Geochemical patterns and metallogenic material source of the Naoyangping-Damogou zinc-fluorite deposits in Pingli County, China

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Abstract
The Naoyangping-Damogou Zinc-fluorite deposits in Pingli County, China, are usually associated with limestone and trachyte rocks. The ore bodies are in closed genetic relationship with fault structures. The results of this study show that the source of the ore-forming elements of the Naoyangping-Damogou zinc-fluorite deposits does not have the characteristics of a deep source; it can be found in the infiltration of meteoric waters along the fractures on alkali trachyte and argillite boundary, water-rock interaction and leaching of ore-forming elements in rocks. The ore-forming elements migrated into favorable position by the precipitation. The results of this work can be used as supportive information during additional geological surveys in the study area.

1. Introduction

North Daba Mountain is an important component of the South Qinling orogen (Wang et al., 2009; Y.P. Dong et al., 2011; Zhang et al., 2004, 2001). Scientific works have revealed remarkable magmatic-tectonic hydrothermal mineralization in the North Daba Mountain region in alkaline rocks or intermediate rocks including niobium-tantalum ore (Jia et al., 2004; S.B. Deng et al., 2003), a magmatic-related hydrothermal zinc-fluorite deposit (Wei et al., 2009), titanomagnete deposits in diabase dikes (Li, 2012; L. Liu et al., 2012), and witherite and barite deposits that are related to volcanics and hydrothermal waters (J.J. Liu et al., 2010; Lü et al., 2004). Therefore, research on the region’s typical deposits has an important significance in regional prospecting for possible discovery of additional deposits. Pre-investigation and detailed studies on the Naoyangping-Damogou zinc-fluorite deposit have been conducted for geological prospecting several times since the 1980s and 2000s, although researches on the genetic mechanism of the deposit and on the regional metallogenic background are limited.

Fluorite of varied color and habit occurs in a wide range of ore deposits, from low-temperature and moderate salinity epithermal veins and replacements to high-temperature and high-salinity magmatic deposits such as greisens, skarns, porphyries, and pegmatite systems (e.g., Bühn et al., 2002; Coniglio et al., 2000; Gagnon et al., 2003; Galindo et al., 1994; Goldring & Greenwood, 1990; Hill et al., 2000; Kesler, 1977; Richardson & Holland, 1979; Subías & Fernández-Neto, 1995; Williams-Jones et al., 2000). Fluorite deposits occur as lenses and veins in many localities in the North Daba Mountain. Based on the structural feature and occurrence, it was suggested that fluorite mineralization has a hydrothermal origin.

The aim of this study is to compare petrochemical data to some isotopic data from Chinese Geological Survey of Shanxi Province, in order to clarify the role of rainwater in the genesis of sphalerite and fluorite mineralization hosted by the Zhuxi group limestone of Late-Triassic age. In addition, this study reports for the first time the REE distribution and patterns of host rocks and sphalerite ore, as well as fluid inclusion analysis of fluorite from different localities of Naoyangping-Damogou area to discuss its origin.

2. Ore deposit geology

2.1 Geological features of the Naoyangping-Damogou ore field

North Daba Mountains is a main component of the South Qinling orogen, confined by Ankang fault in the North and by Chengkou-Fangxian fault in the South. Debates on the magmatic evolution, formation age and tectonic setting about the alkali volcanic rocks still exist due to lack of comparison and systematical research of distribution of alkali volcanic rocks that does not allow a general frame of regional magmatic evolution. The lack of study on mineralization age and ore-forming elements of zinc-fluorite deposit...
constrains the breakthrough of mineral deposit exploration.

Naoyangping-Damogou zinc-fluorite deposit is located to the south-east wing of Pingli anticlinorium, where the anticlinorium is the core strata of Wudang Rock Group Yaoping Rock Formation. The wing part of strata is steeper with the dip angle varying from 42° to 70° and shows a development of secondary reverse antiformal syncline. The mining area rocks are mainly composed of sedimentary rocks from the Middle Silurian Zhuxi group. Lithology is mainly argillite, sandy slate, with intercalate flaggy sandstone and limestone (Shaanxi Province, Bureau of Geology and Mineral Exploration and Development Bureau of the first Geological Brigade, Shaanxi Province, 2012). Local outcrops of marble were observed with silicified alteration. A little area also displays outcrops of the Lower Silurian Meiziya group, which is distributed in the east margin of the mining area.

Within the mining area it is developed, a fracture zone where anticlines of various size can be found. According to its distribution, orientation of tectonic structures can be divided into four groups including nearly EW direction, NW-SE direction, NWW-SEE direction and NE-SW direction. Among them, NW-SE direction is mainly the ore-controlling fracture zone in the mining area. Magmatic rocks in the mining area are well-developed and can be divided mainly into two categories according to the content of SiO2 (Wang, 2007): (1) basic-ultrabasic rocks mostly represented by, pyroxenites, and (2) intermediate acid-acid rocks represented by trachytes.

