Iron and sulfur speciation in some sedimentary-transformation-type of lead–zinc deposits in West Kunlun lead–zinc ore deposit zone, Northwest China

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Abstract Redox conditions are very important for almost all geological processes including ore deposit formation. However, the direct measurement of redox potential (Eh) values for solid materials is difficult. The chemical speciation of redox sensitive elements is one factor which determines the redox conditions. In this study, four groups of ore samples and their host rocks were collected from four sites along the west Kunlun lead–zinc ore deposit zone in northwest China and the iron- and sulfur- species analyzed using Mössbauer spectroscopy and X-ray absorption near edge fine structure (XANES). The results showed systematical change in redox conditions between the ore rocks and their associated host rocks. All ore samples contained more reducing sulfur species than their corresponding host-rocks indicating significantly enhanced reducing conditions in the ore bodies than their host rocks. Such reducing conditions should be more favorable for the sulfidization of metal during the ore formation. In addition very small concentrations of ferrous iron were found in only some of the small samples. This may indicate the removal of iron during metal sulfide ore deposit formation.

Introduction

The formation of ore deposits largely depends on geological surroundings and geochemical processes associated with the supply of ore-forming elements. For the geochemical processes, several factors including temperature (T), pressure (P), acidity–basicity (normally presented by pH value), and redox potential (Eh) are normally considered as key controlling measures. Practitioners have generally focused on these factors and/or parameters to describe and explain the formation mechanism and distribution patterns of ore deposits [5, 23]. In practice, the Eh value is not easily to be measured directly for solid materials. However, by using chemical species or speciation of redox sensitive elements or a couple of elements, it is possible to obtain information about the redox conditions in solid materials including those associated with rare earth elements [20, 21], acidic mining drainage [28], aquatic sediments [12], and also metal ore deposits [1, 2].

The term "chemical speciation" is related here to the distribution of elements among various forms (ions, atoms, molecules, minerals or organo-complexes) or species [14] and their transformation or conversion from one species to another or others [28]. The combination of elemental concentration, isotopic fractionation and chemical speciation has powerful advantages in modern geochemistry and has been used in many fields such as the toxicity of harmful elements [19, 28], positive or negative abnormality of some

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rare earth elements like Ce and Eu in sediments [11, 20, 21], trace element in iron meteorite [22] coal ash evaluation [13]. The study of chemical speciation related to ore deposits is very important because the elemental species not only control the total contents but also the chemical status of certain elements, the latter in turn strongly influence the concentration and also the potential usage of the elements. However, related studies of this type are not so common in ore geology probably because of limited methods and techniques. Along with the rapid development of synchrotron radiation and their implications, chemical speciation has now become available to most elements in many kinds of materials, including solids, even plastic materials.

The species or speciation of sulfur and iron can be used to determine the redox condition of environments for metal ore deposits because these two kinds of elements are redox sensitive and also common in almost all geological materials. Several methods are implacable to determine chemical status of sulfur and iron including XRD and sequential extraction with instrumental measurement [24]. However, X-ray absorption near edge structure (XANES) spectroscopy is one of the most effective methods for the identification of the chemical status of most elements in solid, liquid and even gaseous materials without any chemical preparation whereas Mössbauer spectroscopy (MS) is well suited for iron-containing species [10]. Both XANES and MS have the advantages of high selectivity for certain elements (each element is measured within its own special range of energy), high sensitivity and high resolution, and non-chemical pretreatment. The capacity to examine without chemically breaking down the materials under investigation can supply original information about the chemical status of the target elements. In particular, XANES has found increasing use in the study of laboratory prepared samples as a nondestructive method for identifying chemical species of many elements [8].

In this study, XANES and MS have been used to identify chemical species of sulfur and iron in some selected samples from lead–zinc–copper ore deposits and their corresponding host rocks in the west Kunlun Mountains. The work has been directed towards a better understanding of the formation mechanisms, especially the rule of redox conditions during the ore deposit formation.

