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He-Ar Isotopic Systematics of Fluid Inclusions in Pyrites from PGE-polymetallic Deposits in Lower Cambrian Black Rock Series, South China

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Abstract He-Ar isotopic compositions of fluid inclusions trapped in pyrites from some representative PGE-polymetallic deposits in Lower Cambrian black rock series in South China were analyzed by using an inert gas isotopic mass spectrometer. The results show that the ore-forming fluids possess a low $^3He/^4He$ ratio, varying from 0.43×10^{-8} to 26.39×10^{-8}, with corresponding R/R_a value of 0.003–0.189. The $^{40}Ar/^{36}Ar$ ratios are 258–287, close to those of air-saturated water (ASW). He-Ar isotopic indicator studies show that the ore-forming fluids were mainly derived from the formation water or basinal hot brine and sea water, while the content of mantle-derived fluid or deep-derived magmatic water might be negligible. The PGE-polymetallic mineralization might be related to the evolution of the Caledonian miogeosynclines distributed along the southern margin of the Yangtze Craton. During the Early Cambrian, the formation water or basinal hot brine trapped in Caledonian basins which accumulated giant thick sediments was expelled and migrated laterally along strata because of the pressure generated by overlying sediments. The basinal hot brine ascended along faults, mixed with sea water and finally deposited ore minerals.

Key words: He-Ar isotopic systematics, pyrite, fluid inclusions, PGE-polymetallic deposit, basinal hot brine

1 Introduction

Lower Cambrian black rock series are extensively distributed in South China, within which precious metals, specially platinum group elements (PGE), are extraordinarily enriched (Fan, 1997; Bie and Meng, 1999; Ye and Fan, 2000), and locally formed deposits or ore spots of PGE, such as PGE ore spots around Zunyi, Guizhou Province (Coveney and Chen, 1991, Coveney et al., 1992a and b), PGE and Au ore spots associated with Ni-Mo-V deposits in black rock series distributed in the Zhangjiajie (Dayong) area of northwestern Hunan Province (Li, 1995; Liang and Zhu, 1995; Bao, 1997) (Fig. 1). Thus the black rock series in South China is a significant potential exploration target for PGE. Besides, these black rock series also hint an important anoxic and catastrophic event in the geological history (Zhang et al., 1987; Wu, 2000). In recent years, some researchers studied the genesis and enrichment mechanism of PGE of the black rock series from different aspects: Fan (1983) proposed probable extraterrestrial sources of the PGE based on poly-element composition and Ir abnormal characteristics; Murouchick et al. (1994) measured sulfur isotopic compositions of sulfides in the Lower Cambrian stratabound Ni-Mo-(PGE-Au) ores from South China and proposed that those ores were formed syngenetically with the sedimentary rocks or during the early diagenetic stage. After a measurement of Re-Os isotopic compositions of Ni-Mo-PGE ores from black shale series from Canada and South China, Horan et al. (1994) suggested that a PGE enrichment occurred near the time of sediment deposition or during the early diagenesis. Based on trace elements combination characteristics, Coveney et al. (1992a and b) proposed that the Ni-Mo-PGE-Au ores from South China probably originated as exhalites from submarine springs, and their analytical data did not support extraterrestrial sources of PGE. According to the correlation and normalized pattern of the PGE and Au in the Cambrian black shale series in South China, Li and Gao (2000) proposed that the ores formed by submarine hydrothermal exhalation and the precious metal were originated from Proterozoic mafic to ultramafic rocks, within which submarine hydrothermal fluids convected and absorbed precious metals. Mao et al. (2002a) defined a Re-Os age of 541±16Ma (2σ) with an initial $^{187}Os/^{188}Os$ ratio of 0.78±19 and suggested synsedimentary metal enrichment from seawater and anoxic conditions. Nevertheless, the genesis and source of the precious metals in the black rock series of South China are still in dispute.

