

A FLUID INCLUSION STUDY OF A LARGE MVT BARITE-FLUORITE DEPOSIT: KOMSHECHEH, CENTRAL IRAN*

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Abstract – The Komshech eh barite-fluorite deposit is the product of epigenetic hydrothermal mineralization in dolomitized limestone of Middle Triassic age. The deposit is structurally and lithologically controlled and occurs predominantly as bedded stratabound replacement sheets, although the veins and solution-collapse breccias constitute important modes of occurrence. Brecciation, dolomitization, silicification and mineralization are interrelated. Post-Eocene intrusions and NW-SE and NE-SW trending faults are important ore controls. The ore mineralogy is simple and consists of barite and fluorite with very minor galena, pyrite, chalcopyrite, malachite and azurite. Sulfides are extremely rare in the deposit. At least two episodes of deposition have been identified: an early stage of fluorite precipitation and a later barite-fluorite mineralization event with spatial and temporal variations in salinity and temperature. Thermometric investigations indicate that homogenization temperatures (T_H) for primary and pseudosecondary fluid inclusions in the fluorite range from 89 to 244°C with a mode at 150°C, whereas those for primary fluid inclusions in barite range from 119 to 323°C with two modes at 150 and 250°C. Evidence for boiling is seen during barite deposition. The mean salinities measured are 12 and 10 equivalent weight percent NaCl for fluids in fluorite and barite, respectively. Hydrocarbons in the inclusions hosted by fluorite samples were also detected. Chemical analyses of fluids extracted from inclusions in fluorite and barite show compositions dominated by Na, Ca and Mg ionic species. Barite shows $\delta^{34}\text{S}$ values between 22.6 and 26.7 per mil. The comparatively narrow spread in $\delta^{34}\text{S}$ values suggests very uniform environmental conditions throughout the mineralization field. Consideration of these data in their geologic context favors a basinal source for the ore-forming fluids which have been significantly affected by heating during intrusive emplacement. The deposition of barite and fluorite resulted from physicochemical changes in Ba-F-rich hydrothermal brines during mixing with sulfate-rich formational water and wall rock interaction.

Keywords – Fluorite, barite, fluid inclusion, mineralization, Komshech eh, Iran

1. INTRODUCTION

The style of mineralization at Komshech eh shares many similarities with Mississippi Valley-Type (MVT) deposits. Whereas MVT deposits themselves vary considerably in their shape, size and mineralogy, most authors agree on the basic features of these deposits. They are epigenetic and occur in dolomite or dolomitized limestone sedimentary host rocks with a lack of nearby bodies of igneous rock. Other characteristics of the deposits are the simplicity and often the subtleness of wall-rock alteration effects. Silicification and dolomitization are the common types, but how much is ore-related alteration and how much is pre-ore, or even diagenetic, is unclear [1-4].

The Komshech eh barite-fluorite deposit is located approximately 120 km northeast of Esfahan city, in the Ardestan region of central Iran (Fig. 1). The deposit occupies an area of 400×800 meters and is the largest barite deposit in Iran with more than 1.6 million metric tons of ore at an average grade of 49% barite and 10% fluorite. It is currently mined by an open pit operation. Despite its economic importance,

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very little work has been done on the origin of the Komshecheh deposit, and the nature of mineralization has never been studied. In this paper, the first fluid inclusion and sulfur isotopic data are used in conjunction with field and microscopic observations to derive a genetic model for the mineralization at the Komshecheh deposit.

