

Zajkan intermediate-sulfidation epithermal deposit, NW Iran: Mineral paragenesis, fluid inclusion and oxygen-sulfur isotope

Hossein Kouhestani⁽¹⁾, Mir Ali Asghar Mokhtari⁽¹⁾, Kezhang Qin^(2,3,4), Junxing Zhao⁽²⁾

⁽¹⁾ Department of Geology, Faculty of Sciences, University of Zanjan, Zanjan 45195–313, Iran E-mail: kouhestani@znu.ac.ir

⁽²⁾ Key Laboratory of Mineral Resources, Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing 100029, China

⁽³⁾ CAS Center for Excellence in Tibetan Plateau Earth Science, Beijing 100101, China

⁽⁴⁾ University of Chinese Academy of Sciences, Beijing 100049, China

Abstract

Zajkan is a small (0.2 Mt) epithermal base metal deposit in the Tarom–Hashjin metallogenic belt (THMB), northwestern Iran. It occurs as quartz-base metal sulfide veins hosted by Eocene volcanic and volcanoclastic rocks of the Karaj Formation. Four stages of ore formation are identified at Zajkan: (1) quartz-chalcopyrite-pyrite veins, (2) quartz-galena-sphalerite ± chalcopyrite ± pyrite veins and breccias, (3) quartz-hematite veins and breccias, and (4) barren quartz-carbonate veinlets. Microthermometric measurements of primary LV fluid inclusion assemblages in quartz and sphalerite indicate that the veins were formed at temperatures between 217 and 273 °C from fluids with salinities between 1.7 and 6.4 wt.% NaCl equiv. The oxygen isotopic compositions ($\delta^{18}\text{O}_{\text{water}}$ of +3.7 to +1.1‰) indicate that the ore-forming fluids were mainly derived from magmatic water with the input of meteoric water in the later ore-stages. Sulfur isotopic values of sulfide minerals vary over a narrow range from –5.0 to –0.9‰ (averaging –2.2‰), suggesting that sulfur was derived from a homogeneous magmatic source. The fluid inclusion and stable isotope data indicate that fluid boiling and mixing facilitated hydrothermal alteration and mineralization at Zajkan. Our data suggest that the Zajkan deposit is an intermediate-sulfidation style epithermal mineralization.

Keywords: Fluid inclusion, Stable isotopes, Zajkan, Iran.

Introduction

Boiling and The Zajkan deposit is located in the southeastern part of the THMB, ~50 km northwest of Qazvin. The geological characteristics of the Zajkan deposit indicate that it is a volcanic-hosted epithermal base metal deposit. However, due to lack of systematic geochemical and paragenetic studies, the nature of the ore-forming fluids and mineralization processes are still poorly constrained. In this paper, we present the first detailed field investigations, description of gangue and ore mineral assemblages, and outline the alteration and mineralization of the Zajkan base metal deposit. Linking these data with results of fluid inclusion microthermometric and stable isotopes analysis, our work provides insights into the genesis of the Zajkan base metal deposit and may have implication for the regional exploration of precious and base metal deposits in the THMB.

Material and Methods

Fluid inclusion measurements have been conducted on crystalline quartz, and sphalerite from the early, second, and third stages of ore formation. Microthermometric measurements were performed using a Linkam THMSG-600 heating–freezing stage attached to a Leica microscope in the fluid inclusion laboratory of Institute of Geology, Chinese Academy of Geological Sciences, Beijing, China. The heating rate was 0.1 to 0.2 °C/min between –70 and 0 °C, with an accuracy of ±0.1 °C, whereas rates were about 3 to 5 °C/min at higher temperatures, with an accuracy of about ±1 °C. The heating–freezing stage was calibrated using synthetic fluid inclusion standards.