In recent years, isotopic systematics of inert gases such as He and Ar were extensively used as source indicators of

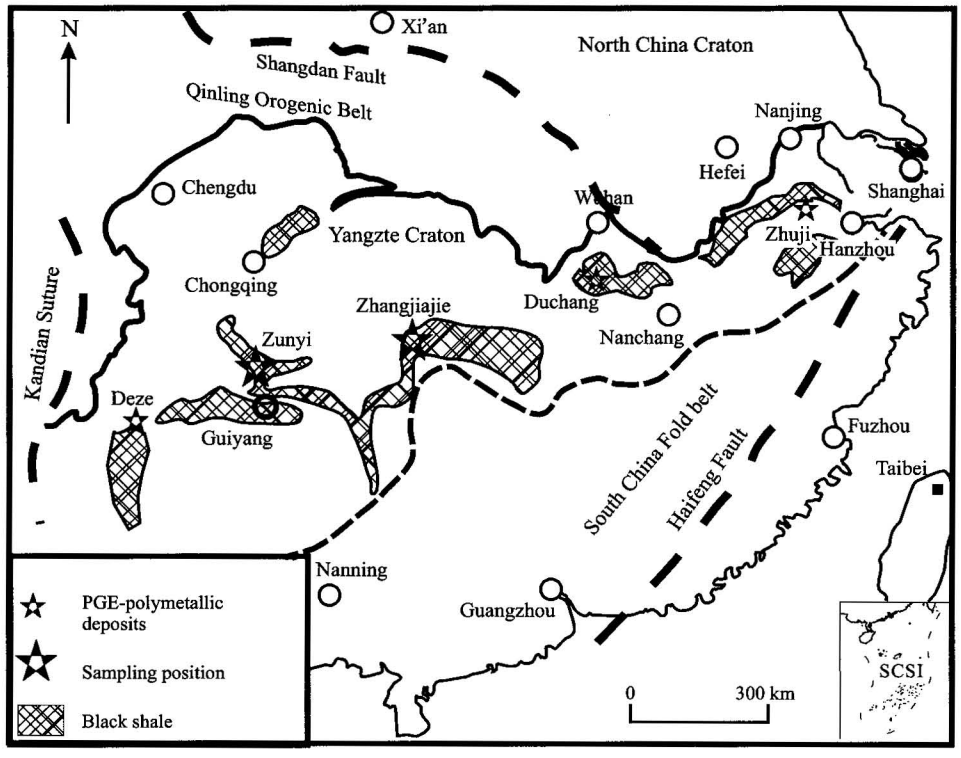

Fig. 1. Geotectonic setting and distribution map of the black shale and related PGE-polymetallic deposits in South China (after Mao et al., 2001).

ore-forming fluids, and many achievements have been made (Simmons et al., 1987; Sturart et al., 1995; Hu et al., 1997; Sun et al., 1999; Burnard et al., 1999; Zeng et al., 2001; Winckler et al., 2001; Zhao et al., 2002; Mao et al., 2002b, 2003). The major reasons include: (1) Inert gases isotopic systematics basically will keep unaffected during water-rock interaction, and thus could retain the original source information of the ore-forming fluids, and (2) The He-Ar isotopic compositions of various sources of ore-forming fluids are quite different, and thus it is easy to make a distinction among them. In this work, He-Ar isotopic systematics of fluid inclusions in pyrites of the Lower Cambrian black rock series from South China was measured, and the metallogenic mechanism was primarily discussed based on the analytical data.

2 Outline of the Host Strata

Although stratohorizons and rock associations of the Lower Cambrian black rock series in South China vary among different areas, the lithologic units from bottom to top generally include: the Sinian dolostone and paleoweathered horizon, the Cambrian black phosphate nodules bearing baritic rocks, the Cambrian black phoshorites, the Cambrian black cherts, the Cambrian Ni-Mo-PGE-bearing black shale ore layers, the Cambrian polymetallic black shale layers and Cambrian black shale layers (Li and Gao, 2000). Precious metals such as PGE predominantly occur in the Cambrian Ni-Mo-PGE-bearing black shale ore layers. The thickness of the ore layers is usually 20–30 cm, locally 50–80 cm. Observations under microscope show that the ores are mainly composed of clay mineral, feldspar, quartz, carbonate mineral, organic matter, jordisite and pyrites. Pyrite, one of the most important ore minerals in diameter of 1–5 mm, mainly occur as laminated and lentiform, occasionally disseminated, structures. The pyrites are usually of euhedral cubic, and locally framboidal crystals.