Geological sites and samples

The west Kunlun Mountains are one of the best potential districts for searching large and ultra large scale metallogenic ore deposits in western China and have attracted domestic and international attention [6, 27]. The Mountains located to the northwestern Tibetan Plateau (also called as Qinghai-Tibet Plateau) and to the southwestern Tarim Basin, are very important in regional tectonic geology in China and central Asia. Tectonically, this area is also one part of the Kunlun orogenic zone, being situated between the ancient Asian structural field and the Tethyan structural field. Associated with the distribution of tectonic zones, there are several huge ore-forming zones passing through the west Kunlun Mountains such as the Kunlun-Qilian-Qinling ore-forming zone, Sanjiang ore-forming zone and middle Asia ore-forming zone [3]. The Sanjiang zone is named to indicate three rivers; the Jinshajiang River, the Lancangjiang River and the Nujiang River, and these three rivers originate from the Tibetan Plateau and flow from north to south in a parallel drainage pattern. The geological conditions of many ore-forming zones including the stratum, the structure and magma activities have indicated that there is a preferred environment for ore formation and a great number of metal ores in different sizes have been discovered in the west part of the Kunlun orogenic zone [6] such as the Tamu lead–zinc deposit, the Kalangu lead–zinc deposit, the Kalama copper deposit, the Kekuxilik Pb–Zn deposit, the Huangyangling Sb deposit, the Heiqia Fe deposit and Sazigou copper deposit [4] etc. These ore deposits (or places) and mineralization points are mainly distributed along the ore-forming belts, which can be further divided into seven sub-metallogenic belts and eighteen mineralization places [26]. The west Kunlun Mountains are one of the best regions for locating large and super-large scale of ore deposits in China.

Based on the regional geology and classification of ore deposits in the study area, four deposits were selected for this study including the Abalieke copper–lead deposit, the Tuohongmulieke lead–zinc–copper deposit, the Kalangu lead-copper ore deposit, and the Damusi lead–zinc deposit from north to south in the study area (Fig. 1). At least two samples were selected from each deposit for this study. Each one was from the ore rocks and another one from the corresponding horst rocks to obtain some information about the significance of redox conditions to mineralization and ore formation.

Experiments

Sample treatment

All ore and horst rock samples were crushed into small pieces and then selected for the experiment. The selected pieces of fresh samples were powdered using an agate mortar and pestle under clean conditions. The powdered samples were stored under dry and hermetic conditions in order to avoid contamination and minimize chemical variations of the elemental components, especially the reactive species of elements under open air conditions [28].
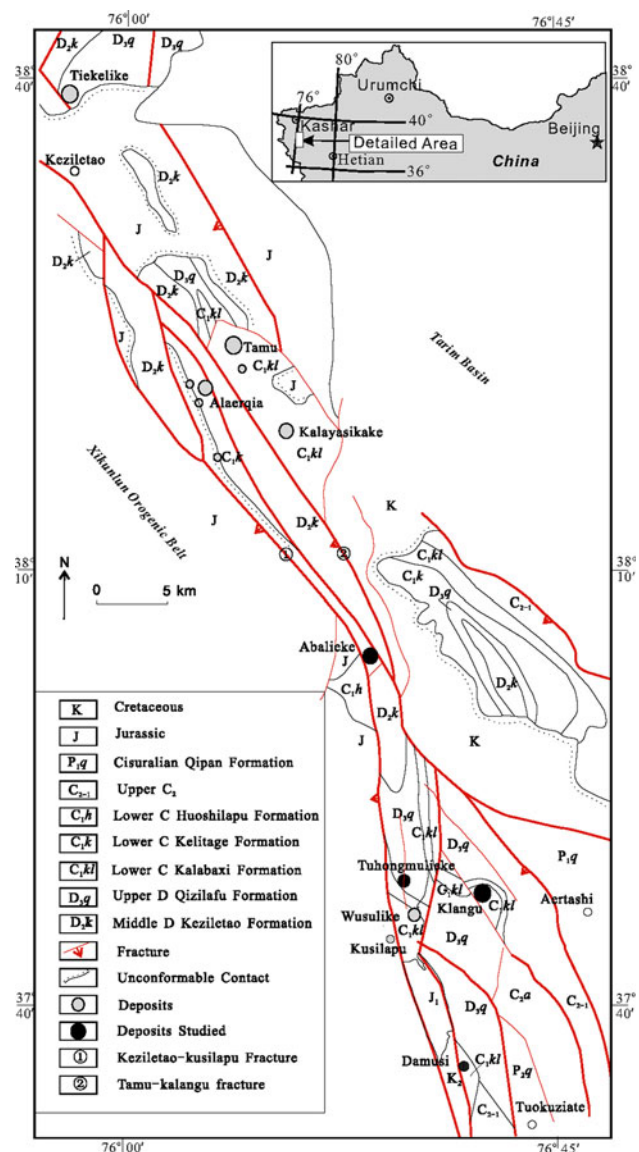
Fig. 1 Map of study area, showing the deposits location in this study