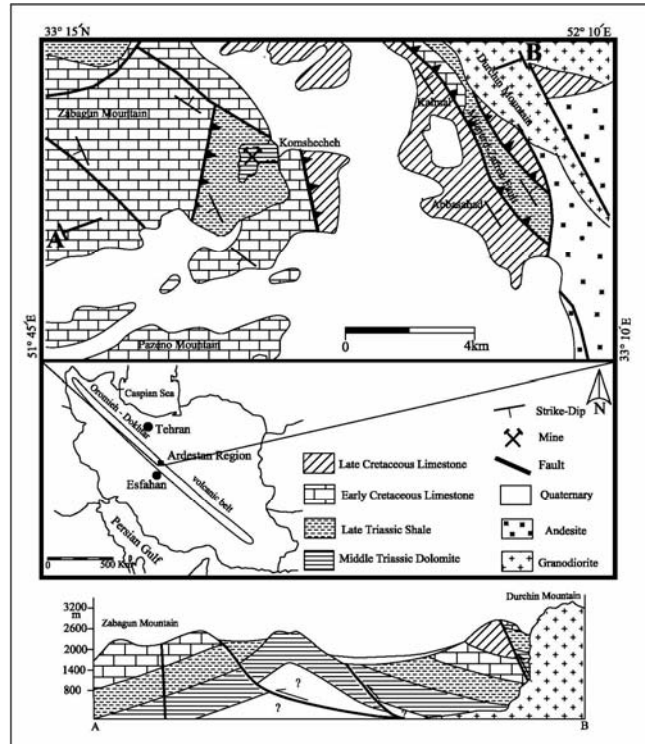


Fig. 1. Simplified geological map and location of the Komshecheh barite-fluorite deposit in Ardestan region, Iran

2. GEOLOGICAL SETTING

The Ardestan region is located in the Oromieh-Dokhtar volcanic belt at the western margin of the Iranian Central Zone (Geological quadrangle map of Kashan No. F7, 1:250000, Fig. 1). This Cenozoic volcanic belt extends for more than 2000 km from northwest to southeast Iran [5-9]. The stratigraphic sequence in the region is largely composed of Mesozoic sedimentary and Cenozoic volcanic rocks (Fig. 1). The order of rock units from youngest to oldest is as follows:

- Andesitic to ryodacitic lava and pyroclastics (Middle-Late Eocene).
- Coarse grained and sandy limestone (Early Cretaceous).
- Shale, marl with intercalations of Orbitolina limestone (Early Cretaceous).
- Shemshak Formation: conglomerate, marl and nummulitic limestone (Early Jurassic).
- Naiband Formation: argillaceous limestone interbedded with marl, coarse grained and sandy limestone (Late Triassic).
- Black shale with thin bands of sandstone and limestone (Late Triassic).
- Shotori Formation: yellow dolomite (Middle Triassic).

The sequence is intruded by numerous mafic to intermediate intrusions of post-Eocene age with the Durchin Mountain 10 km to the NE of the Komshecheh deposit representing the nearest exposed intrusion (granodiorite). Igneous activity during the Cenozoic time (which made the Oromieh-Dokhtar volcanic belt) is due to the still continuing convergence of Afro-Arabian and Iranian plates [7, 9]. Folds in the form

of several parallel anticlines and synclines are the dominant structural forms of the Ardestan region. They strike broadly NW-SE, parallel to the general regional trend of the Zagros belt. Most of the intrusions occur along the Milajer-Zafreh fault, the major NW-SE trending fault in the region. The Komshech deposit is surrounded by second-order related faults.

Mineralization at Komshech is hosted by Middle Triassic dolomitized limestone of the Shotori Formation. On a local scale, the deposit is located in the core of a large NW-SE trending regional anticline (Fig. 1). The dolomite is overlain by Late Triassic shale. Mineralization is epigenetic and lithologically and structurally controlled. Virtually no ore occurs in undolomitized limestone. Silicification generally follows dolomite which replaced original limestone. This phenomenon leads to ground preparation in the host rock for mineralization. The ores occur as bedded stratabound replacement sheets, veins and the solution-collapse breccias. Because of ore deposition by replacement as well as by open-space fillings, ore structures are variable and the minerals vary from fine to very coarse-grained. Evidence of solution activity is common, and it appears that replacement preceded open-space fillings. Open-space fillings occur as veins along faults and breccia cements or as solution cavity fillings (Fig. 2a-d). The maximum length and thickness of the veins reaches 6 m and 1 m, respectively. Dissolution cavities are filled with massive barite and fluorite. Stratabound-replacement mineralization occurs as massive or laminated ores parallel to host rock bedding (Fig. 2e, f). Ore layers are discontinuous, and their thickness is variable even at short distances. They are generally displaced by third order faults. Base metal sulfides are rare in the Komshech deposit. Galena, with very minor amounts of pyrite and chalcopyrite, are present. Post-ore weathering of primary sulfides produced malachite, azurite and very minor cerussite which appear as coatings on exposed barite and fluorite crystal surfaces.