Oxygen isotopes were analyzed at the Beijing Createch Testing Technology Co., Ltd., China, using a laser extraction technique with BrF_3 as the reagent. Samples were heated using a CO_2 -laser, and the isotope analyses were performed using a Thermo Finnigan 253 plus stable isotope ratio mass spectrometer in dual inlet mode. Results are reported in δ notation relative to V-SMOW using values of +10.92‰ for standard GBW04421 quartz. The reproducibility was better than ±0.2‰. Sulfur isotopes were measured at the stable isotope laboratory of the Beijing Createch Testing Technology Co., Ltd., China. Sulfides were combined with V_2O_5 and combusted in a Thermo Scientific Flash 2000 elemental analyzer; the resulting SO_2 flowed directly into a Thermo Finnigan 253 plus mass spectrometer for the sulfur isotope measurement. The analytical reproducibilities are better than ±0.2‰ in the laboratory. Calibration was based on the internationally distributed standards GBW04414 (–0.07‰), GBW04415 (+22.15‰) and IAEA-S-3 (–30.7‰). The $\delta^{34}\text{S}$ values are reported relative to the VCDT standard. The isotopic compositions of the fluid were calculated using the mean value of the fluid inclusion homogenization temperatures.

Results

Geological units around the Zajkan deposit are comprised of Eocene volcanic and volcanoclastic rocks, i.e., tuff units interlayered with andesitic and dacitic lavas and ignimbrite, and late Eocene dacitic domes and quartz monzonite to granodiorite intrusions (Fig. 1). Zircon LA–ICP–MS U–Pb ages of 37.9 ± 1.7 Ma obtained from the andesitic lavas indicate middle Eocene timing of the volcanism, while dacitic domes and granodiorite intrusions, respectively, have ages of 36.8 ± 0.18 Ma and 36.5 ± 0.18 Ma, slightly younger than the surrounding volcanic rocks.

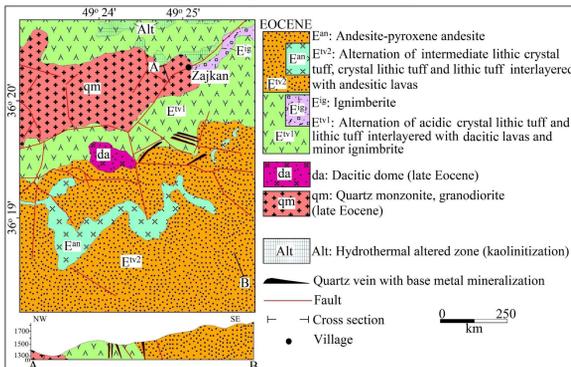


Fig. 1. Geological map of the Zajkan epithermal base metal deposit.

The mineralization is hosted by a series of NW- and NE-trending epithermal base metal quartz-sulfide veins hosted by Eocene volcanic and volcanoclastic rocks of the Karaj Formation (Fig. 2). The main ore vein reaches up to 1000 m in length and ca. 3 m in width, reaching a maximum of 7 m. It generally dips 70–88° to the south with a down-dip extension of about 200 to 250 m. Metal concentrations for outcrop samples average 8 wt.% Zn + Pb, 0.4 wt.% Cu, and reaches up to 5 and 21 g/t Au and Ag, respectively. Four stages of ore formation are identified at Zajkan: (1) quartz-chalcopyrite-pyrite veins, (2) quartz-galena-sphalerite ± chalcopyrite ± pyrite veins and breccias, (3) quartz-hematite veins and breccias, and (4) barren quartz-carbonate veinlets. The primary metallic minerals are pyrite, chalcopyrite, sphalerite, galena, and trace amounts of hematite; gangue minerals are mainly quartz, sericite, chlorite, and calcite. The main wall-rock alteration is silicification, and intermediate argillic, and propylitic alteration.