The basic-ultrabasic rocks (pyroxenites) are distributed in the western part of the ore field and crop out in irregular bands mainly including clinopyroxene rich rocks types and pyroclastic rocks types. There are mainly composed of dark green pyroxene porphyrite. The schistosity is developed and exhibits pyroxene (augite) phenocrysts, with tabular and columnar crystals. The metamorphism and alteration are strong. The alteration includes uralitization of pyroxene and diffuse replacement of microcrystalline matrix by sericite and chlorite. In the mining area, basic subvolcanic rocks are distributed in a small zone, mainly occurring at the west part of Naoyangping. Moreover, in the Zhuxi Group system, there are lenticular and banded. Clinopyroxene rocks in Langao-Pingli are dominated by microcrystalline olivine-bearing pyroxenite.

Trachytes are represented in the study area. They are Alkali trachyte, trachyte breccia, and trachyte porphyry.

**Alkali trachyte**

The most abundant minerals are K-feldspars (mainly orthoclase, with minor microcline). Subordinate minerals are plagioclase, hornblende, biotite and pyroxene.

The quartz content is null or very low (<<5%). The rock is light in color, generally grey and grayish-yellow. The rock exhibits porphyritic texture with phenocrysts of glassy feldspar and a criptocrystalline matrix. In this section, the rock shows a trachyte texture, i.e., alkali feldspar microcrysts oriented along length with a nearly parallel arrangement. Massive structure is dominating, although a vesiculated structure can also be observed.

**Trachyte breccia**

Trachyte breccia compositions are in general relatively complex. It is not only a wall-rock breccia, but often it includes fragments from different, also single-component, and underground sources. Fragments are included in a matrix of fine rock crumbs and powder. Breccia fragments are angular to rounded in shape.

**Trachyte porphyry**

It is mostly composed of K-feldspar group minerals; the rock exhibits porphyritic texture with K-felspar and quartz phenocrysts, and a criptocrystalline matrix.

Based on field evidences, basic and alkaline rock veins show a discontinuous distribution. Among them, trachyte rocks and mineralization have close relationships all within the mining area.

### 2.2 Characteristics of main vein orebodies

In this study, fluorite deposits from eight localities in the Naoyangping-Damogou area, including K1, K2 (Zn), K2 (CaF2), K3, K4, K5, KH7 and K8 areas are investigated (Figure 1). K1, K2 (Zn), K4, K5 and KH7 form the main body of sphalerite ore and K2, K3 and K8 represent the main body of fluorite ore. In the southern part of K2 ore body, a fluorite mineralization has been discovered (Shaanxi Province, Bureau of Geology and Mineral Exploration and Development, Bureau of the first Geological Brigade, Shaanxi Province, 2012). These ore bodies occur without exception in a faulted-fracture zone within NE-SE direction. The orebody morphology and scale are strictly controlled by the fault fracture zone.

#### 2.1.1 The K1 orebody (Damogou)

Damogou (K1) represents the main body of sphalerite ore in the mining area. The orebody is hosted in the Middle Silurian Zhuxi Formation slate rock and alkali trachyte rock fault contact zone. The explored orebody is 384 m in length. Orebody average thickness is about 3.42 m and is stable in Damogou. The average Zn grade is about 10.57% and CaF2 grade is about 11.95%. The dips of orebody vary from 71° to 64°. The orebody outcrops extend from 1142 m to 1212 m above the sea level. The industrial ore type is dominated by primary sulfide ores, associated with
a fluorite resource. A few outcrops of oxidized ore appear discontinuous, with very low amounts of Zn and Pb.

Sphalerite mainly shows allotriomorphic to automorphic granular texture, cataclased and followed by metasomatic replacement. The ore structures are mainly disseminated, massive and brecciated; they are followed by vein structures.

2.1.2 The K3 orebody (Naoyangping)
Naoyangping (K3) constitutes the main body of fluorite ore in the study area. Mineralization was controlled by F1 secondary fracture zones and is closely related to faults (Figure 1). The fracture zone is about 400 m in length and 12 m in width. Fluorite mineralizations found in this area occur mainly in fault zone. Generally ore bodies are NW-trending and limited by F1 fault in the southern part. The outcrops of all ore bodies range from 989 to 1049 m above the sea level. The main orebody is about 320 m in length. Their SE side’s dip angle vary from 20° to 34°, the biggest value is about 48° in the NW side. On the whole, orebody dip angle change direction steepening to the north-west. The dip of orebody is about 71°-42°. The fluorite grade is of about 41.98% on average. Lead and zinc contents are very low. The Pb and Zn grades vary from 0.00% to 0.01% and 0.00% to 0.02%, respectively. The dominant lithological units in the Naoyangping area are represented by quaternary, Middle Silurian Zhuxi Group and alkaline rocks.

