Synchrotron radiation X-ray fluorescence analysis on altered mineral muscovite in gold deposit

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Abstract Synchrotron radiation X-ray fluorescence (SRXRF) microprobe was used to ananlyse altered mineral muscovite and its surrounding feldspar in Yuerya gold deposit. The major, minor and trace elements of the two minerals were detected and analyzed. SRXRF analysis showed that the Yuerya muscovite had a complex chemical composition, containing K, Fe, Ca, Ti, Cr, Mn, Co, Cu, Zn and many trace or ultra-trace elements. Since muscovite resulted from the alteration of hydrothermal ore fluid acting on feldspar (plagioclase), the difference of chemical composition between the two minerals shows the components of ore fluid, which are characterized by the enrichment of alkaline and alkaline-earth metal elements K, Ca and ore-associated elements Fe, Cu, Zn. And gold, silver and platinum, invisible under microscope, were detected in some areas of muscovite, but not found in feldspar. Especially platinum, a mantle material, is rarely seen in the earth crust but now found in the gold deposit of magmatic sources; its appearance approves the idea of mantle flux participating in the gold mineralization, which suggests that the tectonic event controlling gold mineralization in the Yuerya district is a mantle phenomenon.

Keywords Synchrotron radiation X-ray fluorescence, Muscovite, Gold mineralization

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1 Introduction

Gold has been of particular interest because of its noble metal value and its chemical stability. Knowledge of the source of ore fluids and ore materials is fundamental for understanding gold ore formation. In recent years, many analytical methods were applied to gold-bearing mineral such as quartz and pyrite to determine gold state in geological samples and investigate ore material sources, particularly for the identification of so-called “invisible gold”, trapped in the crystal structure of carrier minerals.[1-3] But a gold-carrier mineral muscovite has not been received attention due to its dispersed and tiny characteristics and the problem of separating from feldspar, so general measuring methods are difficult to be used to study it.[4]

Recently, synchrotron radiation X-ray fluorescence (SRXRF) microprobe has been shown to be a promising technique due to the features such as non-destructive and avoiding complex sample pretreatment. And the unique properties of synchrotron radiation such as high brilliance, linear polarization and coherence, provide significant analytical advantages like the possibility of tuning the excitation energy through suitable monochromator devices, thus enhancing the sensitivity for most chemical elements.[4,5] It is very suitable for irradiating as-collected small fragments and making chemical composition analysis.

We have adopted synchrotron radiation X-ray fluorescence technique to determine the altered mineral muscovite and surrounding feldspar of Yuerya gold deposit, Hebei Province, China. The major, minor and trace elements of muscovite and feldspar are determined, and by the comparison of chemical composition of the two minerals, the components of hydrothermal ore fluid was disclosed. Ultra-trace gold, silver and platinum were detected from muscovite crystal and some information about gold mineralization was given.

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2 Geological setting

The Yuerya district, between latitude 118°31' and 118°33' N and longitude 40°29' and 40°30'E, in the eastern part of the northern marginal zone of the North China Craton (NCC) and about 256 km northeast of Beijing, is one of the most important gold-producing areas in China, where the gold deposit is associated with the intrusion of Mesozoic granitic rock. The petrographic evidence indicates that the granitic body of the Yuerya has endured hydrothermally altertion associated with gold mineralization and that primary gold occurs virtually exclusively in granite. Periodic reactivation of the NE-trending faults-magmatic activity zone controls occurrence of Yuerya gold deposit.[6,7]

Gold was first discovered by the local inhabitants in Yuerya district in 1887. Since then, gold has been mined from both primary and secondary deposits. At Yuerya, the primary gold occurs virtually exclusively in granite, with 1.5-km-long and 0.7-km-wide and an area of about 0.59 km^2, and intruding into calcareous dolomitite of Gaoyuzhuang group stratum.[8]

Petrographic evidence indicates that Yuerya granitic rock has been hydrothermally altered by processes that include pyritization, silicification, sericitization, albitization, kaolinization, calcification, and chloritization. Gold mineralization in the district is characterized by structure-controlled gold-bearing pyritic quartz veins. The main alteration types include pyritization, silicification and sericitization, closely related with gold mineralization.

The metallic sulfide mineral assemblage consists of disseminated micron- to submicron-sized gold, pyrite (Fe_2S), chalcopyrite (Cu_2S), galena (PbS), sphalerite (ZnS), and tetrahedrite($Cu_{12}Sb_4S_{13}$). Pyrite is the most common sulfide mineral and occurs as subhedral to anhedral grains, in clusters, and in veins. Gangue minerals include chalcedonic quartz, plagioclase, K-feldspar, muscovite and calcite. Gold often occurs mainly as electrum and native gold, which occur together with sulfide mineral in fracture of pyrite grains or between gangue mineral grains.[6,7]

3 Samples and experimental

The stone samples collected from the Yuerya granite with slight pyritization, silicification and sericitization. The sample comprises quartz, plagioclase, K-feldspar, biotite, with a few pyrite and light brown and/or green muscovite. The stone was cut into a slice of 0.03 mm thickness with a polished surface. Observed under 100× microscope, muscovite occurs in vein along grain boundary of feldspar or interspersed in plagioclase grains. The muscovite veins on the slice were chosen for irradiation after checking under the microscope to ensure no impurity.