In the underlying strata of the Ni-Mo-PGE-bearing black shale ore layers, many stockworks with a thickness of several millimeters were recognized, which were filled with carbonate minerals and quartzes and vertically cut the strata. These stockworks probably represent the remains of ore-forming fluids channel-way of the PGE-polymetallic ores.

3 Samples and Analytical Method

The samples for this study were collected from some typical Ni-Mo-PGE mineralized Lower Cambrian black rock series sections, such as the Xintugou section and Dayuan mine near Zunyi in Guizhou, Daping, Ganziping

and Houping sections in Zhangjiajie (Dayong) in Hunan. The samples were crushed to 0.1–0.2 mm in diameter, sorted by magnetic dressing and heavy liquid, and then the pyrites were handpicked under a binocular miscroscope. X-ray diffraction detection showed that the pureness of the pyrites is more than 99%.

The pyrites were cleaned by acetone and double deionized water in ultrasonic bath for 20 minutes, and then dried over. The samples were heated under vacuum at 120° C for 24 hours to eliminate secondary fluid inclusions and gases absorbed on the mineral surface. The cleaned and dried pyrites were crushed to release trace gases trapped in the fluid inclusions. The released gases were purified successively through two titanium sponge pumps, a Zr-Al pump and an active-carbon cooling trap filled with liquid nitrogen. Active gases were frozen and completely removed. Ar and Xe were frozen, and comparatively pure He and Ne were introduced into the analyzing system. He and Ne were purified again by using a titanium sublimation pump filled with liquid nitrogen to remove trace impurities such as H_2 and Ar. Then the He isotopic compositions were analyzed by using a mass spectrometer. Finally, Ar was released at −78°C and Ar isotopes were analyzed. He and Ar contents were measured according to the weight of the crushed samples. The analytical instrument used is an Ukraine-made MI1201 IG noble gas mass spectrometer in the Isotopic Laboratory of the Institute of Mineral Resources, Chinese Academy of Geological Sciences. The ^3He was detected by an electronic multiplier detector and ^4He by a Faraday cup. The resolutions of the electronic multiplier detector and Faraday cup are 1200 and 760 respectively. The standard gas is air in Beijing and its $^3He/^4He$ is 1.4×10^{-6}.

4 Analystical Results and Discussion

The analytical data of He and Ar isotopic compositions in pyrites from some typical PGE-polymetallic ores in the Cambrian black rock series are presented in Table 1, which shows that: (1) In spite of a quite high variation, the $^3He/^4He$ ratios of all the samples are very low, ranging from 0.43×10^{-8} to 26.39×10^{-8}, and the R/R_a are 0.003–0.189. The sample from Ganziping in Hunan has the highest ratio, while the Daping sample the lowest; (2) The $^{40}Ar/^{36}Ar$ ratios of all the samples slightly vary between 258–287, which is slightly lower than that of air-saturated water (295.5).

Previous studies proved that noble gases such as He and Ar trapped in fluid inclusions in pyrites do not leak or lose because of lack of cleavages (Hu et al., 1997; 1998a and b), thus the He and Ar isotopic compositions may reflect the He-Ar isotopic systematics of ore-forming fluids of PGE-polymetallic ores in black shale series.