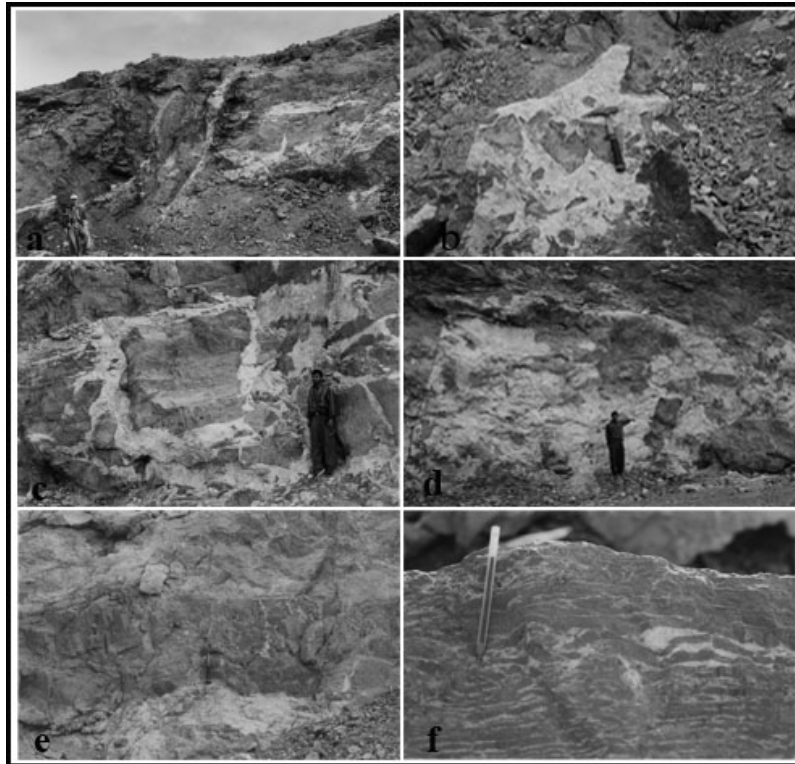


Fig. 2. Ore occurrences at the Komshech deposit: a) barite veins along third-order faults hosted by dolomitized limestone; b) collapse breccia with white barite, fluorite interstitial to brown dolomite; c, d) white and grey barite and fluorite occur as cavity fillings by selective dissolution of dolomite; e) bedded barite (white flecks) is parallel to the host rock bedding; f) laminated barite (white) with brown dolomite

3. PETROGRAPHIC STUDY

Dolomitization and silicification of the original host limestone are indicated by a crosscutting relationship of associated minerals in thin sections. Dolomite generally occurs as euhedral-subhedral grains measuring between 0.5 to 1 mm in diameter, though individual dolomite grains may be as large as 2.5 mm. Although widespread dolomitization of the limestones preceded the main phases of mineralization at Komshech, other less significant dolomitization took place contemporaneously with, or later than mineralization as indicated by grains with curvicular crystalline surfaces and sweeping extinction (Fig. 3a). Such zoned crystals are referred to as saddle dolomites [10]. The dolomite precipitated from hot hydrothermal solutions circulating in fissures and fractures [4], suggesting that the Ca^{+2} content of the fluids changed during crystal growth [11]. Silicification generally favors dolomite that has replaced original limestone. It occurs as veinlets and nodules of fine-grained quartz predating mineralization, and as disseminated coarse-grained euhedral quartz during mineralization. The euhedral zoned quartz replaces fluorite and crosscuts barite (Fig. 3b, c).

