

The Paleozoic Ozbak-Kuh carbonate-hosted Pb-Zn deposit of East Central Iran: Isotope (C, O, S, Pb) geochemistry and ore genesis

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Abstract Lead and zinc mineralization occurs in dolostones of the Middle Devonian Sibzar Formation at Ozbak-Kuh, which is located 150 km north of Tabas city in East Central Iran. The ore is composed of galena, sphalerite and calcite, with subordinate dolomite and bitumen. Wall-rock alterations include carbonate recrystallization and dolomitization. Microscopic studies reveal that the host rock is replaced by galena and sphalerite. The Pb–Zn mineralization is epigenetic and stratabound. The $\delta^{13}\text{C}$ values of hydrothermal calcite samples fall in the narrow range between -0.3‰ and 0.8‰ . The $\delta^{18}\text{O}$ values in calcite display a wider range, between -14.5‰ and -11.9‰ . The $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values overlap with the oxygen and carbon isotopic compositions of Paleozoic seawater, indicating the possible important participation of Paleozoic seawater in the ore-forming fluid. The $\delta^{18}\text{O}$ signature corresponds to a spread in temperature of about 70 °C in the ore-bearing fluid. The $\delta^{13}\text{C}$ values indicate that the organic materials within the host rocks did not contribute significantly in the hydrothermal fluid. The $\delta^{34}\text{S}$ values of galena and sphalerite samples occupy the ranges of 12.2‰ – 16.0‰ and 12.1 – 16.8‰ , respectively. These values reveal that the seawater sulfate is the most probable source of sulfur. The reduced sulfur was most likely supplied through thermochemical sulfate reduction. The sulfur isotope ratios of co-precipitated sphalerite–galena pairs suggest that deposition of the sulfide minerals took place under chemical disequilibrium conditions. The $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios of the galena samples represent average values of 18.08, 15.66, and 38.50, respectively. These ratios indicate that galena Pb likely originated from an orogenic source in which supracrustal rocks with high $^{238}\text{U}/^{204}\text{Pb}$ and $^{232}\text{Th}/^{204}\text{Pb}$ ratios

are dominant. The average lead isotope model age portrays Cambrian age. This model age is not coeval with the host rocks, which are of middle Devonian age. It is probable that the pre-Middle Devonian model age shows the derivation of Pb from older sources either from host rocks of Cambrian age or from deposits previously formed in these rock units. The Pb isotopic composition of galena accords with the occurrence of an orogenic activity from Late Neoproterozoic to Lower Cambrian in Central Iran. The proposed genetic model considers the fact that mineralization formed in fractured and brecciated host rocks along shear zones and faults from metal-bearing connate waters that were discharged due to deformational dewatering of sediments.

Introduction

Iran has large deposits of lead (Pb) and zinc (Zn), among which are the world-class deposits of Mehdiabad, Irankuh, and Angouran (Ghorbani 2002; Leach et al. 2005; Gilg et al. 2006; Taylor et al. 2009). The majority of the deposits are carbonate-hosted with host rocks ranging in age from Devonian to Cretaceous. Despite some recently published studies (Ghazban et al. 1994; Gilg et al. 2006; Reichert 2007; Ehya et al. 2010; Bazargani-Guilani et al. 2011; Mirnejad et al. 2011; Rajabi et al. 2012), there are still many unknown aspects regarding the ore genesis, types of mineralization, and the geodynamic setting of the Iranian Pb–Zn deposits, especially those with host rocks of Paleozoic age, that have to be unraveled.

The Ozbak-Kuh Mountains, located 150 km north of Tabas city in East Central Iran, contains eight Pb–Zn deposits/prospects: Bidu, Ghalleh, Ozbak-Kuh, Gushkamar, Ghouchkuhi, Sibzar, Nignan, and Gerehu, all of which are currently abandoned. The biggest deposit was Ozbak-Kuh. Since the Ozbak-Kuh deposit has been closed in 1968, no

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accurate data are available regarding its grade and tonnage. It has been reported that the ore produced in 1957 and a few ongoing years from the depth of 250 m had a grade of 1–5 mass% Pb, whereas the ore produced in 1965 from deeper levels contained 12 mass% Pb and 2 mass% Zn. The ore concentrate produced from the Ozbak-Kuh deposit during the period of 1954–1968 amounts to 72,395 t. Since a zinc concentrate was also produced during the last 3 years of mining, the aforementioned production includes both lead and zinc concentrates. The ore production was 50 t per day, and it increased to 150 t per day after construction of the flotation plant. During the last years of the mining activity, the ore production decreased to 100 t a day (Haditsch 1982).

The first geological studies in the Ozbak-Kuh area were performed in 1956 by O. M. Friedrich (unpublished data). Three years later, a 1:50000 geological map was prepared by A. Ruttner and F. Misaghi, and this covered the entire Ozbak-Kuh Mountains with 75 km from north to south. This map was later completed by the geologists of the Geological Survey of Iran (GSI; Ruttner et al. *undated*). The geology and mineralogy of the Ozbak-Kuh deposit were studied by GSI (1964) and Haditsch (1982). Although the deposit is now abandoned, the lack of any modern data regarding the mineralization at Ozbak-Kuh encouraged the author to perform this study. The current study presents the geological setting, mineralogical findings, and isotopic (C, O, S, Pb) geochemistry of the Ozbak-Kuh deposit. This database is used to understand the origin(s) of the ore-forming materials and the possible genesis of the ore. The Pb-isotope data are also used to clarify the geodynamic setting of the deposit.