Studies of Burnard et al. (1999) demonstrated that noble gas isotopic compositions of fluid inclusions might be used as indicators to recognize different sources of ore-forming fluids: (1) Air-saturated water (ASW), including meteoric water and sea water. Its $^3He/^4He$ and $^{40}Ar/^{36}Ar$ values are 1 R_a and 295.5 respectively; (2) Mantle-derived or deep-derived magmatic water. Its typical $^3He/^4He$ and $^{40}Ar/^{36}Ar$ values are 6–9 R_a and higher than 400; (3) Crustal fluid, namely, formational water or basinal hot brine. Its characteristic $^3He/^4He$ and $^{40}Ar/^{36}Ar$ respective values are 0.01–0.05 R_a and higher than 295.5. The He and Ar isotopic compositions of the three different sources of fluids mentioned above and those of the fluid inclusions in pyrites from the PGE-polymetallic ores were shown in Fig. 2. In Fig. 2, the pyrites are mainly scattered between ASW and crustal fluids (C), specially near the latter, but quite far from the mantle-derived water (M), suggesting that the ore-forming fluids of PGE-polymetallic ores are probably composed mainly of basinal hot brine and air-saturated water, while the content of mantle- or deep-derived magmatic water may be negligible. Besides, the air-saturated water in the fluid inclusions is probably composed predominantly of sea water, because the host rocks of the PGE-polymetallic ores, namely, the Lower Cambrian black rock series, consist predominately of marine sedimentary rocks.

For the purpose of comparison, $^3He/^4He$ and $^{40}Ar/^{36}Ar$ fields of some typical modern submarine hydrothermal

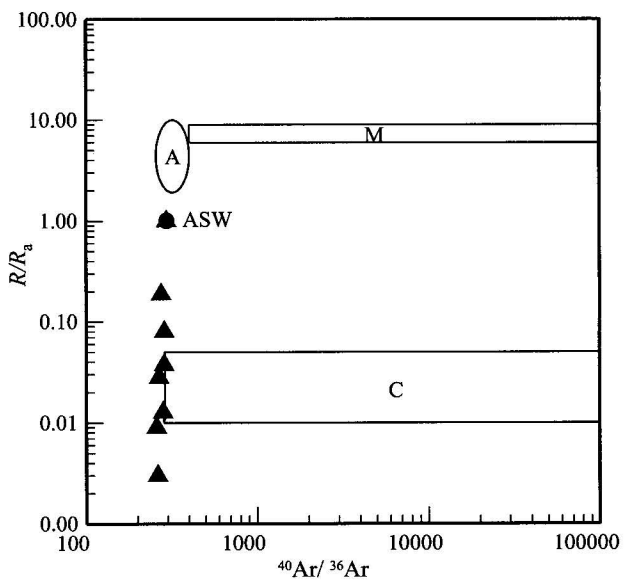

Fig. 2. $^{40}Ar/^{36}Ar$–R/R_a diagram of fluid inclusions in pyrites from Lower Cambrian black rock series, South China (after Zhao et al., 2002).

ASW – air saturated water; A – field of submarine hot brines from Red Sea and TAG in the Atlantic Ocean (after Winckler et al., 2001; Zeng et al., 2001); M – field of mantle fluids; C – field of crust fluid. The filled triangles are pyrites from black rock series in South China.

Table 1 He-Ar isotopic compositions of fluid inclusions in pyrites from PGE ploymetallic ores in Lower Cambrian black rock series of South China

Sample Number	Sampling Location	$^3He/^4He\times10^{-8}$	$^4He\times10^{-6}(cm^3/g)_{STP}$	$^{40}Ar/^{36}Ar$	$^{40}Ar/^{38}Ar$	$^{36}Ar/^{38}Ar$	$^{40}Ar\times10^{-7}(cm^3/g)_{STP}$	R/R_a*
200201	BT304 in Xintugou, Zunyi	5.25±2.08	3.99	286±1	1605±10	5.60±0.05	4.30	0.038
200216	Dayuan Ni-Mo Deposit, Zunyi	11.19±2.12	3.30	287±2	1573±8	5.49±0.01	6.86	0.080
200222	Dayuan Ni-Mo Deposit, Zunyi	1.32	24.67	258±7	1456±67	5.63±0.06	8.18	0.009
200227	Dayuan Ni-Mo Deposit, Zunyi	1.78	1.85	282±5	1548±21	5.50±0.02	18.13	0.013
200240	Daping Mo Deposit, Zhangjiajie, Hunan	0.43	6.23	262±1	1486±1	5.68±0.03	6.45	0.003
200245	Ganziping Mo Deposit, Zhangjiajie, Hunan	26.39±6.01	2.44	275±1	1542±5	5.59±0.03	6.60	0.189
200249	Houping Mo Deposit, Zhangjiajie, Hunan	3.93	3.70	267±1	1541±13	5.74±0.05	1.37	0.028

