mass transfer of elements on the reacted samples. Finally the element zonation of primary halo is ordered by its quantity of mass transfer during the hydrothermal alteration.

2. Materials and methods

2.1. Rock materials

The sample of granite for simulation experiment was collected from Linglong biotite granite located in the Jiaodong Peninsula, China (Gong et al., 2013; Ma et al., 2013). Four columnar samples were made from the granite with length of about 5.1 cm and diameter of approximately 2.6 cm. The detailed size and experiment No. for each sample are listed in Table 1. The granite samples before and after experiments are presented in Fig. 1.

Fig. 1 Photographs of analyzed samples before and after the simulation experiment. (a) Primary sample from Linglong biotite granite; (b) Two of the cores after cutting from the primary granite; (c) No. 1 pre-experiment core without reacted; (d) No. 3 before the simulation experiment; (e) No. 3 after the experiment; (f) No. 3 is cut into 10 sections from the near to the far end to the reaction fluid; (g) No. 4 before the experiment; (h) No. 4 after the experiment; (i) No. 4 is cut into 10 sections from the near to the far end; (j) No. 5 before the experiment; (k) No. 5 after the experiment; (l) No. 5 is cut into 10 sections from the near to the far end. Arrows indicate the movement direction of the reaction fluids.

2.2. Fluid materials

The reaction fluid in S3 is prepared by dilution of standard solution, which represents a geofluid with multiple elements in low contents. In fluids of S4 and S5 which represent hydrothermal fluids with high metal contents, Bi, Cd, Ag and As are made by dilution, while, Cu, Pb and Zn are made from the dissolution of standard solid (nitrate). The element concentrations of fluids adopted in this simulation are listed in Table 2.

Table 1
Experiment No. and sample sizes of granite columns for the experiment.

Test no.	Sample no.	Length (cm)	Diameter (cm)
Pre-experiment	1	5.10	2.60
S3	3	5.14	2.60
S4	4	5.09	2.60
S5	5	5.09	2.61

2.3. Experimental setup

Based on the reactor system reported by Gong et al. (2012), a new core flow-through pressure vessel reactor was constructed to simulate the disperse transfer of elements in water-rock reaction under high temperature and high pressure (Fig. 2). The simulation reactor and the connected wires are made from hastalloy B, which is an alloy mainly made from Ni and Mo.

2.4. Experimental procedure

Temperature, pressure and reaction time were set in these simulation experiments and are listed in Table 3.

In S3, when the fluid−rock interaction had experienced 13 h, the effusion took place at the trailing end of granite core, thus brought S3 to the end of simulation. Accordingly, in the subsequent S4 and S5, the reaction time was set at eight hours to avoid the effusion and model the multi-component dispersed transformation in granite medium, rather than the transformation dominated by fluxion. Remarkably, the S4 and S5 are characterized by the same experimental parameters, indicating that they are repeated experiments.

2.5. Analytical methods

All granite core samples before and after the experiment were respectively cut into 10 sections at 0.5 cm interval from the near to far end to the reaction fluid, with each sample labeled as 1 to 10 (e.g. 101, 102, 103, 104, 105, 106, 107, 108, 109, 110 in Fig. 1).

Granite samples were analyzed at the Hubei Geological Research Laboratory in China. Major oxides (SiO_2, Al_2O_3, TiO_2, Fe_2O_3, Na_2O, K_2O, CaO, MgO, MnO, and P_2O_5) and trace elements of Ba, Cr, Nb, Rb, Sr, and V were analyzed by X-ray fluorescence spectrometry (XRF) on pressed powder pellets. FeO was determined by volumetric analysis, LoI (Loss on Ignition) by gravimetry. Trace elements of Bi, Cd, Co, Cu, Mo, Ni, Pb, Sc, Ta, Th, U, W, Y, Zn, and rare earth elements were analyzed by inductively coupled plasma mass spectrometry (ICP-MS). As, Sb were detected by atom fluorescence spectrometry, Be and Li by inductively coupled plasma atom emission spectrometry, and Ag, B, and Sn by emission spectrometry.

The accuracies of the above-mentioned analyses were monitored using standard materials. Most of the analytical methods yield accuracy higher than 5% for major oxides and 10% for trace elements. The relative errors of repeated sample analyses are less than 10% and most exhibit less than 5% of relative errors.

3. Results

The bulk analyses of major oxides, rare earth elements and other trace elements of the reacted granite samples are listed in Table 1S.

3.1. Major oxides

Major oxide contents (including LoI), WIG, Al_2O_3/TiO_2 and K_2O/SiO_2 values of the before and after reacted granite samples are plotted versus distance from the near to far end to the reaction fluids in Fig. 3.

WIG index is constructed on the major oxides of sample to describe the degree of granite weathering (Gong et al., 2013), which is also suitable to describe the alteration degree of rocks in alteration or mineralization process (He et al., 2014). Al_2O_3/TiO_2 is a ratio between immobile elements (Duzgoren-Aydin et al., 2002) and can be used to trace parent rocks of samples from regolith profiles (Gong et al., 2015). The index of K_2O/SiO_2 is a ratio between mobile