3. Materials and analytical methods
Representative samples of magmatic rocks, limestones, fluorites and sphalerite ores from different localities in the study area, including Naoyangping Figure 1. Geological sketch map of the Naoyangping-Damogou zinc-fluorite deposits 1: Middle Silurian Zhuxi Group (S₂zh), 2: Lower Silurian Meiziya Group (S₁m), 3: Alkali trachyte rock, 4: Basic pyroxenite rock, 5: Limestone bands, 6: Mineralization alteration zone, 7: Zinc orebody, 8: Fluorite orebody, 9: Stratum boundary, 10: Attitude of rock, 11: Fault, 12: Open pit mining pits.
and Damogou areas were collected and crushed. The samples were separated by handpicking under a binocular microscope. Samples were subjected to petrographic, mineralogical, geochemical and fluid inclusion investigations.

Twenty fluorite samples from different localities of the Naoyangping-Damogou area were collected and crushed. Samples were separated by hand picking under a binocular microscope. Thin sections were prepared for these samples (8 samples) and investigated under the optical microscope to investigate the texture of the fluorite. A Nikon Research microscope with attached camera was used to examine the prepared thin sections at State Key Laboratory of Continental Dynamics of Northwest University, Department of Geology of Xi’an.

Fluid inclusion studies were performed on doubly polished fluorite samples taken from the mineralization area. The microthermometric measurements were carried out using a Linkam TH600 heating and cooling stages of the State Key Laboratory of Continental Dynamics of Northwest University, Department of Geology, Xi’an, China following the method described in Ouyang et al. (2014). The heating rate during the phase transitions was controlled manually in the range of 5 to 15°C min^{-1}. Repeated measurements indicated that the reproducibility of the temperature determinations was better than ±0.5°C.

The homogenization temperatures (Th) of fluid inclusions were measured in eight (8) fluorite samples.

Salinities were calculated using the equation of Bodnar (1993) and Hall et al. (1988) for the low- and medium-to high-salinity NaCl-H2O system, respectively.

To analyze the REEs in the magmatic, limestone rocks and Sphalerite ore, the twenty powdered samples were determined by ICP-MS technique by using electron microprobe analysis of the State Key Laboratory of Continental Dynamics of Northwest University, Department of Geology, Xi’an (China).

Nineteen magmatic rocks samples from the Naoyangping-Damogou area were analyzed for major-oxide trace elements contents of magmatic rocks were analyzed by ICP-ES technique at State Key Laboratory of Continental Dynamics of Northwest University of Xi’an. Fluorite, which is main constituent in the study samples, was identified in the X-ray powder diffraction patterns by its characteristic strong reflection. In addition to fluorite, common gangue minerals such as mainly quartz (silica) and followed by clayey mineral, chlorite, sericite, feldspar, calcite, etc., were also detected in the XRD patterns of studied deposits (Figure 3).

Measurement of mineral chemical composition was conducted at the State Key Laboratory of Continental Dynamics of Northwest University of Xi’an by using the EPMA-1600 electron microprobe. The accelerating voltage was 15kV, the beam current was 10nA, and the laser spot size was set to 1 μm.

4. Results

4.1 Occurrence of fluorite

Fluorite deposits in the Naoyangping-Damogou area occurs mainly as veins ranging in thickness from few centimeters up to 10.87 m. The host rocks are magmatic rocks such as pyroxenite, alkali trachyte and limestone. The color of the fluorite varies from grayish-white to purple, followed by white, grey and green. It shows a vitreous luster. Fluorite grains are uniform and about 2–23 mm in size. The fluorite is mainly euhedral (idiomorphic)-hypidiomorphic granular, cataclastic and cryptocrystalline in texture (Figure 2). The fluorite occurs in fluorite-only veins and in hydrothermal quartz veins, quartz carbonate veins along the host rock foliation and fissures. Fluorite also wraps fragments of surrounding rocks. The fluorite is mainly dominated by massive structure, and followed by disseminated, breciated, zoned (zonal pattern) and structures (Figure 2).

4.2 Ore Petrography

Petrographic examinations of fluorites from the studied localities indicate that they show variations. The fluorites were classified into four categories based on the field geology and the alteration zone of the ore deposit, including fluorite alkali trachyte ore-type and fluorite limestone ore-type. Two types of fluorites also are distinguished at Naoyangping-Damogou area: white and purple fluorite. In general, the fluorite ore deposit in the Naoyangping area (K3) typically belongs to the hydrothermally-altered rock, with low grades of fluorite ore. The major common gangue minerals in the studied ores include mainly quartz (silica), followed by clayey minerals, chlorite, sericite, feldspar, calcite (Figure 3).

4.3 Ore mineralogy

The fluorite contents as well as gangue minerals, which calculated based on XRD and chemical (normative calculations) analyses.

The semi-quantitative mineralogical composition of the fluorite samples from Naoyangping-Damogou area is 40% for fluorite, 19% for ferrodolomite, 15% for plagioclase, 10% for quartz, 5% for pyrite and K-feldspar, 4% for muscovite/sericite, 2% for calcite and small amount for phlogopite and chlorite. Traces of zircon and apatite were detected in some of the analyzed samples.