X-ray diffraction (XRD)

Powder X-ray diffraction was used to determine the mineral compositions of the samples without any chemical pretreatment. Conventional XRD was conducted on a new D8 advance, Bruker diffractometer equipped with a graphite monochromator and operated at 40 kV and 40 mA using Cu-Kα radiation at The University of Tokyo, Japan. A portion of sample was further crushed to fine powder using a small clean mortar and then mounted on a plastic holder (φ25 mm, depth 1 mm) for XRD analysis. The oriented samples were scanned over an interval of 5°–60° (2θ) at a scanning speed of 1.4 (to be precise 1.375)°/min for every 0.03° (2θ) step. Divergence, scattering and receiving slits were 0.6 mm, 0.6 mm and 0.10 mm, respectively.

Mössbauer spectroscopy

For ^{57}Fe Mössbauer measurement [9], 250–335 mg of the powdered sample without any chemical pretreatment was gently pressed into a brass sample holder (16 mm in diameter, 1 mm thick). The sample holder was closed at both ends with an iron-free plastic tap. The Mössbauer spectra were obtained with an Austin Science S-600 Mössbauer spectrometer using a γ-ray source of 1.11 GBq ^{57}Co/Rh at constant room temperature (293 K). The obtained spectra were fitted to Lorentzian lineshapes using standard line-shape fitting routines. The half-width (HW) and peak intensity of each quadruple doublet was constrained to be equal. Isomer shifts (IS) were expressed with respect to the centroid of the spectrum of metallic iron foil.

X-ray absorption near-edge structure (XANES)

Sulfur K-edge X-ray absorption near-edge structure (XANES) analysis was performed at the beamline BL-9A of KEK Photon Factory in Tsukuba, Japan [15, 16]. The operating conditions of the storage ring were 2.5 GeV of electron energy and 450–300 mA of electron current. A Si(111) monochromator was used to chromatize the X-radiation from the bending magnet and the beam was focused by a pair of bent conical mirrors coated with Rh. The beam size at the sample position was smaller than 1 × 0.5 mm. All spectra were recorded at room temperature in a fluorescence mode using a Lytle detector. The samples were placed at 45° to the incident X-ray beam. To suppress the absorption of X-rays by air, all the paths, including the I_0 ion chamber and the sample cell, were purged with helium gas. After removal of the linear pre-edge, each spectrum was normalized by defining the absorption at 2.66 keV as equal to unity.