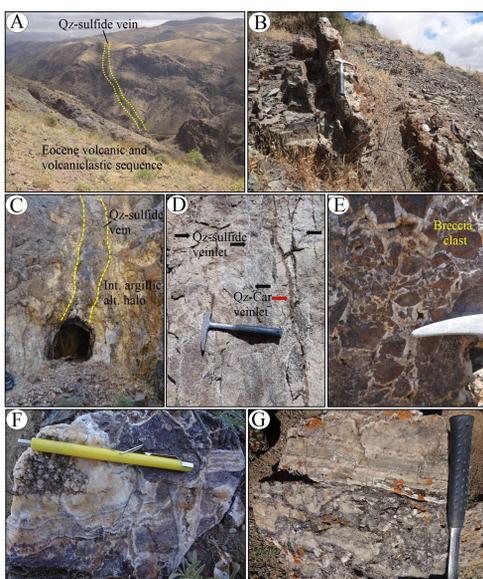


Fig. 2. Field photographs showing representative quartz-sulfide veins and breccias at the Zajkan epithermal base metal deposit. A. General view of the main quartz-sulfide vein, looking east. B and C. Close views of quartz-sulfide veins crosscutting volcanic and volcanoclastic host rocks. In C, the vein is surrounded by 3 m wide intermediate argillic alteration halo. D. Parallel sheeted mineralized quartz-sulfide veinlets (black arrows) crosscut by late stage barren quartz-carbonate veinlets (red arrow). E. Hydrothermally altered breccia ore with quartz-sulfide cement. F and G. Colloform and crustiform texture of quartz vein.

Four types of fluid inclusion are present at Zajkan (Fig. 3): (1) Liquid-rich two-phase (LV) inclusions, (2) Vapor-rich, two-phase (VL) inclusions, (3) Liquid-phase (L) inclusions, and (4) Vapor-phase (V) inclusions. Neither liquid CO_2 nor CH_4 was observed during the freezing experiments. A total of 93 microthermometric measurements were performed on primary LV inclusions. The measured T_{fm} values documented in LV inclusions in stage 1 quartz are –25 to –36 °C. This data set is compatible with the presence of Na and K chlorides in the hydrothermal fluid system (e.g., Roedder, 1984; Goldstein, 2003; Prokofiev et al., 2010). The mean values of $T_{\text{h(total)}}$ of LV inclusions in FIAs of stage 1 quartz (homogenize to the liquid state) range from 235 to 273 °C, with an average of 254 °C. These inclusions have $T_{\text{m-ice}}$ ranging from –1.9 to –5.3 °C indicating bulk salinities of 3.0 to 8.3 (with an average of 6.4) wt.% NaCl equiv. The mean values of $T_{\text{h(total)}}$ of LV inclusions in stage 2 sphalerite (homogenize to the liquid state) range from 217 to 247 °C, with an average of 232 °C. For these inclusions, the data show a range of T_{fm} values from –19 to –28 °C, indicating the dominance of NaCl among the dissolved salts (4). The $T_{\text{m-ice}}$ values range from –0.9 to –3.2 °C with calculated salinities from 1.8 to 5.6 (with an average of 4.1) wt.% NaCl equiv. Similar to stage 2 sphalerite, LV inclusions within stage 3 quartz show a range of T_{fm} from –17 to –25 °C that also suggests the dominance of NaCl among the dissolved salts in the inclusions. The mean values of $T_{\text{h(total)}}$ of LV inclusions from stage 3 quartz range from 219 to 237 °C, with an average of 229 °C. The $T_{\text{m-ice}}$ values obtained for these inclusions range from –0.2 to –2.2 °C, and their bulk salinities range from 0.4 to 3.6 (with an average of 1.4) wt.% NaCl equiv. Microthermometric data show trends of decreasing $T_{\text{h(total)}}$ and salinity through the paragenesis from the stage 1 quartz to stage 2 sphalerite to stage 3 quartz. The two-phase aqueous LV inclusions at the Zajkan deposit have bulk densities of 0.8 to 0.9 g/cm³.