4.4 Major oxides

Nineteen magmatic rock samples were analyzed for major oxide elements. Distribution of major trace
elements in magmatic rocks was analyzed by using ICP-ES technique and the results are shown in Table 1. CaO in the table is that allocated for calcite, while Ca is that for CaF₂. Fluorine controlled the allocation of Ca for fluorite and the rest of Ca is for calcite. SiO₂ contents range between 38.07% and 67.57% with an average of 52.82%. Relatively high SiO₂ contents in many of the studied samples are due to the high quartz content. CaO % varies between 0.07% and 24.87% with an average of 12.47%. Relatively high CaO contents in some of the samples are due to the occurrence of calcite in such samples. Other oxides such as Al₂O₃, TiO₂, TFe₂O₃, MnO, MgO, K₂O, Na₂O, and P₂O₅ occur as traces. Exceptions occur in some samples where some oxides are present in considerably high content, such as samples that show relatively high Al₂O₃, TFe₂O₃, Na₂O and K₂O contents due to the occurrence of orthoclase.

### 4.5 Rare earth elements

Trace element distributions in magmatic rocks, in limestone and sphalerite ore from different localities of Naoyangping-Damogou area are shown in Table 2 and Table 3 respectively. We compare LA-ICP-MS (Magmatic rocks) and LA-ICP-MS (Limestone and sphalerite ore) using Sr, Y, and the lanthanides, which are also detectable in most fluorite grains (Ismail et al., 2014; Mao et al., 2015).

#### 4.5.1 Rare earth elements in magmatic rocks

The ΣREE of magmatic rocks such as alkali-pyroxenite from different localities of the study area ranges between 403.39 ppm and 476.41 ppm, with an average of 438.79 ppm. Chondrite-normalized (Boynton, 1984) REE patterns for ultra-basic pyroxenite and alkali trachyte rocks from different localities are shown in Figures 10a and Figure 10d. The Eu anomaly is calculated as Eu/Eu* = EuN/(SmN.GdN) and Ce anomaly is calculated as Ce/Ce* = (3Ce/Ce*)/(2La/LaN+Nd/NdN). The REE patterns show similar general trends with some exceptions. Chondrite-normalized REE patterns for magmatic rocks such as the ultra-basic pyroxenite rocks (Figure 4a) show LREE enrichment relative to HREE as shown by (La/Sm) N ratios that vary from 6.1 to 10.7. Significant positive Eu anomalies are pronounced, with Eu/Eu* from 0.91 to 1.02 and an average of 0.94. Significant Ce anomalies have been observed in the analyzed samples (Ce/Ce* ranges from 0.96 to 0.99 with an average of 0.98).

#### 4.5.2 Rare earth elements in alkali trachyte rocks

The ΣREE of alkali trachyte rocks ranges between 153.09 ppm and 692.20 ppm with an average of 379.91 ppm. Chondrite-normalized REE patterns for alkali trachyte rocks (Figure 4b) from different localities exhibit LREE enrichment relative to HREE as shown by (La/Yb) N ratios that vary from 16.85 to 30.64 with an average of 20.60. Significant negative

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**Figure 2.** Structure and texture of the Naoyangping fluorite ore. A: Massive pyrite with semi-euhedral granular texture, B: Fluorite veins stricture, C: Pyrite euhedral-semi euhedral granular structure, D: Fluorite-plagioclase pseudomorph (metasomatic pseudomorph structure), E: Fluorite encapsulated (wrapped) gangue minerals, and F: Fluorite cataclastic texture.
Figure 3. The gangue minerals composition of the Naoyangping fluorite ores. A: pyrite-quartz- felsic minerals with pyrite dispersed in felsic minerals gangue, B: pyrite-muscovite sericite, with pyrite dispersed in sericite gangue, C: pyrite- dolomite within pyrite dispersed in dolomite gangue, D: fluorite-pyrite within enclosed in fluorite, E: Purple fluorite which show an uneven distribution of color, F: fluorite-quartz-felsic minerals within fluorite and felsic minerals contact, G: Fluorite- muscovite-sericite within fluorite and sericite contact zone, H: Fluorite- Dolomite within fluorite and dolomite contact zone, and I: fluorite- pyrite within fluorite and pyrite contact zone.