Synchrotron radiation X-ray light used in the experiment cames from the 4W1B beam line at Beijing Synchrotron Radiation Facility.[9] SRXRF spectra were collected during 300s with a Si(Li) detector placed at a distance of 75 mm from the irradiated surface with an incident synchrotron radiation beam of 20 μm×20 μm dimension impinging on sample. In the experimental setup the emergent X-ray fluorescent beam propagated in air until the window of the solid state detector, therefore hindering the analysis of light elements (Na, Mg, Al, Si). The WinQXAS program was used for picking assignment, deconvolution of complex lines, reduction of continuous background caused by scattering and bremsstrahlung in the sample, and estimation of peak area under analytical *K*- or *L*-line.

Fifteen points of muscovite and twelve points of the surrounding feldspar were analyzed after normalized to the intensity of incident X-ray fluorescence. For no suitable mineral standard, rock standards GSR1 (granite), GSR2 (andesite) and GSR3 (basalt) were selected for normalizing the elements of muscovite and feldspar after the standard powders were mixed evenly and then pressed to pieces with similar thickness of the stone slice. The chemical composition analysis was based on peak areas ratios of samples to standards and only semi-quantitative results were obtained since both thickness of the sample slice and coarseness of the sample surface were not comparable to that of the rock standards. Correlation factor analysis was based on X-ray fluorescence counts (peak areas) of every element after normalized to the intensity of incident X-ray fluorescence. If the net peak area of an element was less than three times of the background, this element was considered to be not contained and was ignored in calculation.

4 Result and discussion

4.1 Chemical composition

Muscovite, an aluminous mica-type phyllosilicate with typical chemical formula as $KAl_2[Si_3AlO_{10}](OH,F)_2$, contains a great variety of trace elements according to their availability at the time of mineral formation and during subsequent modification caused by pressure/temperature variations.[10]

Calculated with GSR1, GSR2 and GSR3 as standards, SRXRF analysis showed that muscovite from Yuerya had a complex chemical composition, containing K, Ca, Fe, Ti, Cr, Mn, Co, Cu, Zn as main components, and Ba, Ga, Rb, As, Hg, Sr, Br, Se, Y, Zr, Nb, Mo, In, Sn, Sb, La, Sm, Gd, Tb, Dy, Ta, Re, etc. as trace or sub-trace elements (Fig.1). The feldspar has simple chemical composition, with main components including Fe, only one tenth of that of muscovite, Cr, Mn and Co, whose contents are close to those of muscovite, and Ti, Zn, Cu, Ge, Se, As, Br, Rb and Sr, with very low concentration close to the detection limit and occasionally seen. Since muscovite is an alteration product when hydrothermal ore fluid meets feldspar (plagioclase) and muscovite appears as substitution feldspar crystal selectively, it is obvious that most of these elements in muscovite come from altered hydrothermal fluid, except Cr, Mn and Co mainly from feldspar. By comparing the chemical compositions of plagioclase with those of muscovite,

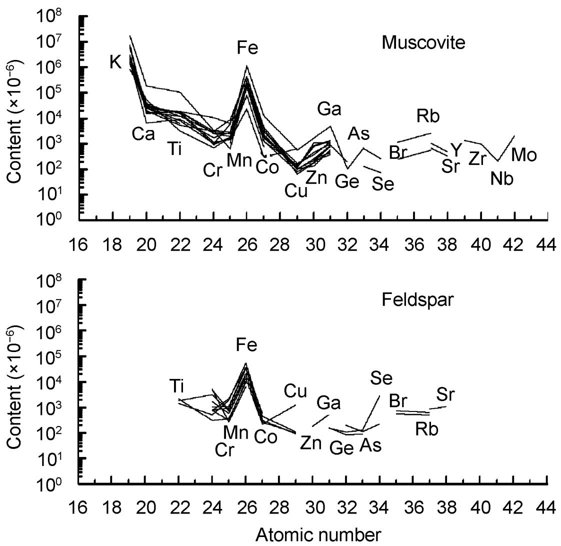

Fig.1 The semi-quantitative analysis results of chemical composition of muscovite and its surrounding plagioclase normalizing by rock standard GSR1, GSR2 and GSR3.

it is shown that the altered hydrothermal fluid is characterized by the enrichment of alkaline and alkaline-earth metal elements K, Ca and transitional metal elements Fe, Ti, Cu, Zn and many trace or ultra-trace elements.