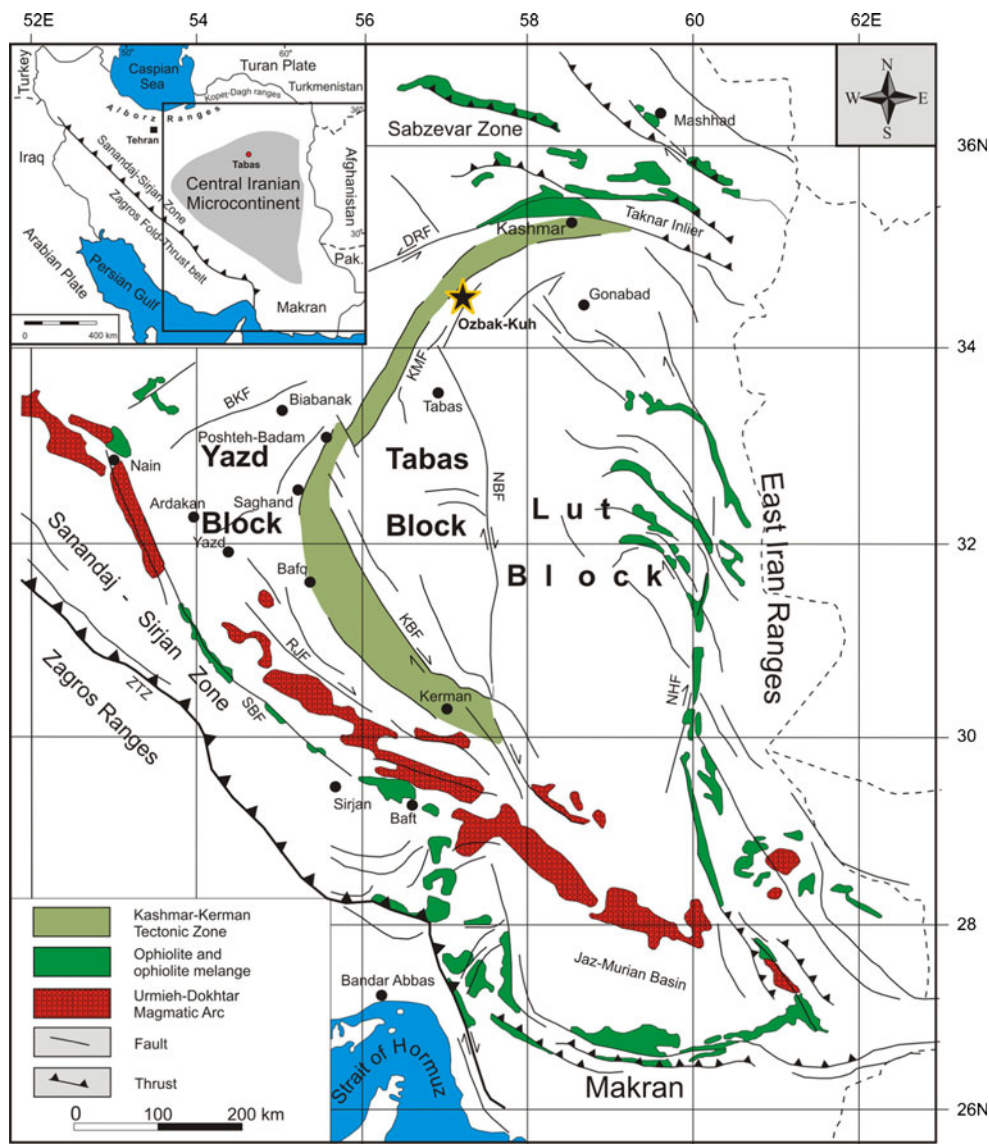
Regional geological setting

The Iranian terrain is located in the middle part of the Alpine-Himalayan Orogen, which extends from western Europe, through Turkey, Iran, and Afghanistan, and continues into Tibet and probably Burma and Indonesia (Aghanabati 2004). This orogen is located at the boundary between Eurasia in the north and Gondwana in the south. The geology and especially the tectonic evolution of Iran are deeply influenced by the development and evolution of the Tethyan region. The geotectonic events that affected the Iranian plate were caused by the opening and closing of the Paleo- and Neo-Tethys oceans (Stöcklin 1977; Berberian and King 1981). The first phase of the Paleo-Tethys rifting in the Late Ordovician–Early Silurian, recorded in northern Central Iran and Alborz, led to the break-up of the Gondwana margin and development of the Paleo-Tethys Ocean in Devonian time (Stampfli 2000; Natal'in and Şengör 2005). So, Iran has been located along the southern

passive continental margin of the Paleo-Tethys Ocean since the Devonian (Bagheri and Stampfli 2008). Convergence at the northern margin of Paleo-Tethys and subduction of its oceanic crust beneath Turan plate commenced from Middle-Late Devonian and was followed by extension and rifting of the northeastern margin of Gondwana in the Lower Permian. This rifting led to the separation of the Iranian Cimmerian Terrains (including Sanandaj-Sirjan and Alborz zones and blocks of the Central Iranian microcontinent) from Gondwana and the spreading of the Neo-Tethys Ocean between them in the Lower Triassic (Stampfli and Borel 2002). Convergence and subduction at the northern margin of the Paleo-Tethys continued until Late Triassic and caused the collision of Iranian Cimmerian Terrains with Turan plate and the beginning of the subduction of Neo-Tethys crust beneath the southern margin of the Iranian Cimmerian Terrains (Stampfli and Borel 2002). From the Early Jurassic to Eocene, the evolution of the present Central Iran was directed by a sequence of back-arc extensional and compressional cycles that were controlled by the north-dipping subduction zone of the Neo-Tethys (Bagheri and Stampfli 2008). The Central Iranian ophiolitic mélanges of Upper Cretaceous age indicate the closure of Central-East Iranian microcontinent ocean during the Late Paleocene–Eocene. From that time on, the Central Iranian microcontinent was under the influence of forces produced by the collision of the Indian and Arabian plates with Eurasia, and was fragmented into the Lut, Tabas, and Yazd blocks. Today, the block is surrounded by ophiolitic mélanges (Fig. 1) and fixed to the Eurasian plate (Bagheri and Stampfli 2008). The Ozbak-Kuh Pb–Zn deposit is located at the northern margin of the Tabas block, close to the Kashmar–Kerman Tectonic Zone (Fig. 1).

Based on the geology, radiometric dating, and geochemical data from magmatic, metamorphic and siliciclastic rocks of the Kashmar–Kerman Tectonic Zone in the Saghand region, Ramezani and Tucker (2003) recognized three main episodes of orogenic activity in Central Iran; i.e. in Late Neoproterozoic–Early Cambrian, Late Triassic, and Eocene times. The Neoproterozoic–Early Cambrian orogeny, which occurred in an active continental margin, was related to a broad-scale magmatic arc that developed along the Proto-Tethyan margin of the supercontinent Gondwana (Ramezani and Tucker 2003). The Late Triassic intrusive bodies of the Saghand region are indicative of a tectonomagmatic period of probably collisional nature, which is consistent with the previously recognized early Kimmerian event in the area. The widespread Eocene metamorphic and magmatic activities coincide with the Early Alpine orogeny, which was caused by the convergence of the Arabian and Eurasian Plates and the Cenozoic closure of the Tethyan oceanic tract by subduction (Ramezani and Tucker 2003).

Fig. 1 Position of the Central Iran Zone relative to the main tectono-stratigraphic units of Iran (after Ramezani and Tucker 2003). The location of the Ozbak-Kuh Pb-Zn deposit at the northern end of the Tabas Block is also shown



Local geology

Various rock units with ages ranging from Precambrian to Recent crop out in the Ozbak-Kuh area (Fig. 2). The oldest rock units are metamorphic rocks composed of mica schist, marble, and amphibolite, as well as shale and slate (Kahar Formation) of Precambrian age. The main part of the rock units in the Ozbak-Kuh area consists of a nearly complete sequence of Paleozoic sedimentary rocks. The overall thickness of the Paleozoic sequence at the Ozbak-Kuh Mountains amounts to 6,000 m (Fig. 3). This sequence begins with Early Cambrian red arkosic sandstones. The propagation of seawater in the Middle Cambrian and its persistence until Late Cambrian led to prevailed deposition of carbonate rocks (dolostones and limestones) during these times. Deposition of siltstone, silty shale and sandstones in the Early to Middle Ordovician reflects the regression of seawater

during this period. The next propagation of seawater during Middle and the Late Silurian resulted in the deposition of coral-bearing limestone and shale. The regression of seawater in the Lower Devonian is indicated by the precipitation of sandstone, dolostone, and gypsum within the sedimentary basin. This seawater regression was the result of the Caledonian tectonic movements during Late Silurian to Lower Devonian. However, the deposition of dolostones and limestones of the Middle and Upper Devonian ages is indicative of seawater propagation during these times.

The Pb–Zn mineralization at Ozbak-Kuh occurs within the dolostones of the Middle Devonian Sibzar Formation. From latest Upper Devonian to Lower Permian, seawater regression resulted in sedimentation of shale and sandstone with limestone intercalations. This seawater regression reflects the Hercynian epeirogenic movements. The propagation of seawater from the Lower Permian to Triassic led to the deposition