Petrographic studies suggest that fluorite was deposited in at least two stages. Fluorites from the first generation are clear or white and are replaced by barite. Those of the second generation are generally purple and occur as open-space fillings with barite. Field observation alone did not allow this distinction. Barite replaces saddle dolomite (Fig. 3d), and this phenomenon is completed by forming the pseudomorph barite. Barite appears in massive or laminated shapes with white, milky, yellowish, grayish and brownish colors. Stratabound massive white barite generally replaces white fluorite (Fig. 3e).

Sulfides clearly post-date the barite, and good evidence for the replacement of barite by galena and chalcopyrite is apparent. Islands of relict barite within the galena and cusped sulfide grain boundaries give the appearance that the sulfides are eating barite and fluorite (Fig. 3f). These relationships suggest that a period of initial galena deposition was followed by a period of chalcopyrite deposition. In the oxidation zone, malachite, azurite and cerussite are produced as weathering products of sulfides forming colloform bands. The paragenetic sequence of mineral assemblages is shown in Fig. 4.

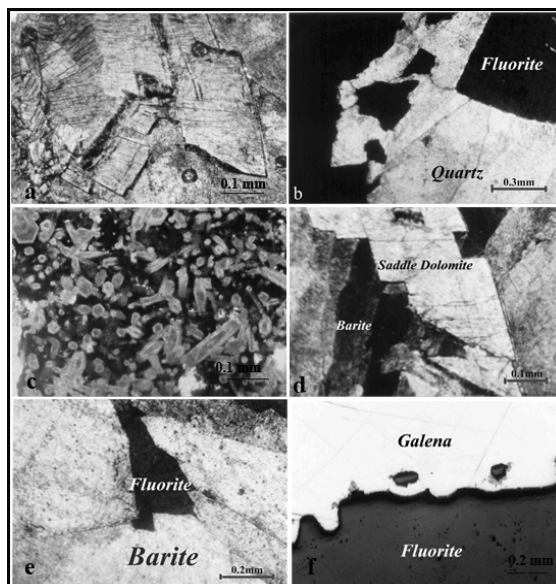


Fig. 3. Plane-polarized transmitted and reflected light photographs of typical textures from Komshech deposit: a) saddle dolomite with curvicular crystalline surfaces; b) fluorite replacement by coarse grained quartz with islands of fluorite in the quartz; c) euhedral zoned quartz (grayish white) replaced fluorite; d) barite replaced saddle dolomite; e) fluorite replacement by massive white barite; f) galena (white) replaced fluorite (dark)

Mineral	Post Ore Stage		Early Stage of Mineralization	Late Stage of Mineralization		Post Stage of Mineralization
Limestone	██████████					
Dolomite		██████████	██████████			
Quartz		██████████	██████████			
Fluorite			██████████			
Barite				██████████		
Galena				██████████	██████████	
Pyrite					██████████	
Chalcopyrite					██████████	
Malachite						██████████
Azurite						██████████
Cerussite						██████████

Fig. 4. Generalized paragenesis of mineral association in the Komshechek deposit

4. FLUID INCLUSION STUDY

Analytical technique

Following microscopic observations, 10 barites and 23 fluorites were selected from the major ore zones of the deposit and were prepared as doubly polished wafers using standard techniques. Microthermometric measurements were made using a Linkam TH-600 combined heating–freezing stage at the Shiraz University Department of Earth Sciences. This device allows the determination of temperatures within a range from -200°C to $+600^{\circ}\text{C}$. The stage was calibrated using K-nitrate, K-dichromate and Benzoic acid. The precision was $\pm 3^{\circ}\text{C}$.