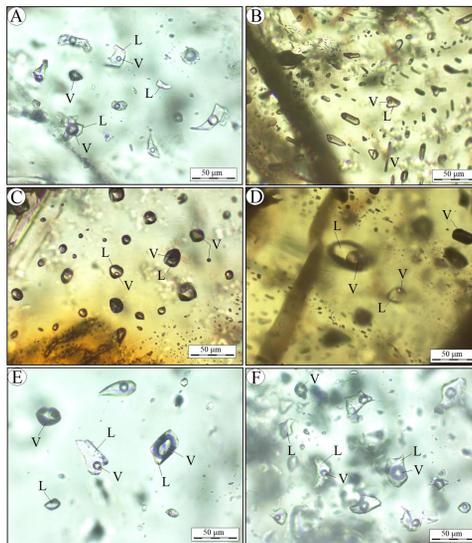


Fig. 3. Photomicrographs of fluid inclusion types from the Zajkan deposit. Inclusions showing representative primary FIAs and variable LV ratio as an evidence for boiling. A. Coexisting primary LV, VL, and V fluid inclusions in stage 1 quartz, probably formed due to boiling. B. Primary LV fluid inclusions in stage-2 sphalerite. C–D. Coexisting elliptical or negative-shaped primary LV, VL, and V fluid inclusions as evidence of boiling in stage-2 sphalerite. E–F. Light-colored and irregularly-shaped, primary LV inclusions coexisting with VL and V fluid inclusions in stage 3 quartz indicating boiling.

The $\delta^{18}\text{O}$ value for quartz from stage 1 veins is +11.5‰, and those for quartz from stages 2 and 3 veins range from +12.0 to +10.8‰, and +10.5‰, respectively. The $\delta^{18}\text{O}$ values of one hematite sample from stage 3 quartz-hematite veins is +3.8‰. Using the mean temperature of fluid inclusion assemblages, the fluids of stage 1 quartz are calculated to have a $\delta^{18}\text{O}_{\text{water}}$ value of about +3.7‰. The calculated $\delta^{18}\text{O}_{\text{water}}$ values of stage 2 veins cover a narrow range from +2.8 to +1.6‰ (average +2.3‰), and that for stage 3 veins is +1.1‰. The calculated $\delta^{18}\text{O}_{\text{water}}$ value for hematite sample from stage 3 quartz-hematite veins is +4.7‰. The $\delta^{34}\text{S}_{\text{sulfide}}$ values vary in a narrow range from –4.8 to –0.5‰. $\delta^{34}\text{S}$ values decrease from galena through chalcopyrite and pyrite to sphalerite. If the mean homogenization temperature of fluid inclusion is then taken as temperature of isotopic equilibrations, the measured compositions imply a $\delta^{34}\text{S}_{\text{H2S}}$ values between –5.0 and –0.9‰, averaging –2.2‰.

Discussion and Conclusions

The Zajkan deposit is an example of volcanic-hosted epithermal base metal deposit. It is structurally-controlled and hosted by Eocene volcanic and volcanoclastic rocks that show medium- to low-temperature hydrothermal alteration assemblages (sericite, illite, epidote, calcite, and chlorite) near the ore veins. Mineralization at Zajkan show sulfide mineral assemblages composed mainly of pyrite, chalcopyrite, galena, and sphalerite hosted by a quartz, sericite, chlorite, and calcite gangue. Epithermal ore textures, such as comb, cockade, colloform/crustiform and plumose textures are well developed at Zajkan. Comparing to typical low (LS)-, intermediate (IS)- and high (HS)-sulfidation epithermal deposits (Hedenquist et al., 2000; Sillitoe and Hedenquist, 2003; Simmons et al., 2005), these mineral assemblages, ore textures, and alteration patterns coincide with those of IS epithermal deposit. In addition, the medium- to high-temperature, moderate- to low-salinity, and low density of ore fluids at Zajkan are typical of IS epithermal precious and base metal systems noted elsewhere. The general absence of adularia, alunite, enargite, and luzonite in mineralized ore veins, and the absence of vuggy quartz, lattice-textured and bladed calcite as well as advanced argillic alteration in this deposit distinguish its base metal veins from LS and HS epithermal deposits. Moreover, paleodepth of ~500 m is characteristic of silver- and base metal-rich of epithermal systems of the IS category (Hedenquist et al., 2000; Sillitoe and Hedenquist, 2003).