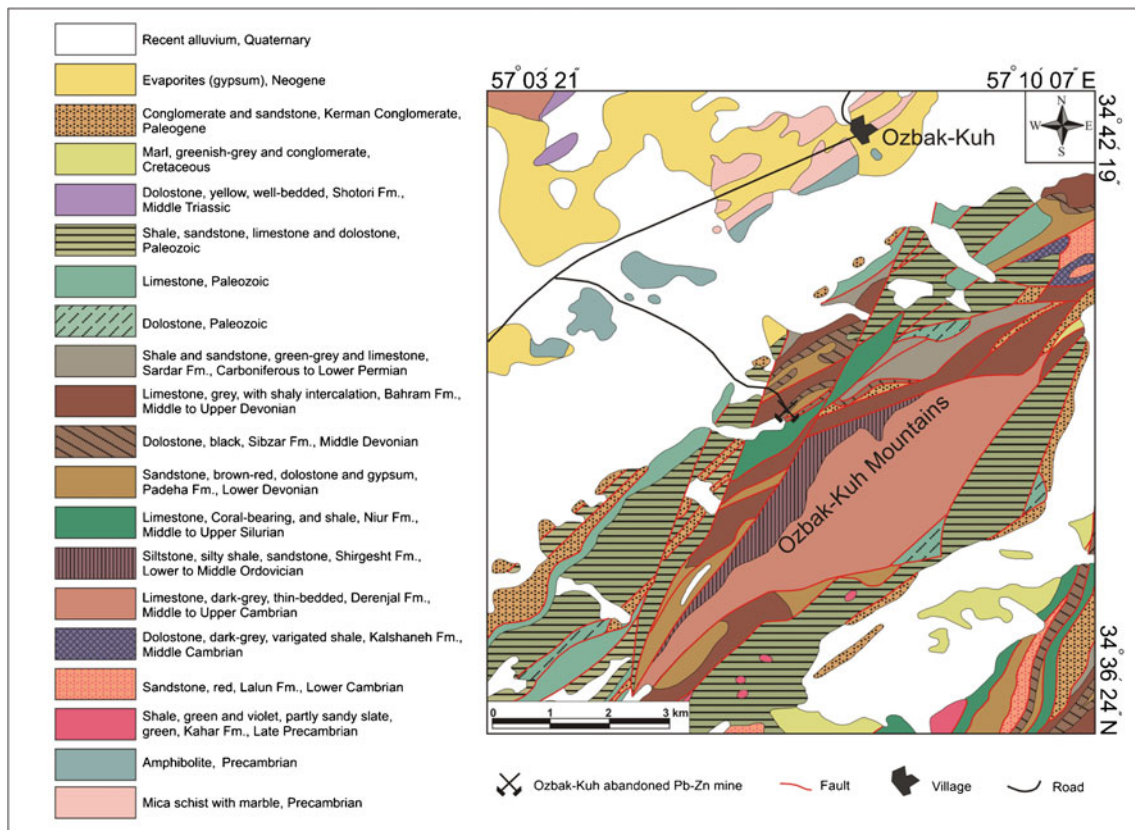


Fig. 2 Simplified geological map of the Ozbak-Kuh area (after Ruttner et al. undated)

of limestones (Fig. 3). The Paleozoic sedimentary rocks in the Ozbak-Kuh area are not limited to the formations mentioned above. Besides those formations, rock units composed of dolostone, limestone, as well as shale and sandstone with limestone and dolostone intercalations are exposed in the study area (Fig. 2). The precise ages of these units are not known, but they are attributed to the Paleozoic based on their geologic and stratigraphic positions (Ruttner et al. undated). Dolostones of Middle Triassic age, as well as marl and conglomerate of Cretaceous age compose the Mesozoic sedimentary units in the Ozbak-Kuh area. Tertiary deposits include Paleogene conglomerate and sandstone and Neogene evaporites. The youngest sedimentary deposits in the study area are recent alluviums (Fig. 2).

The Ozbak-Kuh mountain ranges are located in a zone of extremely intense folding and faulting. This is due partly to a change in the trend of the structures that turn about 90° from the north-northwest direction dominating in the Kuh-e-Shotori Mountains east of Tabas to east-northeast in the mountain ranges southeast of Doroneh (GSI 1964). In the region peripheral to the Ozbak-Kuh deposit (Fig. 2), the general trend of the structures is southwest-northeast. As seen in Fig. 2, lens-shaped rock bodies consisting of various Paleozoic formations are combined into a tectonic mixture by numerous faults. The faults bordering these rock bodies

are either vertical or steeply inclined toward northwest and southeast (GSI 1964). The Ozbak-Kuh deposit lies between two big NNE-SSW-trending faults (Fig. 2). The deformation of the rocks in the Ozbak-Kuh ranges is certainly younger than Lower Cretaceous (Aptian-Albian), because ammonite-bearing marls of that age and conglomerates associated with these marls are also affected by those deformations. The orogenic phase is most probably Upper Cretaceous or Lower Tertiary in age (GSI 1964).

The host rocks of the Ozbak-Kuh deposit are black and light-gray dolostones of the Sibzar Formation. The bedding planes of the dolostones are either vertical or steeply inclined towards northwest. Parallel to the bedding planes of the Sibzar dolostone, a crushed and brecciated zone is cemented by galena, some sphalerite, and calcite; so, the deposit is concordant and stratabound. As to be seen on Fig. 4, the brecciated zone is related to a reverse fault system at the base of the Sibzar Formation that thrust it over the younger Bahram Formation, indicating that it is a tectonic breccia. Hence, the planar structure that controls the stratabound ore deposit is considered a tectonic shear zone. This mineralized breccia is associated with an ore vein that is 0.5 to 3.0 m thick (Fig. 4). The vein was mined over a length of 250 m and down to a depth of 280 m. The Sibzar dolostone is cut off in depth by the thrust fault that separates

	Formation	Age	Lithology	Description	Thickness (m)
Tabas Group	Sorkh Shale Fm.	Lower Triassic		Shale	122
	Jamal Fm.	Permian		Limestone and dolostone	473
Ozbak-Kuh Group	Sardar Fm.	Carboniferous to Lower Permian		Shale, sandstone and limestone.	582
	Shishtu Fm.	Upper Devonian to Lower Carboniferous		Shale and alternating limestone	543
	Bahram Fm.	Middle to Upper Devonian		Limestone with shale intercalation	300
	Sibzar Fm.	Middle Devonian		Dolostone	100
	Padeha Fm.	Lower Devonian		Sandstone, dolostone and gypsum	492
Gushkamar Group	Niur Fm.	Middle to Upper Silurian		Limestone and shale	446
	Shirgesht Fm.	Lower to Middle Ordovician		Siltstone, silty shale, sandstone	1236
Mila Group	Derenjal Fm.	Middle to Upper Cambrian		Limestone	823
	Kalshaneh Fm.	Middle Cambrian		Dolostone, variegated shale	1000
	Lalun Fm.	Lower Cambrian		Sandstone	600
	Kahar Fm.	Late Precambrian		Shale, partly sandy slate	1600

Fig. 3 The stratigraphic column of the Paleozoic sediments in the Ozbak-Kuh area (data from Aghanabati 2004; Ruttner et al. undated)

the Ozbak-Kuh and Mila Groups at the surface, southeast of the Ozbak-Kuh deposit (GSI 1964). Indications of Pb-Zn mineralization in the Sibzar dolostone have been found elsewhere around the Ozbak-Kuh deposit (e. g. Gushkamar, Ghouchkuhi, Sibzar and Ghalleh prospects), but none of these orebodies is comparable with that of Ozbak-Kuh from

regarding its size. Similar to Ozbak-Kuh, these orebodies occur in or close to fractured zones within the Sibzar dolostone. At Gushkamar, for example, the brecciated zone follows a trend more or less parallel to the bedding planes. However, joints which are oblique or perpendicular to the bedding have also been found to be mineralized (GSI 1964). Thus, all mineralizations are structurally controlled and situated within, or close to shear zones and subvertical faults on the western side of the Ozbak-Kuh ranges.

In the Ozbak-Kuh ranges, the vertical faults and thrust zones are sometimes associated with volcanic rocks. These volcanics occur as small lens-shaped bodies and form only occasionally bigger masses. The common occurrence of the volcanic rocks is in the form of impregnations in tectonically crushed rocks. The impregnated rocks are mostly affected by contact metamorphism. A third type of volcanic rocks are sills which are planar to the bedding planes of non-crushed rocks. Such sills of andesite and trachyte can be observed especially at the base and within the Sibzar dolostones (Fig. 4) (GSI 1964). According to Bagheri and Stampfli (2008), this volcanic activity, as well as the deposition of dolostones, evaporites, and terrigenous rocks of the Padeha and Sibzar Formations are related to the opening of the Paleo-Tethys Ocean at the north of Tabas, Yazd, and Alborz blocks.

Samples and methods

In the current study, sixty-one mineral and rock samples were collected from old tunnels and small remaining mine dumps. Since most parts of the tunnels are now unsafe, the samples were collected from those parts that are accessible without the use of heavier mining equipment. Care was taken to select representative ore samples. Routine mineral-optical examinations were conducted on polished sections from twenty ore samples using a polarizing microscope.