Results and discussion

Mineral composition

The XRD patterns of ore samples associated with their corresponding host rock samples are illustrated in Fig. 2. The mineral compositions of the samples studied were simple, there being just two or three types of minerals determined for each sample and the mineral types were also limited. However, there were some differences in mineral compositions between the ore rock samples and their host rocks not only in the compositions but also their relative contents (Table 1). For samples collected from the Tuohongmulieke lead–zinc–copper (Fig. 2a), the ore sample th-809 was dominated by galena and nantokite with less dolomite whereas the host rock sample th-815 was

dominated by dolomite with less nantokite. Their relative contents were different from each other. For samples from the Damusi lead–zinc deposit (Fig. 2b), the ore sample dms-9 was dominated by galena with less dolomite and pyrochlore whereas the host rock sample dms-7 was dominated by dolomite with small amount of ankertite. For samples from the Kalangu lead–copper ore deposit, the ore sample klg-1 was dominated by galena with less quartz whereas the host rock sample klg-2 was dominated by dolomite with less ankeritie. These differences in the mineral composition between the ore rocks and their host rocks may indicate some ore formation processes under special geochemical conditions.

The mineral composition of samples from the Abalieke copper–lead deposit is special as compared to the other three deposits. Galena and less kombatite were present in the ore rock sample whereas pyrochlore and diopside were found in the host rock sample without any dolomite being detected.

Iron speciation

The ^{57}Fe Mössbauer spectra of all samples at room temperature (RT, constant at 293 K) were shown in Fig. 3. Little iron was detected in most samples as their spectra

showed no clear absorbing peaks, indicating these samples may contain iron in concentrations lower than the detection limit. According to our experience and some references in the literatures [7, 9, 10, 29], spectra can be obtained with information about iron species and relative contents can be obtained when the total iron concentration (tot-Fe) is about 5 mg Fe cm^{-2} in the tested sample. Otherwise data points obtained are distributed horizontally as was found in most samples in this study (Fig. 3c, d).

However, two samples (th-815 and klg-2) showed weak signals for ferrous iron in the spectra (Fig. 3a, b) and their Mössbauer parameters are listed in Table 2. The curve fitting with iron components was robust, with sufficiently small Chi squared values from samples th-815 and klg-2. Only one weak doublet was obtained in sample th-815, which should be ferrous iron sulfide (pyr-Fe^{2+}). Two species were measured in sample klg-2. One doublet was ascribed to the ferrous iron in siderite [18, 25, 13] or other kind of carbonate minerals. In some cases, the ferrous iron in calcite and dolomite may also display as the iron in siderite (sid-Fe^{2+}). The sample klg-2 may contain higher total iron than klg-1. At the same measuring conditions and same weight of samples the large peaks represent higher contents of iron, which can be determined using the Mössbauer peak areas normalized by sample weight and