Table 1. Major oxide concentrations (Wt. %) in the analyzed magmatic rocks samples of the Naoyangping-Damougou area.

| Sample No. | Sample Name  | SiO2  | TiO2  | Al2O3 | Fe2O3 | MnO  | MgO  | CaO  | Na2O | K2O  | P2O5 | LOI  | Total (%) |
|------------|--------------|-------|-------|-------|-------|------|------|------|------|------|------|------|------|
| XTWL01     | Trachyte     | 58.50 | 1.11  | 22.43 | 4.25  | 0.10 | 1.80 | 0.66 | 1.57 | 7.62 | 0.18 | 1.42 | 100.51 |
| XTWL04     | Diabase      | 65.89 | 1.04  | 16.63 | 3.61  | 0.08 | 0.73 | 0.29 | 6.27 | 3.92 | 0.11 | 0.89 | 99.46 |
| XTWL05     | Diabase xenoliths | 40.72 | 5.12  | 10.75 | 14.18 | 0.22 | 6.98 | 14.92 | 3.29 | 0.10 | 0.77 | 2.74 | 99.79 |
| XTWL10     | Felsic Mylonite | 67.57 | 0.75  | 15.11 | 3.41  | 0.09 | 0.05 | 0.52 | 5.95 | 4.30 | 0.08 | 1.57 | 99.40 |
| XTWL11     | Diabase      | 50.54 | 0.42  | 7.60  | 2.95  | 0.21 | 1.12 | 2.36 | 6.50 | 4.42 | 0.17 | 4.55 | 99.14 |
| XTWL12     | Volcanic bomb | 60.09 | 0.91  | 18.00 | 3.31  | 0.14 | 0.54 | 1.90 | 6.88 | 5.53 | 0.11 | 2.05 | 99.46 |

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Eu anomalies are pronounced, with Eu/Eu* from 0.30 to 0.62 and with an average of 0.52. Significant Ce anomalies have been observed in the analyzed samples (Ce/Ce* ranges from 0.82 to 0.95 with an average of 0.93).

### 4.5.3 Rare earth elements in limestone and sphalerite ore

The ΣREE of limestone rocks from the different localities of the study area ranges from 32.39ppm to 89.28ppm with an average of 61.50ppm. Chondrite-normalized REE patterns of limestone rocks (Figure 4c) are enriched in LREE. The ΣLREE/ΣHREE ratio values ranges from 3.39 to 12.78 with an average of 10.81. The La/Yb ratios range from 4.00 to 41.87 with an average of 18.80. Significant negative anomalies as shown by (La/Sm) _N_ ratios that vary from 8.41 to 10.23 indicate the order of difference of degree of fractionation. Eu anomalies ratios range from 0.87 to 2.12 with an average of 1.30. Those of Ce anomalies range between 0.80 and 1.77 with an average of 1.13.

All samples of sphalerite ore in the mining area were collected in the open pit bottom of the Damogou K1 orebody. REE concentrations range between 481.85ppm and 603.72ppm with an average of 535.19ppm. Chondrite-normalized REE patterns of the sphalerite are shown in Figure 10d. They both have enrichment LREE distribution patterns while the ΣLREE/ΣHREE values range from 12.52 to 13.95, with an average of 13.09. La/Yb ratios range from 18.75 to 31.21 with an average of 23.28. LREE and HREE indicate relatively negative difference degree of fractionation by (La/Sm) _N_ ratios that vary from 3.73 to 17.45 and (Gd/Yb) _N_ ratios that vary from 1.21 to 5.75. Significant negative Eu anomalies are pronounced with Eu/Eu* ratios range from 0.46 to 0.59 with an average of 0.52. Ce anomalies have been observed in the analyzed samples (Ce/Ce* ranges from 0.99 to 1.00 with an average of 1.00).

### 4.6 Fluid inclusion petrography and microthermometry

Fluid inclusions were studied in fluorite (Figure 5). Four types of fluid inclusions were identified in our samples based on their phase composition at room
temperature and according also to the classifications of Nash and Theodore (1971) and Roedder. The result of petrographic observations indicates that the inclusions are mainly of gas–liquid two-phase, pure gas phase, pure liquid phase, and \( \text{CO}_2\text{-H}_2\text{O} \) three-phase daughter mineral-bearing type (Figure 6). Microthermometry of fluid inclusions from Damogou area reveals that the homogenization temperatures range from 295°C to 340°C with salinities from 0.53% to 1.33% \( \text{NaCl}_{eq} \), and the homogeneous temperatures of fluid inclusions in fluorite from Naoyangping area range from 289°C to 329°C with high salinities (Table 4). Liquid-rich two-phase inclusions are common in the grain boundary or present as trails penetrating crystal boundaries, suggesting a secondary origin (Figure 6A and Figure 6B). The primary fluid inclusions are usually 5–10 mm in size and are spherical to semi-spherical in shape (Figure 6C and Figure 6D). The Damogou inclusions are dominated by fluids that show low salinities.

Homogenization temperatures of all these fluids in Naoyangping-Damogou are mostly in the range 289°C to 340°C. Most of the inclusions have freezing point values ranging from −0.3°C to −8.0°C. All these inclusions show low salinity, which ranges from 0.53 wt. % to 1.33 wt. % \( \text{NaCl}_{eq} \).

5. Discussion
The data obtained by cross plot of the Naoyangping-Damogou fluorites on a Tb/Ca versus Tb/La variation diagram (after Moller et al., 1976) (Figure 7) are compatible with a structurally controlled, sedimentary-hydrothermal origin. The relative positions of fluorite-rich samples on the Tb/Ca vs. Tb/La diagram are consistent with this late crystallization environment. According to Dolniecek and Slobodnik (2001), fluorite of hydrothermal origin is homogeneous without any growth zones.