4.2 Gold occurrence

By SRXRF, gold, silver and platinum, invisible under microscope, were detected in some area of muscovite; but they are not found in feldspar. From Fig.2 we have found that a complex population of trace elements gives rise to interferences on the characteristic Au-*L*α line and Pt-*L*α, from *K*-lines of lighter elements (Cu-*K*α, Zn-*K*, Ge-*K*α, Ga-*K*α, As-*K*α, Se-*K*α) and from the *L*-lines of Hg, Tl, Pb and Bi, which were accounted for in data processing. Moreover, the experiment was based on the non-destructive analytical methodology and no suitable gold reference samples could be used. So the exact and precise quantification of the detected gold, silver and platinum is difficult to realize.

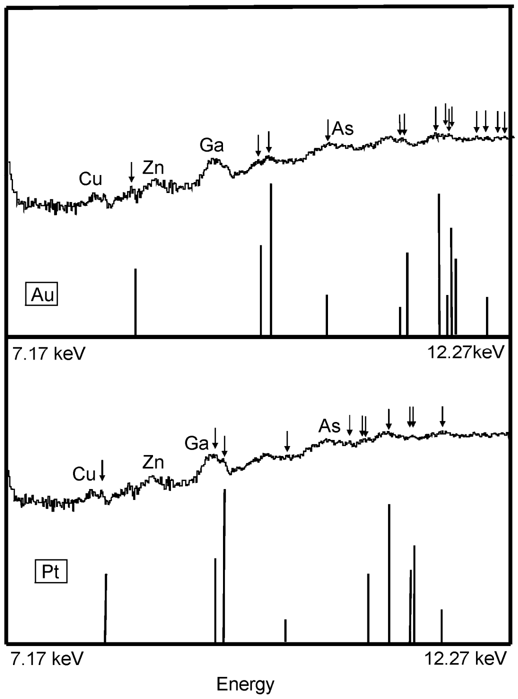

Fig.2 Part of a typical synchrotron radiation X-ray fluorescence spectrum of muscovite, from which the characteristic Au-*L* line and Pt-*L* line are illustrated.

Based on synchrotron radiation X-ray fluorescence counts, the statistical analyses were performed by means of the SPSS version 10.0 software and a correlation factor was used to indicate the correlation and strength of the relationship between every two elements (Table 1). Most of the elements in muscovite reveal excellent/very good correlations with potassium (K), an intrinsic component of the muscovite. Ca, Ti, Fe, Co, and Cu have correlation coefficients r of more than 0.8; and for Cr, Mn and Zn, r is between 0.70 and 0.8. Apparently, these elements occur as isomorphous substitution in the crystal lattice of the mica minerals. The mica crystal structures display a diversity of interstitial sites ranging from (a) Si-O tetrahedral site, occupied by Si and Al, plus trace Fe, Ga, Ti, and through (b) Al-O octahedral site, filled with Al and some Fe, Mn, Mg, Ti and other cations with suitable ionic radii and valence such as Ni, Zn, Ta, Nb, Ge, rare earth elements (REE), to (c) the large interlaminar site, filled by K with minor abundances of both alkaline cations Na, Rb and divalent cations of large radius, such as Ca, Ba and Pb.[11] The correlation of these elements may be attributed to the ions formed in hydrothermal fluid which come into the mica crystal structure together.

Table 1 Correlation coefficient analysis of some elements in muscovite

Elements	Components of muscovite									Noble metal		
	K	Ca	Ti	Cr	Mn	Fe	Co	Cu	Zn	Ag	Pt	Au
K	1.000	0.898	0.966	0.730	0.704	0.818	0.856	0.959	0.776	-0.043	-0.063	0.520
Ca	0.898	1.000	0.970	0.636	0.779	0.886	0.923	0.961	0.583	-0.249	0.140	0.735
Ti	0.966	0.970	1.000	0.701	0.782	0.893	0.929	0.985	0.677	-0.140	-0.034	0.603
Cr	0.730	0.636	0.701	1.000	0.831	0.811	0.790	0.663	0.514	-0.046	-0.180	0.165
Mn	0.704	0.779	0.782	0.831	1.000	0.976	0.952	0.732	0.269	-0.124	-0.120	0.327
Fe	0.818	0.886	0.893	0.811	0.976	1.000	0.993	0.849	0.409	-0.163	-0.101	0.453
Co	0.856	0.923	0.929	0.790	0.952	0.993	1.000	0.896	0.465	-0.166	-0.080	0.497
Cu	0.959	0.961	0.985	0.663	0.732	0.849	0.896	1.000	0.706	-0.125	0.039	0.632
Zn	0.776	0.583	0.677	0.514	0.269	0.409	0.465	0.706	1.000	0.053	-0.124	0.355
Ag	-0.043	-0.249	-0.140	-0.046	-0.124	-0.163	-0.166	-0.125	0.053	1.000	0.017	-0.247
Pt	-0.063	0.140	-0.034	-0.180	-0.120	-0.101	-0.080	0.039	-0.124	0.017	1.000	0.655
Au	0.520	0.735	0.603	0.165	0.327	0.453	0.497	0.632	0.355	-0.247	0.655	1.000