Ten samples of hydrothermal calcite were analyzed for carbon ($\delta^{13}\text{C}$) and oxygen ($\delta^{18}\text{O}$) isotopes. The samples were chosen from ore samples in which textural relationships indicate that calcite deposited contemporaneously with sphalerite and galena (see next). The pure calcite samples were prepared by hand picking from crushed samples under a binocular microscope, or by using a dental microdrill. Carbon and oxygen isotope composition of the samples was determined at the Environmental Isotope Laboratory (EIL), University of Waterloo (Ontario, Canada), using a GVI IsoPrime Continuous Flow Isotope Ratio Mass Spectrometer (CF-IRMS). The apparatus was calibrated based on the international IAEA-CO-1 ($\delta^{13}\text{C}=2.49$ and $\delta^{18}\text{O}=-2.40$), IAEA-CO-8 ($\delta^{13}\text{C}=-5.76$ and $\delta^{18}\text{O}=-22.70$), and in-house EIL-21 ($\delta^{13}\text{C}=-0.19$ and $\delta^{18}\text{O}=-15.68$) standards. All carbon and oxygen isotope data are expressed in the δ notation in per mil (‰) relative to V-PDB (Vienna Pee Dee Belemnite). The

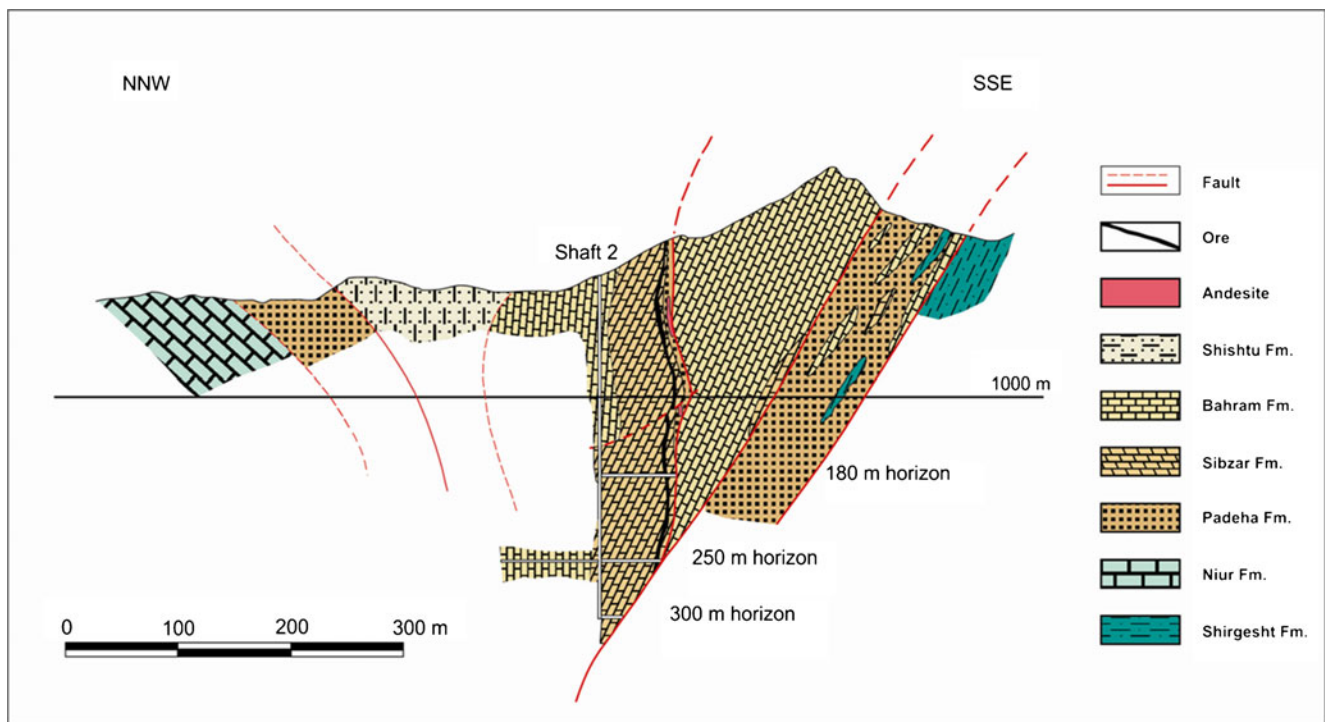


Fig. 4 A vertical section displaying the shape and position of the Pb-Zn ore body relative to rock formations in the Ozbak-Kuh area (after GSI 1964)

measurements were carried out in duplicate. The uncertainties associated with these analyses were $\pm 0.2\%$ for carbon and $\pm 0.4\%$ for oxygen isotopes.

Twenty monomineralic sulfide samples of sphalerite and galena were analyzed for sulfur isotopes. These samples include ten coexisting sphalerite and galena pairs. The sulfidic pairs were selected from those samples in which textural evidences imply the contemporaneous precipitation of sphalerite and galena. In order to prepare monomineralic samples, the ore samples were first crushed, and clean sphalerite and galena pieces were then picked up under a binocular microscope. The sulfur isotope analyses were performed using an Isochrom Continuous Flow Stable Isotope Ratio Mass Spectrometer (GVInstruments/Micromass-UK), coupled to a Carlo Erba Elemental Analyzer (CHNS-O EA1108-Italy) by the EIL. The results are presented in the δ notation as per mil (‰) that is relative to the Vienna Canyon Diablo Troilite standard ($\delta^{34}\text{S}_{\text{V-CDT}}$). Precision and reproducibility was typically better than $\pm 0.3\%$.

Lead isotope compositions of eleven carefully selected galena samples from the ore body were determined. Clean galenas were picked up from crushed samples under a binocular microscope. The isotopic analyses were performed at Actlabs (Activation Laboratories Ltd., Canada), using a high-resolution ICP-MS (Element2, Thermo Finnigan, Bremen, Germany) instrument. The NBS SRM-981 common-Pb standard was used for the mass-discrimination correction. The U.S. Geological Survey's BCR-2 standard was used to test the accuracy and external reproducibility of Pb-isotope ratios

during the analyses. The external reproducibility of the Pb-isotope ratios are $^{206}\text{Pb}/^{204}\text{Pb}=0.3\%$, $^{207}\text{Pb}/^{204}\text{Pb}=0.2\%$, and $^{208}\text{Pb}/^{204}\text{Pb}=0.5\%$ at the 2 sigma level.

Results

Ore mineralogy and wall rock alteration

The Pb-Zn mineralization at the Ozbak-Kuh deposit occurs within dolostones of the Sibzar Formation. The simplified paragenetic sequence of the host rock, ore, and gangue minerals is shown in Fig. 5. At the abandoned mine site, thin intercalations of shale with high fissility are also found within the Sibzar Formation. The color of these rocks is commonly black, due to the abundance of organic matter (bitumen). The abundance of the bituminous materials is sometimes so high (up to 50 %) that

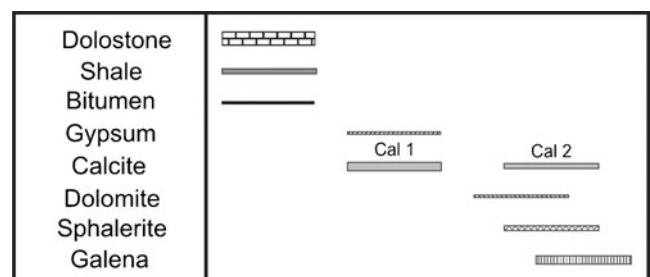


Fig. 5 Simplified paragenetic sequence of the host rock, ore, and gangue minerals in the Ozbak-Kuh deposit

it blackens the hand. The presence of frequent white calcite veins gives a zebra structure to the host rocks. These veins form as stylolites within the dolostones and are oriented parallel as well as perpendicular and oblique to the bedding planes. This calcite is considered to be the first-generation calcite (Cal 1). The host rocks are sometimes crushed and brecciated due to faulting. The host rock fractures are rarely filled with gypsum.

The mineralogy of the ore is very simple. The ore minerals are galena and sphalerite. Calcite is the main gangue mineral. Mineralogically and texturally, the ore is clearly heterogeneous. Galena is much more frequent than sphalerite, and commonly is the only ore mineral present. Galena is usually found within the host rock as patches (0.5–3 cm in diameter) composed of crystals with perfect cubic cleavage. Moreover, galena is present in veins and veinlets within the rocks. Sphalerite, where present, is found as sugar-grained aggregates, ranging in diameter from 1 to 3 cm. Sphalerite in the Ozbak-Kuh deposit is commonly yellowish brown and lacks zoning and colloform features. Galena and sphalerite are sometimes enclosed within calcite, indicating that they are coeval. This second-generation calcite (Cal 2) (Fig. 5) is present as patches (1–2 cm in diameter) and veins, having perfect rhombic cleavage. Since sphalerite is not massive and calcite patches are not large enough, suitable samples for fluid inclusion studies were not found. Bitumen is rarely found in the ore.