Prismatic mantle trace elements diagram of the Naoyangping-Damogou area are illustrated in
From them, it can be discovered that the trace elements contents of ultra-basic pyroxenite (Figure 8a) samples are similar, whereas two samples had significantly higher Pb content, much likely caused by the late hydrothermal alteration of the area.

Primitive mantle trace elements spider diagram of alkaline trachyte and sphalerite ore are shown in Figures 8b and Figure 8d, respectively. A comparison of those two diagrams shows a certain similarity. Sr values are significantly depleted and the trace elements in the...
This may be interpreted as an indication that the material sources of alkaline trachyte and sphalerite ore are analogous. It also shows that in the mining area the ore-forming elements of sphalerite ore and alkaline trachyte are closely related.

The Figure 9 display δD and δ¹⁸O characteristics of the fluid inclusion water in Naoyangping-Damogou zinc-fluorite deposits obtained by the Geological Survey Institute of Shaanxi province. On the same diagram, it is shown that the hydrogen and oxygen compositions of the studied samples are located between meteoric water line and kaolinite weathering line, which is just below the field of regional primary magmatic waters. Thus, it is not easy to determine the source of hydrothermal ore-forming solutions of this deposit. Isotopic data indicate that most probably they derived from magmatic water with mixed rainwater. This result clearly shows that the Naoyangping-Damogou area hydrothermal ore-forming solution

### Table 4. Microthermometric data of fluid inclusions from the Naoyangping-Damogou study area.

| Sample No. | Sampling location | Samples lithology characteristics | Type of fluid inclusions | Range of Th (°C) | Freezing point (°C) | Range of salinity | Density of fluid |
|------------|-------------------|-----------------------------------|---------------------------|------------------|--------------------|-----------------|-----------------|
| LT01       | K1-1085 middle-stage | Purple fluorite                   | Gas-liquid two-phase      | 295 – 335        | 300 – 320 (Damogou)| ~0.3 – ~0.8     | 0.53 – 1.33     |
| LT03       | K1-1136 middle-stage | White fluorite                    | Gas-liquid two-phase      |                  |                    |                 |                 |
| LT04       | K1-1136 middle-stage | White fluorite                    | Gas-liquid two-phase      |                  |                    |                 |                 |
| LT05       | K1-open pit        | White fluorite                    | Gas-liquid two-phase      | 310 – 340        |                    |                 |                 |
| LT06       | K1-open pit        | White fluorite                    | Gas-liquid two-phase      |                  |                    |                 |                 |
| LT09       | K3-PD10            | Purple fluorite                   | Gas-liquid two-phase      | 289 – 329        | 289 – 329 (Naoyangping) |                 |                 |
| LT10       | K3-PD10            | Purple fluorite                   | Gas-liquid two-phase      |                  |                    |                 |                 |
| LT11       | K3-PD10            | Purple fluorite                   | Gas-liquid two-phase      |                  |                    |                 |                 |

Figure 6. Morphology of the Naoyangping-Damogou fluid inclusions. A, B and C: secondary fluid inclusions; D: pure gas fluid inclusions, and E: inclusions containing daughter crystal F: daughter crystal.

Figure 7. Plot of the Naoyangping-Damogou fluorites on a Tb/Ca versus Tb/La variation diagram (After: Moller et al., 1976). Trends are taken from Geological Survey of Shaanxi Province (2009)
mainly originated from the intraformational-evolution of rainwater. Sulphur isotopic determinations for pyrite and sphalerite from Damogou area (see histogram in Figure 10) display δ34S values concentrated in the range between 13‰ and 15‰, and the sphalerite ore deposit are characterized by enrichment in heavy sulfur δ34S. Sulfur isotopic characteristics in Sphalerite are significantly different from that in the mantle source of sulfur (0‰). Additionally, the same histogram (Figure 10) shows that the source of sulfur in the ore deposits is not characteristic of a deep source. The most probable source of sulfur in ore-forming fluid can be the alkali trachyte or the thermo-chemical sulfate reduction in sedimentary rocks (Zeng, 2013).

6. Conclusion
As one of the ore deposit types in the south-east wing of Pingli Anticlinorium of the North Daba Mountain,
fluorite occurs in a number of localities as veins in a fracture zone within NE-SE direction. Petrography as well as REE geochemistry and fluid inclusion suggest that the source of the ore-forming materials of the Naoyangping-Damogou zinc-fluorite deposits do not have the characteristics of the deep-sourced hydrothermal deposits; it can be the atmospheric precipitation along the fracture infiltration of alkali trachyte and argillite boundary location, and occurrence of water-rock interaction with metasomatic extraction of ore-forming elements in rocks. Subsequently, the ore-forming elements migrated into favourable position for their precipitation during the late stages of magmatic-hydrothermal crystallization conditions. Fluid inclusions investigations indicated that these deposits have high temperatures and low salinities.