Fig. 2 Powder X-ray diffraction pattern of selected samples from the West Kunlun Mountains. In the figure, *Dol* dolomite, *Qtz* quartz, *Gal* galena, *Nan* nantokite, *An* ankerite, *Pyr* pyrochlore, *Di* diopside, *Ko* kombatite. **a** Samples from the Tuhongmulieke Pb–Zn–Cu deposit; **b** samples from the Damusi Pb–Zn–Cu deposit; **c** samples from the Kalangu Pb–Zn–Cu deposit; **d** samples from the Abalieke Pb–Zn–Cu deposit
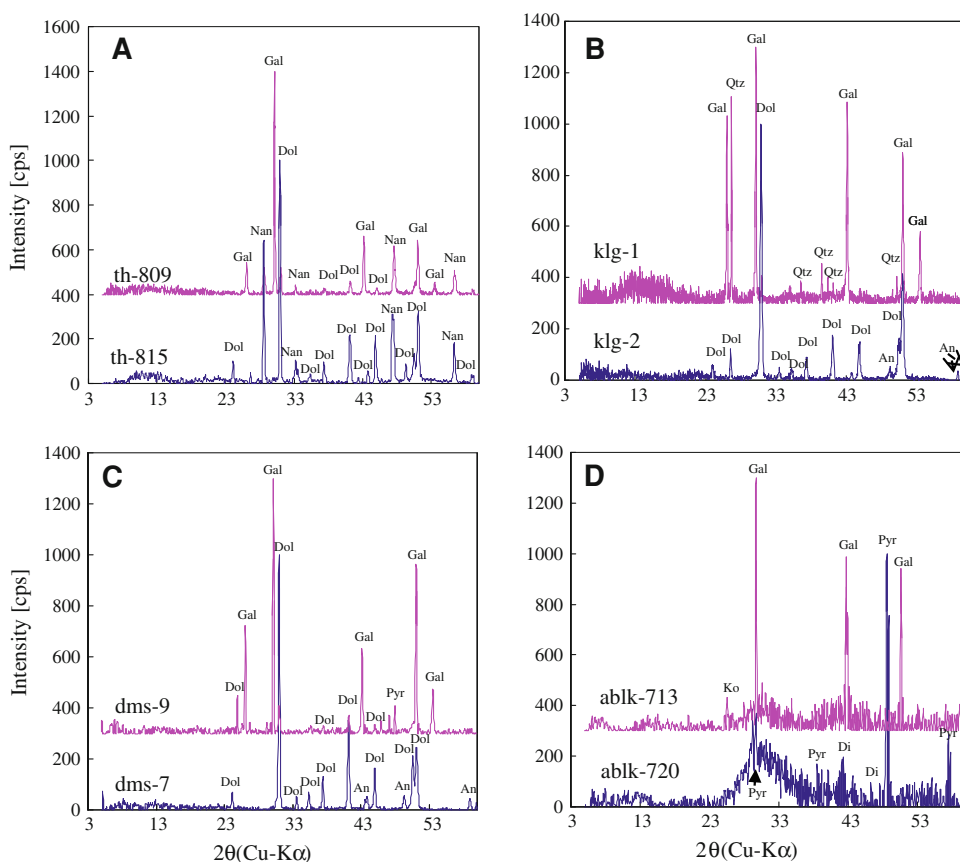
Table 1 Mineral composition (%) of samples studied

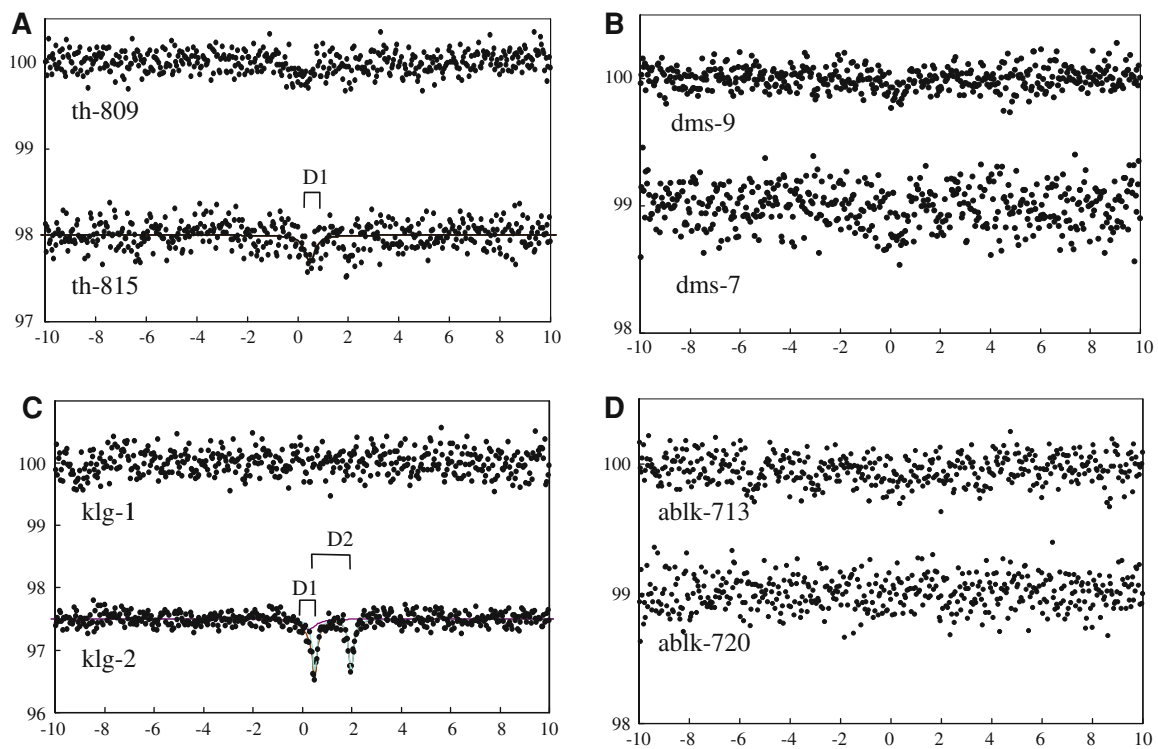| Sample no	Dolomite	Quartz	Galena	Nantokite	Ankerite	Pyrochlore	Diopside
th-809	4.36		79.48	17.16			
th-815	81.91			18.09			
klg-1		16.35	83.65				
klg-2	87.86		8.16		3.98		
dms-7	15.26		82.53			2.21	
dms-9	91.27				8.73		
ablk-713			92.65			7.35	
ablk-720						83.76	16.24