The oxygen isotope composition of quartz from the Zajkan deposit demonstrated that the main ore-forming fluids were largely magmatic in origin, but progressively mixed and cooled by dilute meteoric water during later ore-stages. The stage 3 fluids are more depleted in ^{18}O suggesting a significant input of meteoric water into the fluid system. The narrow range of $\delta^{18}\text{O}_{\text{water}}$ values from the Zajkan deposit suggests that the isotopic characteristics of the ore fluids did not change significantly during the mineralization process; however, we cannot fully rule out the interaction between hydrothermal fluids and the altered volcanic wall-rocks. Estimates of fluid salinities show that the ore-forming fluids at Zajkan were diluted from early to late, which are in accord with the oxygen isotope evidences for dilution by meteoric water. Salinities of the LV fluid inclusions of the early, second and third ore-stages in the Zajkan deposit are up to 6.4, 4.1 and 1.7 wt.% NaCl equiv., respectively. This indicates that the initial ore-fluids were likely sourced from a magmatic system progressively diluted by meteoric water during later ore-stages.

Sulfides from the Zajkan deposit have a narrow range of $\delta^{34}\text{S}_{\text{sulfide}}$ compositions, suggesting they formed under stable physical and chemical conditions and were derived from a relatively homogeneous source. They have low $\delta^{34}\text{S}_{\text{H2S}}$ values range from –5.0 to –0.9‰, averaging –2.2‰, consistent with a magmatic and magmatic-related source of sulfur (Hoefs, 2015) under conditions sufficient oxidizing to stabilize SO_2 (Ohmoto and Rye, 1979). Considering that the host rocks at Zajkan are igneous, it is likely that the metals and sulfur have a magmatic origin and were scavenging from magmatic host rocks or, less probably, from a magma driving the system.

The total homogenization temperature of fluid inclusions in stage 1 quartz from the Zajkan deposit vary between 235 and 273 °C, with an average temperature of ca. 254 °C. Compared with the $T_{\text{h(total)}}$ of fluid inclusions in stage 1 quartz, a narrower range of $T_{\text{h(total)}}$ in stage 2 sphalerite (217 and 247 °C) and stage 3 quartz (219 and 237 °C) were obtained, with an average $T_{\text{h(total)}}$ of 232 and 229 °C, respectively. Plotting these data on the homogenization temperature versus salinity diagram (Fig. 4) shows positive correlation between salinity and homogenization

temperatures implying that mineralization at Zajkan involved mixing of magmatic fluids and a dilute, cooler meteoric fluid. In addition, the evolutionary path of the Zajkan fluid inclusion data could be the result of boiling. This process would result in strong partitioning of salts into the liquid-like phase, which becomes more saline (Wilkinson, 2001; Canet et al., 2011). Based on these arguments, it is suggested that fluid mixing occurred during the fluid evolution, as well as fluid boiling, and it seems clear for the Zajkan deposit that fluid mixing played a more important role in base metal precipitation than fluid boiling.

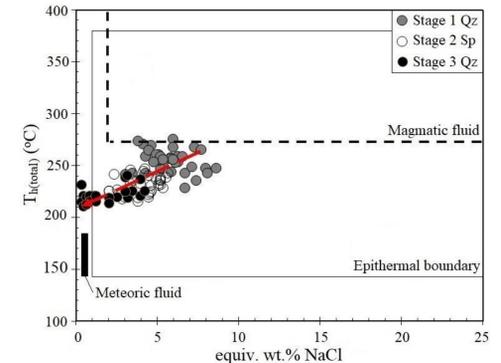


Fig. 4. Total homogenization temperatures vs. equivalent salinity diagram reflecting the mixing and/or boiling trend of fluid inclusion populations at the Zajkan deposit.

Coexistence of LV, VL, and V inclusions in the same quartz and sphalerite growth zones at the Zajkan deposit (Fig. 2) suggests that the inclusions were trapped from a heterogeneous boiling fluid. The possibility of boiling is also consistent with the presence of plumose and colloform/crustiform banded textures within ore-stage quartz veins at Zajkan. Fluid boiling is further supported by the occurrence of the ore-hosting hydrothermal breccias, which are commonly evidence for periods of sharp pressure drops. These may have caused intermittent boiling in a hydrothermal system (Canet et al., 2011; Kouhestani et al., 2015).