Disclosure statement

There are no relevant financial or non-financial competing interests to report.

References

Bodnar, R. J. (1993). Revised equation and table for determining the freezing point depression of H₂O-NaCl solutions. *Geochemistry et Cosmochimica Acta*, 57(3), 683–684. https://doi.org/10.1016/0016-7037(93)90378-A

Boynton, W. V. (1984) Geochemistry of Rare Earth Elements: Meteorite Studies. In: Henderson, P., Ed., *Rare Earth Element Geochemistry*, Elsevier, New York, 63–114. http://dx.doi.org/10.1016/B978-0-444-42148-7.50008-3

Bühn, B., Rankin, A. H., Schneider, J., & Dulski, P. (2002). The nature of orthomagmatic, carbonatic fluids precipitating REE,Rich fluorite: Fluid-inclusion evidence from the Okorusu fluorite deposit, Namibia. *Chemical Geology*, 186(1–2), 75–98. https://doi.org/10.1016/S0009-2541(01)00421-1

Coniglio, J., Xaver, R. P., Pnottu, L., & D’Eramo, F. (2000). Ores-forming fluids of vein-type fluorite deposits of the Cerro Aspero Batholith, southern Cordoba Province, Argentina. *International Geology Review*, 42(4), 368–383. https://doi.org/10.1080/0020610009465088

Deng, S. B., Wang, W. J., & Wang, X. J. (2003). The geological characteristics of the alkali-intermediate rocks and their ore-bearing (columbo-tantalite) features in the Ziyang–Langao areas. *Geology of Shaanxi*, 21(in Chinese with English abstract), 19–26.

Dolnicz, Z., & Slobodnik, M. (2001). The neoideous fluorite mineralization in the Brno Massif: Interaction between fluid and rock. *Geoines*, 13, 51–52.

Dong, W., Ximin, C., & Bangchao, W. (2009). Geological characteristics and ore prospects of zinc-fluorite deposit in Pingli Damogou. *Shaanxi. Northwestern Geology*, 46(3), 77–85.

Dong, Y. P., Zhang, G. W., Neubauer, F., Liu, X. M., Genser, J., & Hauzenberger, C. (2011). Tectonic evolution of the Qinling orogen, China: Review and synthesis. *Journal of Asian Earth Sciences*, 41(3), 213–237. https://doi.org/10.1016/j.jseaes.2011.03.002

Gagnon, J. E., Samson, I. M., Fryer, B. J., & Williams-Jones, A. E. (2003). *COMPOSITIONAL HETEROGENEITY IN FLUORITE AND THE GENESIS OF FLUORITE DEPOSITS: INSIGHTS FROM LA ICP MS ANALYSIS*. *The Canadian Mineralogist*, 41(2), 365–382. https://doi.org/10.2113/gscamin.41.2.365

Galindo, C., Tornos, F., Darbyshire, D. P. F., & Casquet, C. (1994). The age and origin of the barite-fluorite (PbZn) veins of the Sierra del Guadarrama (Spanish Central System, Spain): A radiogenic (Nd, Sr) and stable isotope study. *Chemical Geology*, 112(3–4), 351–364. https://doi.org/10.1016/0016-7037(94)90034-5

Geological Survey of Shaanxi Province, (2009). Damogou Zn-CaF₂ ore: Structure Magmatic hydrothermal (in Chinese with English abstract).

Goldring, D. C., & Greenwood, D. A. (1990). Fluorite mineralization at Beckermet iron ore mine, Cumbria, north England.–Trans. *Institution of Mining Metallurgica (Sect. B: Applied Earth Science)*, 99, B113–B119.

Hall, D. L., Sterner, S. M., & Bodnar, R. J. (1988). Freezing point depression of NaCl-KCl-H₂O solutions. *Economic Geology*, 83(1), 197–202. https://doi.org/10.2113/gsecongeo.83.1.197

Hall, H. D., & Petersen, U. (1979). Element dispersion, element concentration and ore deposits. *Annales de la Société Géologique de Belgique*, T102, 407–415.

Ismail, R., Ciobanu, C. L., Cook, N. J., Schmidt Mumm, A., Wade, B., Giles, D., & Teale, G. S. (2014). Rare Earths and other trace elements in minerals from skarn assemblages Hillside iron oxide-copper-gold deposit, Yorke Peninsula, South Australia. *Lithos*, 184–187, 456–477.

Jia, R. X., He, Y., Guo, J., Lin, Y., & Song, H. P. (2004). Geochemical characteristics of rare metal and REE for subvolcanic alkaline rock in Hongyang area, Zhenping, Shaanxi. *Geology and Prospecting*, 40(in Chinese with English abstract), 56–60.