The examination of polished sections from the ore under a polarizing microscope also suggests that the ore is mineralogically and texturally very simple. Anhedronal and coarse-grained (up to 5 mm) galena is the most frequent sulfide mineral that is sometimes found along with sphalerite. Galena is also found as dispersed fine grains (up to 50 μm) and small veinlets within the host rock. Recrystallization of dolomite crystals resulted in the formation of relatively coarse idiomorphic crystals (up to 2 mm). These dolomite crystals are sometimes replaced by galena and sphalerite (Figs. 6a, b). Sphalerite is found as anhedronal grains (0.5–2 mm) within the host rock; it contains abundant host rock relicts (Fig. 6c), indicating that it replaced the host rock and that the ore is epigenetic. The galena patches enclose rounded sphalerite islands, revealing that at least some galena is paragenetically younger than sphalerite (Fig. 6d). In addition to the minerals mentioned earlier, pyrite, marcasite, and quartz were reported in small amounts by Haditsch (1982).

Wall rock alteration at the Ozbak-Kuh deposit is represented by recrystallization of carbonates and dolomitization; it is limited to the immediate contact of the ore body with host rocks. Wall rock alteration only extends several centimeters into the host rock is rare and, if present, is usually associated with disseminated galena and sphalerite. Wall rock recrystallization resulted in the coarsening of the host rock minerals, especially dolomite.

Carbon and oxygen isotopes

The $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of ten calcite samples associated with sulfide minerals are listed in Table 1 and presented in Fig. 7. The $\delta^{13}\text{C}$ values fall in the narrow range between -0.3‰ and 0.8‰ , fairly close to 0‰ . The $\delta^{18}\text{O}$ values show a wider range than $\delta^{13}\text{C}$; they are between -14.5‰ and -11.9‰ .

Sulfur isotopes

The $\delta^{34}\text{S}$ values of ten galena samples from the main ore body at Ozbak-Kuh occupy a narrow range between 12.2‰ and 16.0‰ with an average of 13.8‰ (Table 2). The $\delta^{34}\text{S}$ values for ten sphalerite samples show a narrow range of 12.1‰ – 16.8‰ with an average of 14.0‰ (Table 2). Hence, the sulfur isotopic composition of galena and sphalerite is almost identical.

Lead isotopes

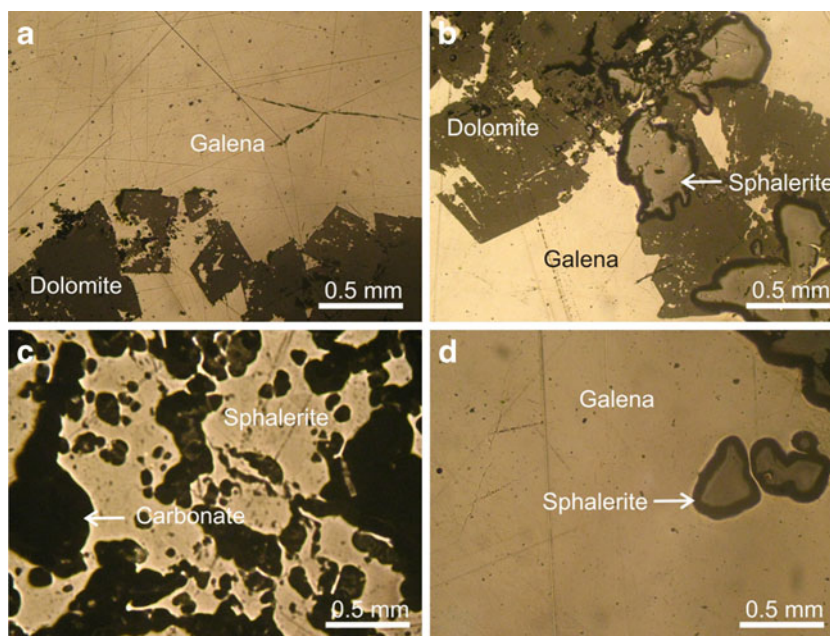
The lead isotope composition of galena samples from the Ozbak-Kuh deposit is presented in Table 3 and shown in Fig. 8. The $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios of the analyzed samples display the ranges of 17.97–18.25, 15.49–15.90, and 38.00–38.82, respectively. Lead isotope data from the Ozbak-Kuh deposit are distributed along steep northeast-southwest linear arrays with a slope of ~ 1.5 , as depicted in Fig. 8. Leach et al. (2005) commented that such arrays are analytical artefacts and are caused by mass discrimination errors due to slight variations in filament temperatures and sample loads; therefore, according to these authors these arrays are geologically meaningless. Thus, the Ozbak-Kuh lead is isotopically much more homogeneous than it appears to be from the spread of values shown in Fig. 8. The average Pb-isotope composition ($^{206}\text{Pb}/^{204}\text{Pb}=18.08$, $^{207}\text{Pb}/^{204}\text{Pb}=15.66$, and $^{208}\text{Pb}/^{204}\text{Pb}=38.50$) of the Ozbak-Kuh galenas is also plotted in Fig. 8 as red squares.

Discussion

Conditions and mechanisms of Pb–Zn sulfide deposition

The sulfur isotope signature of sulfide and sulfate minerals that precipitated contemporaneously within ore deposits can yield important information regarding the involved sulfur species, as well as the rate and mechanism of sulfide–sulfate deposition, regardless of the ultimate sulfur origin (Ohmoto and Goldhaber 1997). Since sulfate minerals are not present in the Ozbak-Kuh deposit, the equilibrium–disequilibrium constraints between sulfide pairs such as sphalerite–galena that deposited contemporaneously have the most significance. The

Fig. 6 Photomicrographs of ore samples. **a** Replacement of idiomorphic dolomite crystals by galena; **b** replacement of idiomorphic dolomite crystals by galena and sphalerite; **c** carbonate relicts in sphalerite indicating replacement of the host rock by sphalerite; and **d** sphalerite inclusions within galena. All photomicrographs were taken in reflected light under plane polarized light



studies of equilibrium–disequilibrium constraints between coprecipitated sphalerite and galena can provide important data about the S concentration in ore-forming fluid, as well as the rate and mechanism of sulfide deposition (Ohmoto and Goldhaber 1997). The $\delta^{34}\text{S}$ difference of seven sphalerite–galena pairs ranges from -1.2‰ to -0.1‰ (Table 2). For these sulfide pairs, the relation $\delta^{34}\text{S}_{\text{galena}} > \delta^{34}\text{S}_{\text{sphalerite}}$ indicates the possible deposition of sulfides under disequilibrium conditions (Ohmoto 1986). The $\delta^{34}\text{S}$ difference between three sulfide pairs is in the range 1.0–4.6‰. The relation $\delta^{34}\text{S}_{\text{sphalerite}} > \delta^{34}\text{S}_{\text{galena}}$ for these pairs suggests that at least these three mineral pairs could reflect chemical equilibrium conditions (Ohmoto 1986).

The isotopic fractionation between H_2S in a hydrothermal fluid and a sulfide mineral is strongly related to temperature, and it decreases rapidly with increasing temperature; the effect

of pressure is negligible at pressures below 10 kbar (Ohmoto and Goldhaber 1997). Assuming sulfide deposition under chemical equilibrium conditions, the observed fractionation for three sphalerite–galena pairs in the Ozbak-Kuh deposit corresponds to mineral formation temperatures of 127 °C, 465 °C, and 557 °C (Table 2). The fact that the Ozbak-Kuh deposit occurs in a sedimentary setting and that no high-temperature alteration is developed at the contact of the ores to the carbonate host rocks render the high temperatures of 465 °C and 557 °C for two sulfide pairs unrealistic. So, these fractionations were probably caused by deposition under incomplete chemical equilibrium conditions. Only the temperature of 127 °C for one sulfide pair would be geologically reasonable; only this pair could have been deposited under conditions near complete chemical equilibrium. In summary, the $\Delta\delta^{34}\text{S}$ values between sphalerite and galena in the Ozbak-Kuh deposit reveal that the deposition of sulfides mostly occurred under chemical disequilibrium conditions.