Because the Zajkan fluids boiled, the trapping pressure of the fluid inclusions can be estimated based on microthermometric data for samples where vapor is the last phase to homogenize. Consequently, the highest temperatures of the LV inclusions are used for pressure and depth estimation for the Zajkan deposit. Based on the experimental data of Haas (1971), Urusova (1975), and Bodnar et al. (1985), the calculated entrapment pressures range from 35 to 79 bar, equivalent to a depth of 358 to 810 m below the paleowater table, which were nearly identical to those of the epithermal deposits worldwide.

It seems that the dilational sites along the NE-, and NW-trending faults provided a focus for upward migration of metal-bearing moderate-salinity magmatic fluids to a sufficiently shallow depth to allow efficient fluid mixing with the low-salinity and low-temperature meteoric waters (Fig. 5). Through the reaction of mineralizing magmatic fluids with wall-rocks and heat recharge by magma, fluids could have extracted significant amounts of metallogenic materials from volcanic and volcanoclastic host rocks. Fluid mixing changed the conditions of the ore-forming fluid system, destroying the chemical equilibrium of solutions and initiating important chemical reactions, ultimately resulting in the precipitation of base metals from solution during the mineralization process. Consequently, the fluid mixing hypothesis is the main mechanism that could explain the deposition of base metal sulfides in mineralized ore veins at Zajkan. Pervasive fluid boiling lead to the temperature decrease of the ore-forming system and vapor H_2O escape, which are both favorable mechanisms for base metal precipitation (Drummond and Ohmoto, 1985; Fan et al., 2011; Zhong et al., 2018). Increase in pH that accompanied boiling also enhanced chalcopyrite, sphalerite and galena deposition (e.g., Thiersch et al., 1997).

The relatively lower temperature and salinity of fluid inclusions in later ore-stages at Zajkan suggest that the ore-forming fluids were predominantly meteoric waters that have reacted with the volcanic and volcanoclastic host rocks. Significant increase in the oxygenated meteoric water component would eventually increase oxygen fugacity, which agrees with the presence of specular hematite in stage 3 quartz veins. This interpretation is consistent with models for the formation of other epithermal precious and base metal deposits in the THMB.

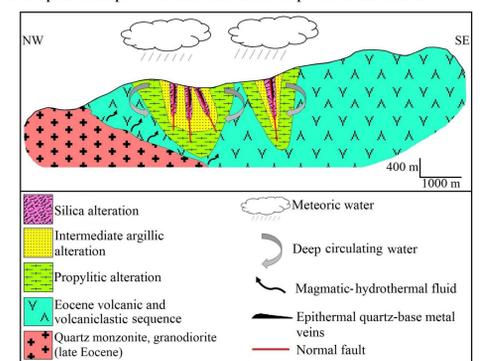


Fig. 5. Conceptual model of Zajkan hydrothermal system integrating the fluid inclusion and the stable isotope interpretations. The model shows magmatic-hydrothermal fluids derived from magma that mix with deeply circulating meteoric water, forming the epithermal ore veins.

Acknowledgements

Financial support of this research was provided by the Key Laboratory of Mineral Resources, Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing, China (Grant No. KLMR2017-01), and the office of Vice Chancellor for Research and Technology, University of Zanjan, Zanjan, Iran; both grants are gratefully acknowledged. We are most grateful to the Roy Godard Company, Zanjan, Iran, for the logistical supports and close cooperation and unlimited access to collect the samples from the Zajkan deposit.