5. DESCRIPTION OF FLUID INCLUSIONS

Fluid inclusions are generally abundant in fluorite but are scarce in barite. The inclusions in fluorite are primary, pseudosecondary or secondary in character and have varying shapes including rod, flat, lens, very irregular, perfect and defect negative (Fig. 5). Primary and pseudosecondary inclusions in fluorite are consistently simple two-phase liquid-vapor types with no daughter mineral or separated CO_2 phase at room temperature. The vapor makes up less than 15 Vol%. The inclusions vary from 5 to 400 microns in diameter, averaging 80 microns. Hydrocarbons are present in some of the inclusions as a brownish-yellow liquid or as a black solid (Fig. 6a, b). Secondary inclusions in fluorite show highly variable vapor/liquid ratios which indicate that the inclusions were affected by post ore events. They are two-phase liquid-rich, two-phase vapor-rich, two-phase bubble in bubble (CO_2) and monophasic (only vapor phase) types (Fig. 6c, d).

Some small primary and pseudosecondary fluid inclusions are found in barite. The inclusions are generally lensoid without daughter minerals and some appear along cleavage planes. The inclusions within barite can be divided into four groups: 1) two-phase liquid-rich; 2) two-phase vapor-rich; 3) monophasic (only liquid phase) and 4) monophasic (only vapor phase) (Fig. 7).

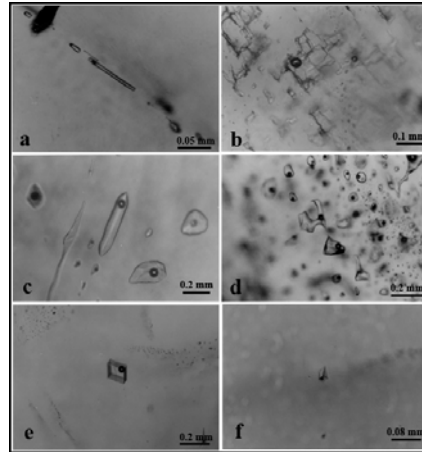


Fig. 5. Microphotographs of representative primary fluid inclusions in fluorite show different shapes and sizes: a) rod shape; b) ultra-flat shape; c) lens shape; d) irregular shape; e) perfect negative shape; f) defect negative shape

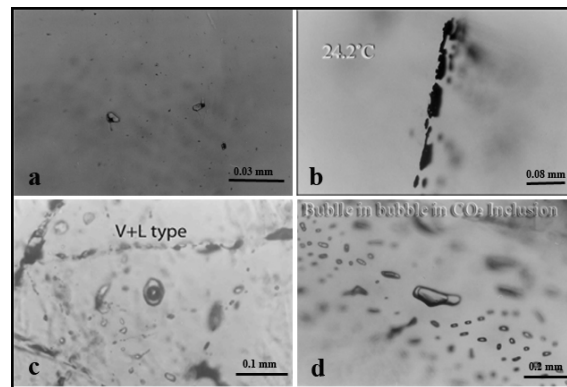


Fig. 6. Microphotographs of hydrocarbon inclusions and some secondary fluid inclusions in fluorite: a) two brownish-yellow hydrocarbon fluid inclusions; b) black solid inclusion at room temperature; c) two phase vapor-rich secondary fluid inclusions; d) two phases bubble in bubble fluid inclusion