In order to obtain an equilibrium sulfur isotope fractionation in a hydrothermal fluid, the formation temperatures have to exceed 120 °C, and the total concentration of H_2S should be much higher than the total concentration of metals (Ohmoto 1986). In addition, the equilibrium fractionation is related to the rate and persistence of mineral deposition (Ohmoto and Goldhaber 1997). If metals and sulfur are allowed to coexist, namely the residence time of two components in the system increases, it is more likely that they achieve temperature-related equilibrium fractionation. If these three requirements are not or only partly achieved, the fractionation between H_2S and sulfide precipitates is considerably smaller than that under equilibrium conditions (Ohmoto and Goldhaber 1997).

Table 1 Analytical results of C and O isotopes in calcite samples from the Ozbak-Kuh deposit

Sample No.	$\delta^{13}\text{C}_{\text{V-PDB}}$ (‰)	$\delta^{18}\text{O}_{\text{V-PDB}}$ (‰)
OZ-CO-01	0.6	-12.8
OZ-CO-02	-0.2	-14.3
OZ-CO-03	0.8	-13.8
OZ-CO-04	0.6	-13.0
OZ-CO-05	-0.2	-12.4
OZ-CO-06	0.8	-12.9
OZ-CO-07	-0.3	-11.9
OZ-CO-08	0.7	-12.1
OZ-CO-09	-0.1	-13.8
OZ-CO-10	-0.1	-14.5

Fig. 7 Carbon and oxygen isotope data from the Ozbak-Kuh deposit (solid circles) compared with the isotopic composition of the Phanerozoic seawater (colored boxes; Veizer et al. 1999)

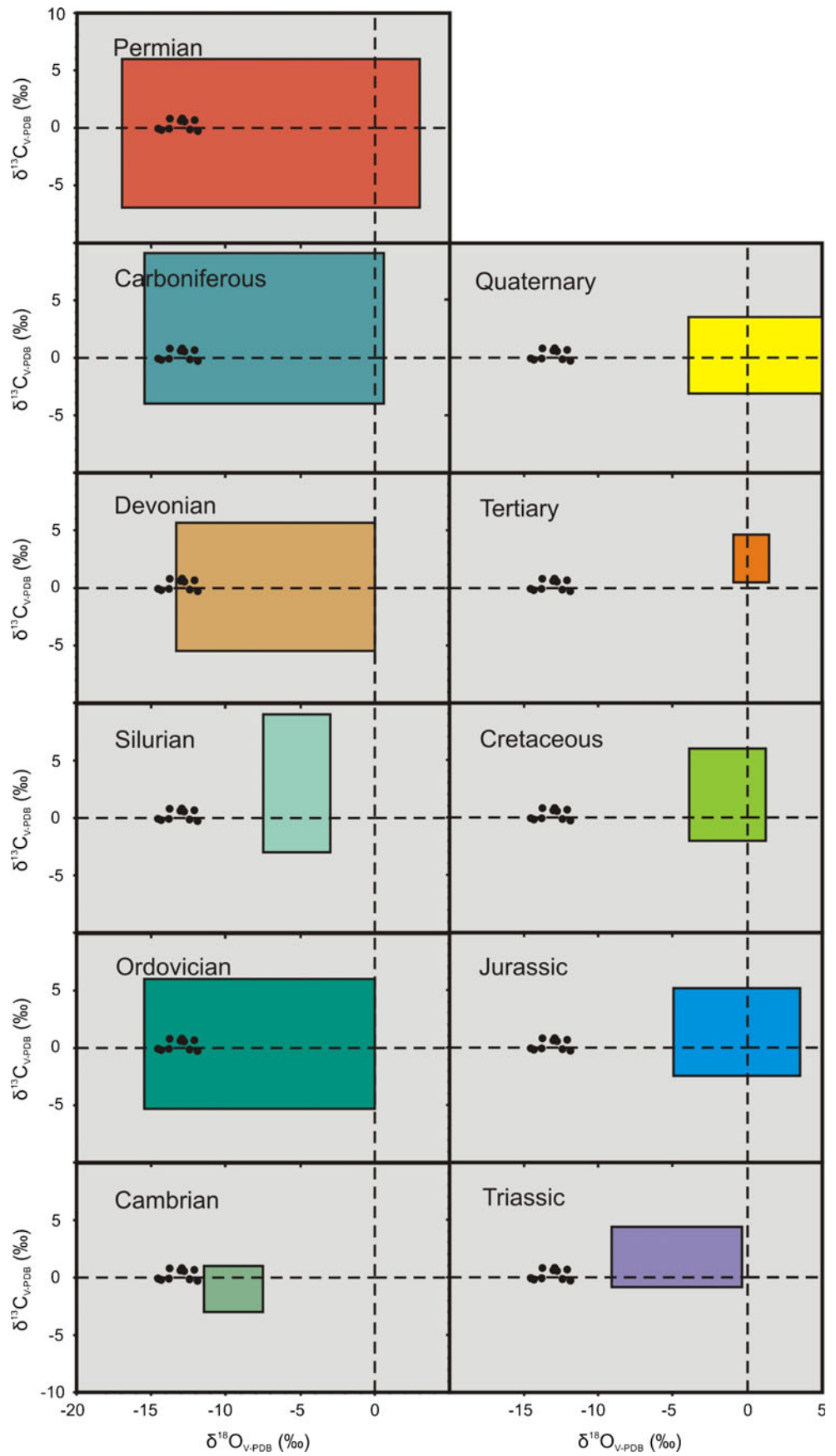


Table 2 Sulfur isotope data from sulfide minerals of the Ozbak-Kuh deposit

Sample No.	Mineral	$\delta^{34}\text{S}_{\text{V-CDT}}$	$\Delta\delta^{34}\text{S}$	Temperature ($^{\circ}\text{C}$)
OZ-SPS-GAS-01	Sphalerite	12.8	-1.2	Disequilibrium
	Galena	14.0		
OZ-SPS-GAS-02	Sphalerite	13.3	-1.1	Disequilibrium
	Galena	14.4		
OZ-SPS-GAS-03	Sphalerite	14.3	1.0	557
	Galena	13.3		
OZ-SPS-GAS-04	Sphalerite	12.1	-0.7	Disequilibrium
	Galena	12.8		
OZ-SPS-GAS-05	Sphalerite	12.7	-0.2	Disequilibrium
	Galena	12.9		
OZ-SPS-GAS-06	Sphalerite	15.0	-1.0	Disequilibrium
	Galena	16.0		
OZ-SPS-GAS-07	Sphalerite	14.4	-0.1	Disequilibrium
	Galena	14.5		
OZ-SPS-GAS-08	Sphalerite	14.1	-0.6	Disequilibrium
	Galena	14.7		
OZ-SPS-GAS-09	Sphalerite	14.8	1.4	465
	Galena	13.4		
OZ-SPS-GAS-10	Sphalerite	16.8	4.6	127
	Galena	12.2		

The precipitation of sulfide minerals in the Ozbak-Kuh deposit under disequilibrium conditions means that the requirements mentioned earlier have not been achieved. This could indicate that the concentration of H_2S in ore-forming fluid was equal or considerably lower than that of metals, and/or that the precipitation rate of sulfide minerals was preferentially fast (Ohmoto and Goldhaber 1997). The different recorded fractionations for sulfide pairs in the Ozbak-Kuh deposit could also be caused partly by temperature variation in the hydrothermal fluid (e.g. Schaefer 2002).