Fig. 3 Mössbauer spectra for some selected samples from four sites in the study area measured at room temperature (298 K). The upper indicator bars show the peak position of each iron species. D1-doublet for low-spin ferric iron or iron in pyrite, pyr-Fe^{2+}; D2-doublet for paramagnetic high-spin ferrous iron in siderite, sid-Fe^{2+}. Samples numbers are the same as Fig. 2

cited as the Index of total iron by total peak area of Mössbauer spectra (IM). IM was proportional to iron content semi-quantitatively in the tested samples and was used for the fast estimation of iron content [7, 29].

Sulfur speciation

Sulfur K-edge XANES were obtained for all samples (Fig. 4). The spectra were compared with selected reference samples including pyrrhotite (FeS), pyrite (FeS_2), elemental sulfur (S^0) and calcium sulfate ($CaSO_4$). The influence of self-absorption for the reference materials was examined by using powdered reference samples containing sulfur at various concentrations. Self-absorption effects were not observed for S < 0.5 wt%. Positions of the peaks found in the ore rocks and their corresponding host rocks were located at similar energies to those found in the spectra of sulfides including pyrite and most horst rocks either in the energy range for sulfate or to the right in the sulfide range.

The samples showing peaks corresponding to sulfate and some reduced sulfur species are most likely sulfide compounds in metal sulfides such as galena and pyrite. Generally, the ore rock samples showed more reducing sulfur than the corresponding host rocks and may indicate the important process of sulfidization during the ore formation. Some host rocks contained sulfate in correlation

Table 2 Mössbauer parameters of the iron compounds in samples (measured at 293 K)

Sample ID	Total peak area/ % mm s^{-1}	Species	Relative content %	IS/mm s^{-1}	QS/mm s^{-1}	HW/mm s^{-1}	Explanation
th-809	n.d.						
th-815	0.15 ± 0.03	para-Fe^{2+}	100.00 ± 0.00	0.479 ± 0.054	n.d.	0.482 ± 0.158	FeSO$_4$
klg-1	n.d.						
klg-2	0.52 ± 0.03	para-Fe^{2+}	77.96 ± 2.64	1.241 ± 0.158	1.474 ± 0.158	0.240 ± 0.158	FeCO$_3$
		para-Fe^{2+}	22.04 ± 2.64	0.269 ± 0.158	n.d.	0.690 ± 0.158	FeSO$_4$
dms-9	n.d.						
dms-7	n.d.						
ablk-713	n.d.						
ablk-720	n.d.						

n.d. no detected

with carbonate, probably indicating the parallel process of sulfate and carbonate formation during the geothermal process in the host rocks.