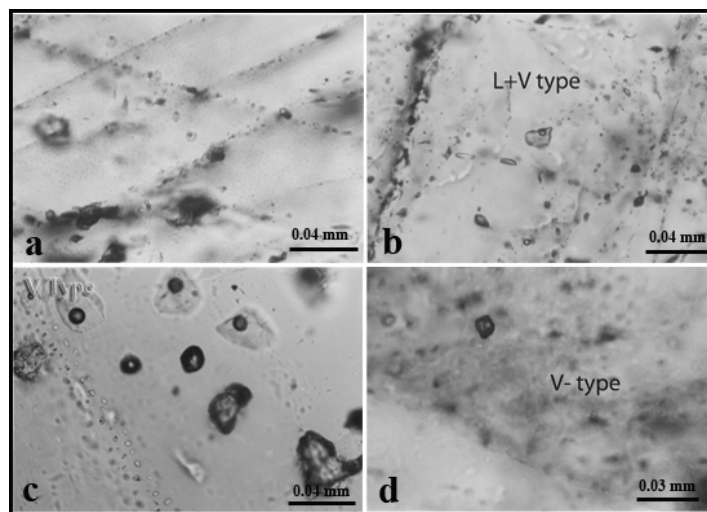


Fig. 7. Microphotographs of representative primary fluid inclusions within barite show different types: a) two phase liquid-vapor inclusions along the cleavage planes; b) two phase liquid-rich and some monophasic (liquid phase) primary fluid inclusions; c) two phase liquid-rich and some monophasic (vapor phase) primary fluid inclusions; d) monophasic (only vapor phase) fluid inclusion

5. FREEZING DATA

In freezing runs, three temperatures can be recorded: 1) the freezing temperature of inclusion (T_f); 2) the initial ice-melting temperature or eutectic temperature (T_{fm} or T_e), and 3) the last ice-melting temperature (T_m). In this study, freezing data were obtained with a 1°C/min cooling rate. Inclusions were initially frozen before subsequent warming to the first ice-melting temperature and then finally to the temperature at which the last ice crystal disappeared. Of the many hundreds of primary and pseudosecondary fluid inclusions in the fluorite samples, 250 were of sufficient size and were positioned so that within the sample they could be adequately observed. The measured temperatures vary from -100°C to -35°C, from -70°C to -20°C and from -22°C to 0°C, for T_f , T_{fm} and T_m , respectively (Fig. 8). The last ice-melting temperatures (T_m) indicate salinities of between 0 and 25.4 wt% NaCl equivalent (Fig. 9a) in terms of the system NaCl-H₂O [12]. The extremely low initial ice-melting temperatures are characteristics of all inclusions. As these values are clearly far below the eutectic temperature in the pure NaCl-H₂O system (-20.8°C), it is suggested that other ions (e.g. Ca²⁺ and Mg²⁺) are present in the fluids, and thus the ore solutions are likely in the H₂O-NaCl-CaCl₂ ± MgCl₂ system [13, 14]. Such a composition may be expected in view of the lithological context of the Komshechek deposit. The absence of daughter minerals at room temperature indicates that the magmatic waters can not be regarded as mineralizing fluids. In freezing runs the hydrocarbon-bearing primary fluid inclusions are not frozen, even below temperatures of -100°C. It is suggested that the black solid inclusions are waxes or bituminous materials [15]. However it would necessitate FT-IR microspectroscopy to obtain the exact composition of the hydrocarbons. The formation of clathrates during freezing runs in some secondary fluid inclusions in fluorite suggests that carbonic phases are present in the secondary fluids [16]. The inclusions are apparently two-phase liquid-rich, with T_m varying from -6°C to +13°C. Regarding the presence of the double-bubble inclusions, it is suggested that such inclusions can be put in the mixed NaCl-salt-CO₂ system [16].

The fluid inclusions in barite are scarce and appear in small sizes. Freezing temperatures indicate salinities around 0 to 20.6 equivalent weight percent NaCl (Fig. 9b). The data on fluid inclusions in barite show that the mineralizing fluids are also within the H₂O- NaCl-CaCl₂ ± MgCl₂ system. 15 measurements on the inclusions show temperatures from -90°C to -45°C, from -70°C to -27°C and from -24°C to 0°C, for T_f , T_{fm} and T_m , respectively (Fig. 10).