The observed isotopic disequilibria also argue against fast sulfide-producing mechanisms and high H_2S concentrations in the ore-forming fluid. For instance, transport of reduced sulfur along with metals in a hydrothermal fluid to

Table 3 Lead isotope data of the analyzed galena samples from the Ozbak-Kuh deposit

Sample No.	$^{208}\text{Pb}/^{204}\text{Pb}$	$^{207}\text{Pb}/^{204}\text{Pb}$	$^{206}\text{Pb}/^{204}\text{Pb}$
OZ-GAPB-01	38.48	15.63	17.97
OZ-GAPB-02	38.29	15.75	18.17
OZ-GAPB-03	38.57	15.67	18.10
OZ-GAPB-04	38.62	15.57	18.18
OZ-GAPB-05	38.82	15.69	18.17
OZ-GAPB-06	38.73	15.90	18.25
OZ-GAPB-07	38.52	15.66	17.99
OZ-GAPB-08	38.60	15.49	18.02
OZ-GAPB-09	38.80	15.63	18.08
OZ-GAPB-10	38.16	15.66	18.00
OZ-GAPB-11	38.00	15.61	17.97

the site of deposition, or gaining a large amount of reduced sulfur at the site of ore deposition (e. g. mixing of the metal-bearing fluid with a reduced sulfur-carrying solution), leads to fast supply of required H_2S for the formation of sulfide minerals and, therefore, their precipitation under equilibrium conditions. In contrast, slow sulfide generation by hydrothermal fluid in the host rock (via pyrite decomposition or mobilization of organically bound sulfur) is probably too slow to generate the sufficient H_2S fast enough in order to approach the equilibrium conditions. As a result, the concentration of H_2S in such a system is low and at any given time, only one sulfide mineral precipitates, which will result in the formation of rather monomineralic ores in which the $\delta^{34}\text{S}$ of minerals is nearly equal to that of H_2S (Ohmoto and Goldhaber 1997). The fact that galena is significantly more frequent than sphalerite, and that other sulfide minerals are absent in the Ozbak-Kuh deposit, are in accordance with this conclusion. Supply of sulfur via decomposition of host rock pyrite is unlikely because of the very low pyrite content of the host rock. Another possibility is the acquisition of H_2S by gradual sulfate reduction at the site of ore deposition.

Sulfur and metal sources

Sulfur within natural environments originates ultimately from either igneous or seawater sources (Ohmoto and Rye 1979). Since the $\delta^{34}\text{S}$ values of sulfides in magmatic hydrothermal deposits fall between -3 and $+1\%$ (Hoefs 2009), the strongly positive average $\delta^{34}\text{S}$ values of galena (13.8%) and sphalerite (14.0%) from the Ozbak-Kuh deposit do not confirm the derivation of sulfur from a magmatic source. The alternative

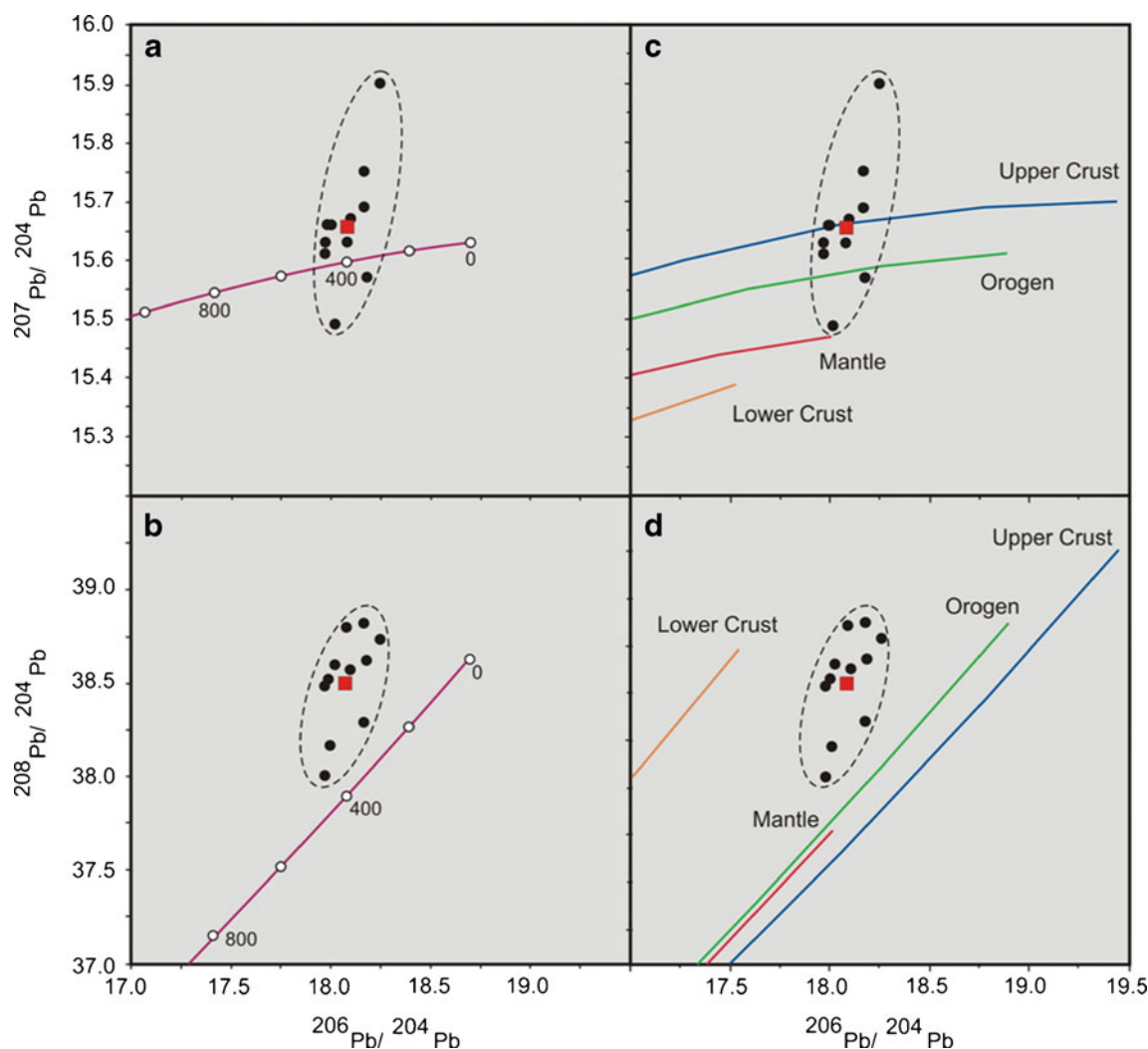


Fig. 8 Pb-isotopic ratios of galenas from the Ozbak-Kuh deposit plotted in diagrams showing the model curves for the Pb isotope evolution of the average crust (**a** and **b**) (Stacey and Kramers 1975),

and in the plumbotectonic diagrams (**c** and **d**) (Zartman and Doe 1981). The red squares correspond to the average Pb-isotope composition of the analyzed samples

sulfur source is, thus, seawater sulfate. The gypsum beds contained in nearby Lower Devonian Padeha Formation would appear to be an easily accessible source of marine sulfate for mineralization at Ozbak-Kuh (Figs. 2 and 3). However, any other sulfate-bearing strata, or even sulfate-carrying connate waters entrapped within the rock units of various ages in the region, could have provided the required sulfate. Since no method is known to decide on the actual sulfate sources (Bouabdellah et al. 2012), all should be considered potential sources.

The reduction of sulfate to sulfide could be either caused by bacterial sulfate reduction or nonbacterial sulfate reduction through a reaction with organic materials (thermochemical sulfate reduction). The narrow ranges of $\delta^{34}\text{S}$ in the sulfides and the strongly positive values indicate that they have not been produced by bacterial sulfate reduction. Bacteriogenic sulfides are commonly depleted in ^{34}S

relative to the source and display a wide range of $\delta^{34}\text{S}$ values (Seal 2006). On the other hand, the temperature of 127 °C calculated for one coexisting sphalerite–galena pair renders bacterial activity also unlikely. Therefore, it seems that thermochemical sulfate reduction is the most probable mechanism of sulfate reduction at the Ozbak-Kuh deposit. The occurrence of Pb-Zn mineralization in those parts of the Sibzar Formation that contain abundant organic material confirms this view. It is, thus, concluded that the sulfate, transported most likely in the ore-forming fluid, reacted with organic matter present in the carbonate host rocks at temperatures >120 °C and it was converted into H_2S . Reaction of the H_2S with metal complexes then resulted in the precipitation of metal sulfides.

The average Pb isotopic composition of Ozbak-Kuh galenas plots above the Stacey and Kramers (1975) model curves for the Pb isotope evolution of the average crust

(Figs. 8a, b). If the $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios are considered source-indicative parameters, the fact that Pb isotope data are located above the Stacey and Kramers (1975) evolution curves clearly suggests a crustal source for Pb. Moreover, the probable source(s) of Pb was investigated using the plumbotectonic curves of Zartman and Doe (1981) (Figs. 8c, d). As illustrated on Fig. 8c, the mean $^{206}\text{Pb}/^{204}\text{Pb}$ - $^{207}\text{Pb}/^{204}\text{Pb}$ value plots on the upper crust curve. On Fig. 8d, the data plot between the reference curves of lower crust and orogenic lead, but closer to the orogen lead curve.