*R_a represents the $^3He/^4He$ of air in Beijing, and the value is 1.4×10^{-6}.

fluids such as Red Sea and TAG area in the ridge zone of the Atlantic Ocean (A) (Winckler et al., 2001; Zeng et al., 2001) were marked in Fig. 2. The scattered points of the PGE-polymetallic ores are also quite far from A, suggesting that the tectonic setting of the PGE-polymetallic mineralization was probably not oceanic ridge, and the ore-forming fluids contain a little mantle-derived components.

Excepting He-Ar isotopic compositions analyses, systematic observations and measurement were made on fluid inclusion in the PGE-polymetallic ores and the carbonate and quartz of the stockworks beneath the ore layer. Two kinds of fluid inclusions, with homogenization temperatures of 150–200°C, were recognized. The first kind is organic matter-rich ones, with salinity usually higher than 15 wt% (NaCl)eq. The second contains a little organic matter, with salinity lower than 5 wt% (NaCl)eq. The characters of fluid inclusions also demonstrate that the ore-forming fluids of the PGE-polymetallic ores are composed mainly of basinal hot brines with medium to high salinity and air-saturated water with low salinity. The measured data of fluid inclusions are in accordance with the He-Ar isotopic components analyzed.

Measurements of He-Ar isotopic compositions of fluid inclusions in pyrites highlights the genesis of the PGE-polymetallic ores: evolution of sedimentary basins and the associated basinal hot brines probably played an important role in the genesis of the Ni-Mo-PGE ores. During the Neoproterozoic to the Early Cambrian, Caledonian miogeosynclines distributed along the southern margin of the Yangtze Craton received very thick fine-granied clastic and lime sediments. The great pressure caused by the overlying sediments would expel and force the formational water or basinal hot brines trapped in the sediments in the miogeosynclines to migrate laterally along contact zones of the strata. The expelled formational water would absorb ore-forming elements such as Ni, Mo, V and PGE, forming mineralizing fluids with medium to high salinity and high content of organic matters. The basinal hot brines ascended along faults, mixed with sea water, and finally deposited PGE-polymetallic ores in the black rock series during the Early Cambrian (541.3±16 Ma, Mao et al., 2001). The nearly vertical stokworks underlying the ore layers, which were usually filled with carbonate and quartz, probably represent remains of ascending channel-way of the basinal hot brines.

5 Conclusions

(1) The $^3He/^4He$ ratios of ore-forming fluids of PGE-polymetallic ores in the Lower Cambrian black rock series from South China are quite low, varying from 0.43×10^{-8} to 26.39×10^{-8}, and the R/R_a are 0.003 to 0.189, while the $^{40}Ar/^{36}Ar$ ratios are 258–287, near those of the air-saturated water.

(2) The ore-forming fluids of the PGE-polymetallic ores are composed predominately of basinal hot brines and air-saturated water or sea water, which contain a little mantle-derived water.

(3) Basinal hot brines probably played an important role in the PGE-polymetallic mineralization. During the Early Cambrian, formation water trapped in thick sediments, which were accumulated in the Caledonian miogeosynclines distributed along the southern margin of the Yangtze Craton, was expelled and migrated laterally along strata or vertically along fault, and finally mixed with sea water and deposit PGE-polymetallic ores.

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