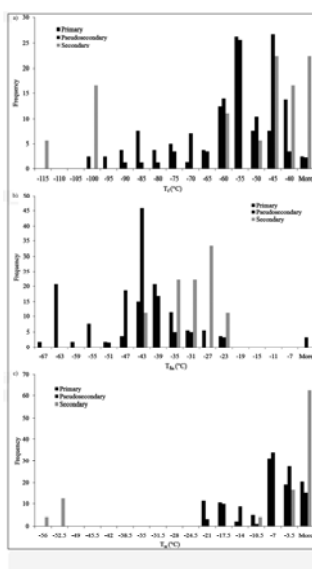


Fig. 8. Histograms of a) freezing temperature, b) initial ice melting temperature and c) last ice melting for fluid inclusions in fluorites of the Komshechek deposit

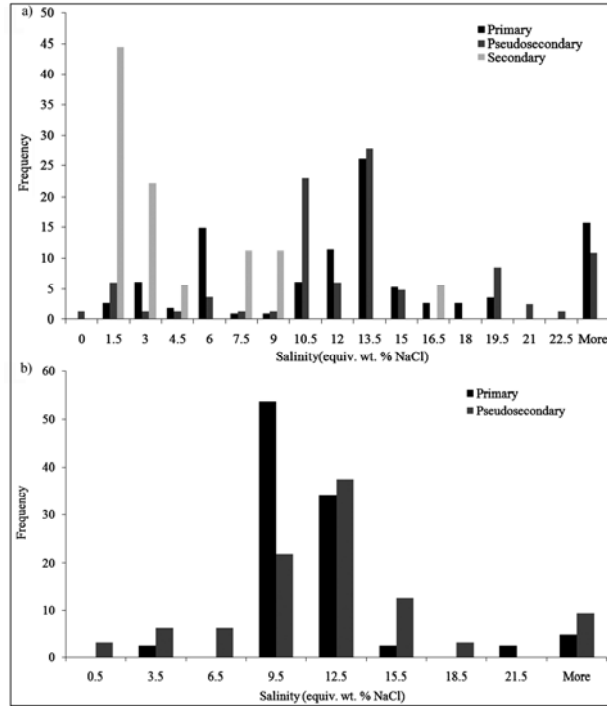


Fig. 9. Histograms of salinities within fluorite (a) and barite (b) fluid inclusions from Komshech deposit

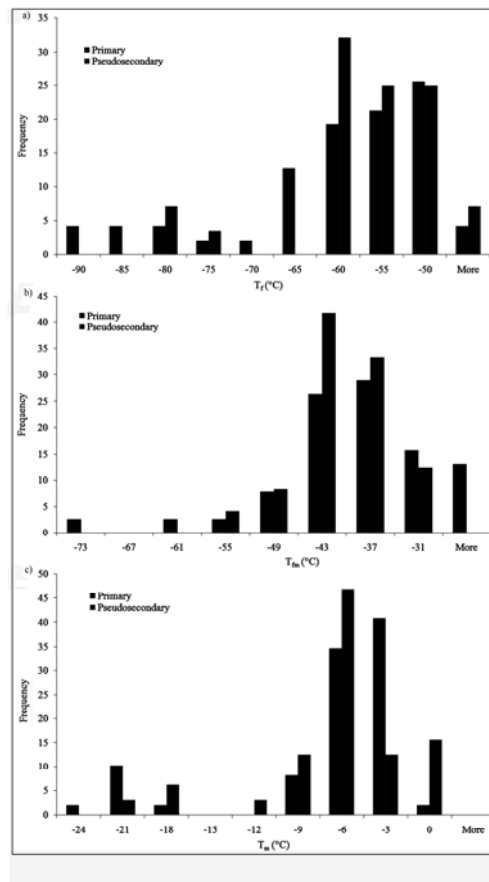


Fig. 10. Histograms of a) freezing temperature, b) initial ice melting temperature and c) last ice melting for fluid inclusions in barites of the Komshech deposit