The calculated average values of μ ($^{238}\text{U}/^{204}\text{Pb}$), ω ($^{232}\text{Th}/^{204}\text{Pb}$), and κ ($^{232}\text{Th}/^{238}\text{U}$) based on the Stacey and Kramers (1975) model are 10.00, 41.50, and 4.14, respectively. These values indicate that Pb was dominantly derived from rocks with high U/Pb and Th/Pb ratios, which are characteristic of the upper crust (Zartman and Doe 1981). Therefore, the Pb isotope data indicate an orogenic lead reservoir with a significant contribution of supracrustal rocks for galena Pb at the Ozbak-Kuh deposit. The homogeneity of the lead isotopes together with their upper crustal signature suggest persistent circulation of ore-forming fluids within a source reservoir dominated by supracrustal rocks.

The Pb isotope model age calculated based on the Stacey and Kramers (1975) model yields an average age of 502 Ma, indicating a Cambrian age. However, this model age is older than the host rocks, which are of Middle Devonian age. Because the Pb isotopic composition of probable source rocks in the Ozbak-Kuh area is not known, the ultimate source of Pb cannot be determined. However, the pre-Middle Devonian model age reveals that galena mineralization at Ozbak-Kuh occurred due to remobilization of Pb from an older source possibly of Cambrian age. These could either have been Cambrian host rocks or older ore deposits previously formed within these units. The conclusions that galena Pb at Ozbak-Kuh derived from an orogenic source with high affinity to crustal rocks, and that the model age portrays a Cambrian age, are in accordance with Ramezani and Tucker (2003), who found a major period of orogenic activity in an active continental margin setting during Late Neoproterozoic to Early Cambrian in Central Iran.

Source of ore-forming fluid

The $\delta^{18}\text{O}$ values plotted against $\delta^{13}\text{C}$ for hydrothermal calcite samples are shown in Fig. 7. The oxygen isotopic fractionation between a given mineral and fluid from which it precipitates is dependent on several factors, including temperature and composition (salinity) of the fluid, as well as the water/rock ratio (Taylor 1997). Unfortunately, the lack of a realistic estimation of the temperature(s) of ore formation in the Ozbak-Kuh deposit does not allow calculation of the $\delta^{18}\text{O}$ values of the hydrothermal fluid.

However, since the Ozbak-Kuh deposit is situated in a sedimentary setting, the oxygen and carbon isotopic composition of the calcites can be compared with that of Phanerozoic seawater (Veizer et al. 1999; Fig. 7). The isotopic composition of the Ozbak-Kuh hydrothermal calcites overlaps either completely or partly with those of seawater of Ordovician, Devonian, Carboniferous, or Permian ages. Similar to sulfur isotope composition, the available data do not permit an unequivocal identification of the ultimate source of the mineralizing fluid. Paleozoic seawater entrapped within the rock units as basinal brines would be a strong candidate that could serve as the major source of the hydrothermal fluid which caused mineralization at the Ozbak-Kuh deposit.

The calcite from the Ozbak-Kuh deposit exhibits very uniform $\delta^{13}\text{C}$ values, but slightly more variable $\delta^{18}\text{O}$ values (Table 1 and Fig. 7). The $\delta^{13}\text{C}$ values close to 0‰ indicate that the organic material within the host rocks did not involve in the hydrothermal fluid. The $\delta^{18}\text{O}$ variation suggests that the temperature and possibly the isotopic composition of the fluid did not remain constant, in both space and time (Golyshev et al. 1981). The observed oxygen isotopic composition would correspond to a spread in temperature of about 70 °C, assuming precipitation from a single fluid. The data further indicate that the fluid was not in thermal equilibrium with the host rock. This could indicate high fluid flow rates and high proportions of hydrothermal fluid.

Ore genesis

It has been proposed that the Ozbak-Kuh ore body is a result of hydrothermal-metasomatic activity, because of the presence of andesitic and trachytic volcanic rocks in the Sibzar Formation (GSI 1964; Haditsch 1982). However, a direct spatial relationship between igneous rocks and mineralization is lacking, and a link with magmatic processes is also not supported by the isotopic evidence provided in this paper.

Lead isotope data are indicative of formation of the Ozbak-Kuh deposit in an orogenic setting. They indicate a rather radiogenic lead reservoir such as supracrustal rocks. Oxygen and carbon isotopic data of carbonates indicate that basinal brines originated from Paleozoic seawater are the most probable source of the ore-forming fluids. The sulfur isotopic data indicate that the source of sulfur likely was seawater sulfate and that higher temperature thermal sulfate reduction was the dominant process providing reduced sulfur. It appears that homogenization of lead and sulfur isotopes was achieved by circulation of large fluid volumes along structural pathways (see below). The prolonged circulation of fluids could be due to high heat flow in the basin. Presence of minor extrusive rocks in the stratigraphic sequence (e. g. within the Sibzar Formation) may also be an expression of this. The hydrothermal leaching

of metals from wall rocks could have taken place effectively during this long-lasting fluid percolation, resulting in the production of metal-rich connate fluids.

Taking into account the above findings, the Ozbak-Kuh deposit is comparable to Mississippi Valley-Type (MVT) Pb-Zn deposits (Sangster 1990; Leach et al. 2005) in terms of tectonic setting, type of host rock, wall rock alteration and sources of ore-forming fluids and materials. Nevertheless, it displays a set of characteristics that contrast with those of typical MVT deposits. These include the distinct ore-controlling tectonic structure, the concordant nature of the ore, the dominance of Pb relative to Zn, and the lack of sparry dolomite and collapse breccia.

An alternative model is that accepted for carbonate-hosted Pb-Zn deposits that occur along faults and tectonic shear zones (e. g. Han et al. 2007; Kamona and Friedrich 2007). As previously discussed, tectonic deformation of the rocks in the Ozbak-Kuh Mountains is post-Early Cretaceous. Because the ores are not affected by deformation, it is concluded that ore formation is post-kinematic. It is probable that post-Lower Cretaceous deformation of the sediments through intense folding and faulting resulted in dewatering of the basin. The discharged metal-rich connate waters, driven by pressure gradients, then moved into the compressional shear zones, which represent the ore-hosting structures within the Sibzar dolostone, while they continuously leached the ore-forming materials along their channel ways. Changes in physico-chemical conditions resulted in precipitation of the ore minerals and formation of the Pb-Zn deposits at Ozbak-Kuh. The most suitable shear zones for precipitating ore minerals were apparently those places where carbonate host rocks are present that contain a lot of organic materials required for sulfate reduction. The mineralization occurred as an epigenetic process through cementing the breccia fragments and replacing the dolostone itself. However, the exact age of mineralization remains unclear.

Conclusions

Lead and zinc mineralization in the Ozbak-Kuh deposit is hosted by dolostones of the Middle Devonian Sibzar Formation. The ore is structurally controlled by a steep tectonic zone, in which fault-associated breccia fragments were cemented by galena, sphalerite, and calcite. The $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of the hydrothermal sulfide-bearing calcites indicate that Paleozoic seawater possibly was an important component of the ore-forming fluid. The $\delta^{34}\text{S}$ value of sulfides in the Ozbak-Kuh deposit indicates a marine source of sulfate, including evaporite-bearing strata and/or sulfate-bearing connate waters. Thermochemical sulfate reduction is the most likely process of supplying reduced sulfur for sulfide deposition at Ozbak-Kuh. Lead isotope studies indicate that galena

Pb in the Ozbak-Kuh deposit originated from an orogenic source, which was dominated by upper crustal rocks with high $^{238}\text{U}/^{204}\text{Pb}$ and $^{232}\text{Th}/^{204}\text{Pb}$ ratios. The Ozbak-Kuh deposit was probably formed along a tectonic shear zone due to expulsion of metal-rich connate waters from Paleozoic strata during a post-Early Cretaceous orogenic event.

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