Both platinum and silver are the only two analyzed elements that show no correlation with potassium and these substituting elements. And there is no correlation between platinum and silver. One can conclude, therefore, that platinum and silver are introduced as discrete particles into muscovite. This agrees with geological exploration report about silver,[6,7] though no platinum is detected.

Trace gold was detected by SRXRF with very low ratio of peak to background. The low concentration of gold hinders the application of spectroscopic techniques like EXAFS, which would otherwise be capable of checking both valence and coordination of Au in mica-type silicates. Gold is correlated, either with potassium and these substituting elements, or with platinum, though the correlation coefficients are not very high. From Fig.3, the peak area of X-ray fluorescence count of potassium plotted against that of gold shows a liner correlation except some points with high gold X-ray fluorescence counts. Apparently, dissolved or solid gold from various sources co-exist in the muscovite.

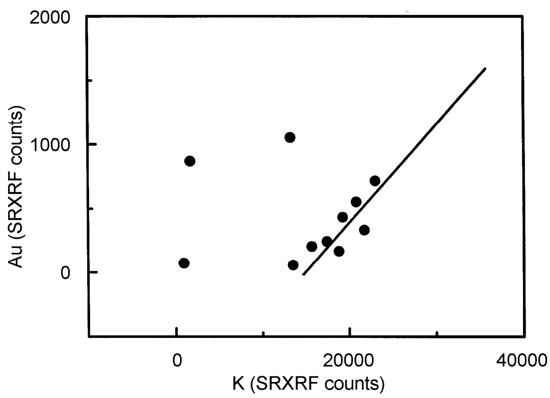

Fig.3 Correlation between the peak areas of potassium and gold in muscovite based on synchrotron radiation X-ray fluorescence counts.

4.3 Ore fluid source

Knowledge of the source of ore fluids and ore materials is fundamental for understanding ore formation. Hydrothermal fluids and ore materials are always considered to originate from magmatic systems since the deposit was discovered.[6-8] Now a new idea is generated that mantle flux, which is composed of hydrogen, halogen elements, alkali metal, carbon, oxygen, nitrogen and sulfur, possibly participates in the gold mineralization in Yuerya, especially in the terminal stage.[12,13] Values of fluid $\delta^{18}O$ and δD from the former studies, when calculated from measurements made on O- and H-bearing hydrothermal silicates, are 0.703% and –8.84% respectively, just in the range of typical magmatic fluid, which show the magmatic source of ore fluid.[6] But sulfur isotopic data for sulfides reveal that sulfur in the ore fluids was mainly derived from deep mantle source.[8,12] By comparison of chemical composition of muscovite and feldspar, enrichment of alkali metal in hydrothermal fluid associated with gold deposit is disclosed. Fluid inclusion studies of gold-bearing pyrite–quartz ores indicate that hydrothermal fluid associated with gold deposit contains abundant CO_2 and H_2O.[7] Both are characteristic of mantle flux and support the possibility of mantle flux participating in gold mineralization. Considering platinum, a mantle component and seldom seen in the earth crust, we can guess that some mantle flux participating in the formation of gold deposit or ore fluids were derived from magmatic water dehydrated from mafic magmas that were derived from an enriched mantle source.

5 Conclusion

Synchrotron X-ray fluorescence spectrometry is a highly-sensitive technique for the chemical analysis of geological materials at a microprobe scale, whose advantages have already been emphasized for silicate-hosted elements.[4,14] From chemical composition analysis of muscovite, we have known that hydrothermal ore fluid contains abundant alkaline and alkaline-earth metal elements K, Ca, ore materials Fe, Cu, Zn and many kinds of trace elements at the phase of muscovite formation in the late stage of gold sericitization. And invisible gold, silver and platinum are found in muscovite. Enrichment of alkali metal elements and abundant CO_2 and H_2O in hydrothermal ore fluid brings forward a possibility of mantle flux participating in gold mineralization; and platinum in muscovite and analytical result of sulfur isotope further support the idea. The mantle source of part of ore fluids indicates that the tectonic event controlling gold mineralization in the Yuerya district is a mantle phenomenon (i.e., a portion of the ore fluids originated from mantle-derived magmas).

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