Redox conditions

For the sedimentary-transformation-type of lead–zinc deposits, geothermal fluids are the basic carrier and solution for the precipitation of metals, in which redox

Fig. 4 Sulfur K-edge X-ray absorption near-edge structure (XANES) for some selected samples from four sites in the study area. Samples numbers are the same as Fig. 2

condition take place in the rock-fluid interactions. Almost all thiophile elements, like many metals, are mostly precipitated under reducing conditions, especially those metals which combine with sulfur to form metals sulfides. Based on the distribution of sulfur and iron species between the ore rocks and their host rocks, a relatively much stronger reducing condition occurs in the ore bodies compared with their host rocks, indicating that reducing conditions are essential and important for the ore formation even though reducing conditions occur in both the ore bodies and their host rocks.

For each pair of samples, more reducing species of sulfur presented in the ore samples than the corresponding horst rocks, especially metals sulfides, indicating strong sulfurization of metals including lead, zinc, or copper during the ore formation. On the other hand, there was no iron species in all the samples from the ore deposit, probably indicating some removal or depletion of iron during metal ore formation.

In general, there were more carbonate minerals including dolomite and/or calcite and also ankerite in the host rocks than the ore deposit rocks, probably indicating strong carbonation process occurring in the host rocks along with the deposit formation. Carbonation processes in the horst rocks, indicate that lead–zinc–copper ore deposits belong to recovered type of deposit because of the secondary carbonate mineral formation. The conversion of carbon dioxide into carbonate is an important role in the metal sulfide accumulation as the formation of gold deposits [17].
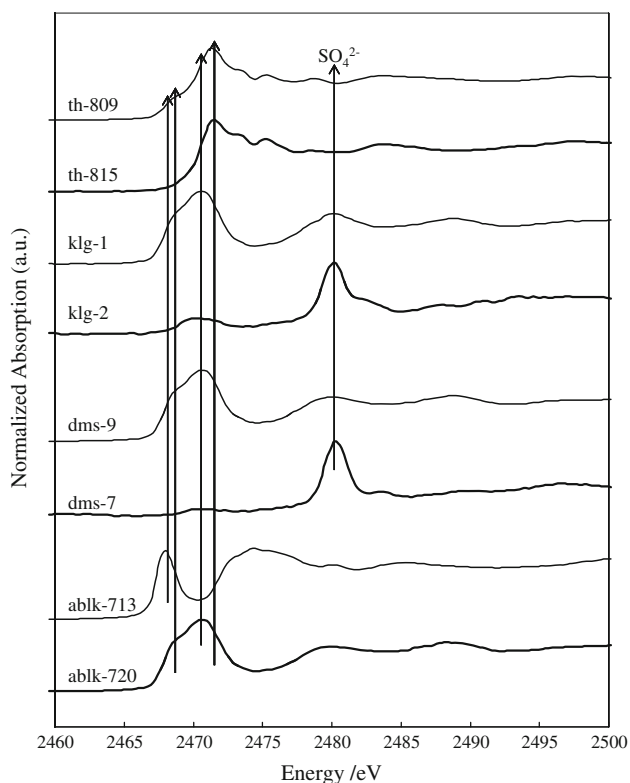
Summary

Based on sulfur and iron speciation combined with mineral compositions, some information about the ore formation of lead–zinc–copper in the study area can be determined.

1. There is more reducing species of sulfur in the ore rocks than their corresponding host rocks, and less iron in ore samples than their host rocks, probably indicating some process of heavy metal sulfidization and iron-removal or depletion during the lead–zinc–copper ore formation in all the four sties studied

2. Strong carbonation processes occur in the host rocks along with metal ore formation, especially the mineralization of dolomite and ankerite. This may indicate special interactions between geothermal fluids and the host rocks during the ore forming processes

3. Relatively stronger reducing conditions reflected by the distribution patterns of sulfur species occur in the ore body than their corresponding host rocks, indicating that reducing conditions should be an essential environment for metal sulfide formation

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