References

- Bodnar, R.J., Burnham, C.W., Sterner, S.M., 1985. Synthetic fluid inclusions in natural quartz. III. Determination of phase equilibrium properties in the system H_2O – NaCl to 1000 °C and 1500 bars. *Geochim. Cosmochim. Acta* 49, 1861–1873.
- Canet, C., Franco, S.L., Prol-Ledesma, R.M., González-Partida, E., Villanueva-Estrada, R.E., 2011. A model of boiling for fluid inclusion studies: Application to the Bolanos Ag–Au–Pb–Zn epithermal deposit, Western Mexico. *J. Geochem. Expl.* 110, 118–125.
- Drummond, S.E., Ohmoto, H., 1985. Chemical evolution and mineral deposition in boiling hydrothermal processes in the light of studies in rock-buffered systems: I. Iron-copper-zinc-lead sulfide solubility relations. *Econ. Geol.* 87, 1–22.
- Fan, H.R., Hu, F.F., Wilde, S.A., Yang, K.F., Jin, C.W., 2011. The Qiyugou gold-bearing breccia pipes, Xiong'ershan region, central China: Fluid-inclusion and stable-isotope evidence for an origin from magmatic fluids. *Int. Geol. Rev.* 53, 25–45.
- Goldstein, R.H., 2003. Petrographic analysis of fluid inclusions. In: Samson, L., Anderson, A., Marshall, D. (Eds.), *Fluid Inclusions: Analysis and Interpretation*. Min. Assoc. of Can., Short Course 32, 9–55.
- Haas, J.L., 1971. The effect of salinity on the maximum thermal gradient of a hydrothermal system at hydrostatic pressure. *Econ. Geol.* 66, 940–946.
- Hedenquist, J.W., Arribas, A.R., González-Urrien, E., 2000. Exploration for Epithermal Gold Deposits. *Rev. Econ. Geol.* 13, 245–277.
- Hoefs, J., 2015. *Stable Isotope Geochemistry*, 7th edition. Springer International Publishing, Switzerland.
- Kouhestani, H., Ghaderi, M., Chang, Z., Zaw, K., 2015. Constraints on the ore fluids in the Chah Zard breccia-hosted epithermal Au–Ag deposit, Iran: Fluid inclusions and stable isotope studies. *Int. Geol. Rev.* 65, 512–521.
- Ohmoto, H., Rye, R.O., 1979. *Isotope of sulfur and carbon*. In: Barnes, H.L. (Ed.), *Geochemistry of Hydrothermal Ore Deposits*. John Wiley and Sons, New York, p. 509–567.
- Prokofiev, V.Y., Garofalo, P.S., Bortnikov, N.S., Kovalenko, V.A., Zorina, L.D., Grichuk, D.V., Selektor, S.L., 2010. Fluid inclusion constraints on the genesis of gold in the Darasun district (eastern Transbaikalia), Russia. *Econ. Geol.* 105, 395–416.
- Roedder, E., 1984. *Fluid inclusions*. *Rev. Mineral.* 12, 644 p.
- Sillitoe, R.H., Hedenquist, J.W., 2003. Linkages between volcanotectonic settings, ore fluid compositions, and epithermal precious-metal deposits. *Econ. Geol.* Spec. Pub. 10, 315–342.
- Simmons, S.F., White, N.C., John, D.A., 2005. Geological characteristics of epithermal precious and base metal deposits. In: Hedenquist, J.W., Thompson, J.E.H., Goldfarb, J.R., Richards, J.P. (Eds.), *Econ. Geol.* 100th Ann. Vol., pp. 485–522.
- Thiersch, P.C., Williams-Jones, A.E., Clark, J.R., 1997. Epithermal mineralization and ore controls of the Shasta Au–Ag deposit, Toadoggonne District, British Columbia, Canada. *Miner. Deposita* 22, 44–57.
- Urusova, M.A., 1975. Volume properties of aqueous solutions of sodiumchloride at elevated temperatures and pressures. *Russ. J. Inorg. Chem.* 20, 1717–1721.
- Wilkinson, J.J., 2001. Fluid inclusions in hydrothermal ore deposits. *Lithos* 55, 229–272.
- Zhong, J., Chen, Y.J., Chen, J., Qid, J.P., Dai, M.C., 2018. Geology and fluid inclusion geochemistry of the Zijinshan high-sulfidation epithermal Cu–Au deposit, Fujian Province, SE China: Implication for deep exploration targeting. *J. Geochem. Expl.* 184, 49–65.