Kesler, S. E. (1977). Geochemistry of manto fluorite deposits, northern Coahuila, Mexico. *Economic Geology*, 72(2), 204–218. https://doi.org/10.2113/gsecongeo.72.2.204

Lü, Z. C., Liu, C. Q., Liu, J. J., & Wú, F. C. (2004). Geochemical Studies on the Lower Cambrian Withitherite-Bearing Cherts in the Northern Daba Mountains. *Acta Geologica Sinica*, 78(in Chinese with English abstract), 390–406.

Li, F. Z. (2012). Geology of titanomagnetite deposit in Zhiuxhe, Ziyang County of Shaanxi. *Geology of Shaanxi*, 30(in Chinese with English abstract), 35–40.

Liu, J. J., Wu, S. H., Liu, Z. J., Su, W. C., & Wang, J. P. (2010). A discussion on the origin of witherite deposits in large-scale barium metallogenic belt, southern Qingling Mountains, China: Evidence from individual fluid inclusion. *Earth Science Frontiers*, 17(in Chinese with English abstract), 222–238.

Liu, L., Gao, J. L., & Shang, X. S. (2012). Geological characteristics of Tiefosi titanium-magnetite deposit and prospecting potential, Shaanxi. *Mineral Exploration*, 3(in Chinese with English abstract), 638–643.

Mao, M., Simandel, G. J., Spence, J., & Marshall, D. (2015). Fluorite trace-element chemistry and its potential as an indicator mineral: Evaluation of LA-ICP-MS method. In G. J. Simandel & M. Neetz (Eds.), *British Columbia Ministry of energy and mines, british columbia geological survey paper 2015-3* (pp. 251–264). Symposium on
Strategic and Critical Materials Proceedings, November 13-14, 2015, Victoria, British Columbia.

Moller, P., Parekh, P. P., Schneider, H. J. (1976). The application of Tb/Ca-Tb/La abundance ratios to problems of fluorspar genesis. Min. Depos. 11, 111–116. https://doi.org/10.1007/BF00203098

Nash, J. T., & Theodore, T. G. (1971). Ore fluids in the porphyry copper deposit at Copper Canyon, Nevada: ECON. GEOL. 66, 385–399.

Ouyang, H., Wu, X., Mao, J., Su, H., Santosh, M., Zhou, Z., & Chao Li, C. (2014). The nature and timing of ore formation in the Budunhua copper deposit, southern Great Xing’an Range: Evidence from geology, fluid inclusions, and U–Pb and Re–Os geochronology. Ore Geology Reviews, 63, 238–251. https://doi.org/10.1016/j.oregeorev.2014.05.016

Richardson, C. K., & Holland, H. D. (1979). Fluorite deposition in hydrothermal systems. Geochimica et Cosmochimica Acta, 43(8), 1327–1335. https://doi.org/10.1016/0016-7037(79)90122-4

Shaanxi Province, (2012) Bureau of geology and mineral exploration and development bureau of the first geological brigade. Subias, L., & Fernández-Nieto, C. (1995). Hydrothermal events in the Valle de Tena (Spanish western Pyrenees) as evidenced by fluid inclusions and trace-element distribution from fluorite deposits. Chemical Geology, 124(3–4), 267–282. https://doi.org/10.1016/0009-2541(95)00060-Y

Wang, Y., (2007). Geological characteristics and significance of Early Paleozoic Alkali volcanic in South-Qinling, Langao-Pingli, Shaanxi Province. A dissertation submitted to Chang’an University, Xi’an for the Master Degree, 68p (in Chinese with English abstract)

Wang, Z., Q., Yan, Q. R., Yan, Z., Wang, T., Jiang, C. F., Gao, L. D., Li, Q. G., Chen, J. L., Zhang, Y. L., Liu, P., Xie, C. L., & Xiang, Z. J. (2009). New division of the main tectonic units of the Qinling orogenic belt, Central China. Acta Geologica Sinica, 83(in Chinese with English abstract), 1527–1546.

Wei, D., Chen, X. M., & Wu, B. C. (2009). Geological characteristics and ore prospects of Zinc-Fluorite deposit in Pingli Damogou, Shaanxi. Northwestern Geology, 42(in Chinese with English abstract), 77–85.

Williams-Jones, A. E., Samson, I. M., & Olivo, G. R. (2000). The genesis of hydrothermal fluorite-REE deposits in the Gallinas Mountains, New Mexico. Economic Geology, 95(2), 327–342. https://doi.org/10.2113/gsecongeo.95.2.327

Zeng, W., (2013) Sulfur Isotopic Geochemistry of Pb-Zn Deposits in NW Guizhou Province, SW China (in Chinese with English abstract).

Zhang, G. W., Dong, Y. P., & Lai, S. C. (2004). Mianlüe tectonic zone and Mianlüe suture zone on southern margin of Qinling–Dabie orogenic belt. Science in China Series D, 47(4), 300–316. https://doi.org/10.1360/02YD0526

Zhang, G. W., Zhang, B. R., Yuan, X. C., & Xiao, Q. H. (2001). Qinling Orogenic Belt and Continental Dynamics (pp. 1–855). Science Press.