6. HEATING DATA

The fluid inclusions in both fluorite and barite were examined for their homogenization temperatures (T_H) at heating rates of 5-9°C/min for fluorite and 1-3°C/min for barite samples. The presence of the monophasic inclusions (only vapor phase) and open-space fillings in the Komshecheh deposit suggest that the pressure corrections under these conditions would be very small and thus were not applied in this study. The T_H for 250 primary and pseudosecondary fluid inclusions within fluorites ranges from 89°C to 244°C with a mode at 150°C (Fig. 11a). The nearly uniform vapor/liquid ratios in primary fluid inclusions in fluorites show no evidence of the fluid boiling, and all the inclusions are found to homogenize into the liquid phase. More than 61 primary and pseudosecondary inclusions in barite were examined for their homogenization temperature. The T_H for the inclusions in barite ranges from 119°C to 323°C and displays two modes at 150°C and 250°C (Fig. 11b). The liquid-rich inclusions homogenize into the liquid phase while vapor-rich inclusions homogenize into the vapor phase. The existence of the two major fluid inclusions together in barite indicates fluid boiling. As there is no correlation between the fluid inclusion size and the homogenization temperature in the studied inclusions, it is suggested that the fluid inclusions are not stretched during over-heating and that the T_H values are a good approximation for the mineralization temperatures.

Twenty secondary fluid inclusions from the same fluorites give higher homogenization temperatures, generally above 170°C. The close agreement between homogenization temperatures of the secondary inclusions in fluorite and of the primary fluid inclusions in barites strongly suggests that secondary fluid inclusions in fluorite were affected by later fluids after deposition, and that barite precipitates after fluorite. This situation is compatible with the petrographic observations.

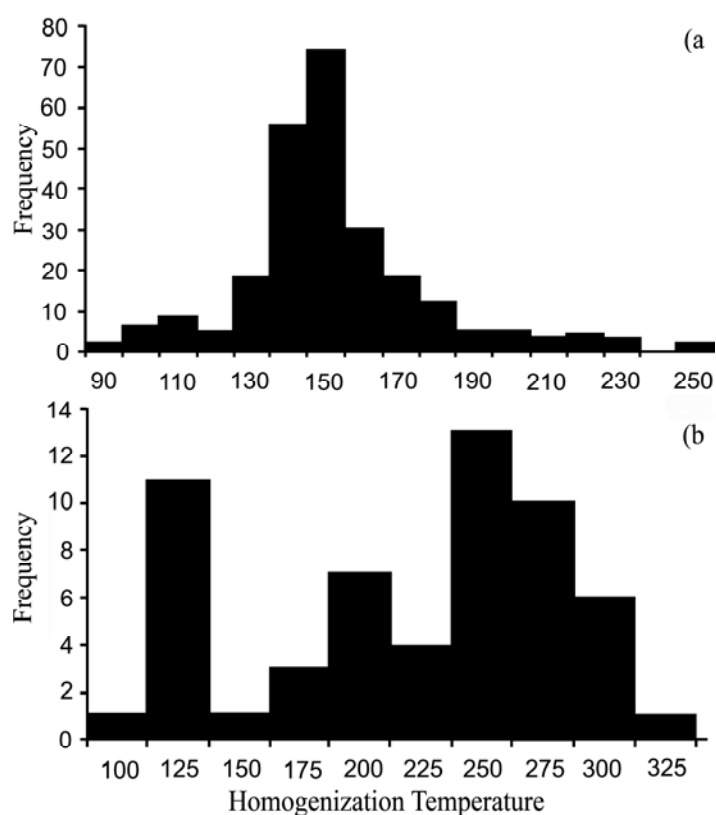


Fig. 11. Fluid inclusion microthermometric results versus frequency from the Komshecheh deposit: a) homogenization temperature histogram of aqueous liquid-vapor primary fluid inclusions in fluorite; b) homogenization temperature histogram of primary fluid inclusions hosted in barite

7. CRUSHING – LEACHING ANALYSIS

The crush-leach method [14] was used to collect the fluids contained in the inclusions. Twenty grams of each sample (5 fluorites and 2 barites) were washed using pure HCl to remove contaminations and then were crushed, screened and powdered. The powders were leached with 25 ml of distilled water. Atomic absorption spectroscopy and flame photometry techniques were used for the elemental analysis (Table 1). Because samples with different fluid inclusion densities were used in the leach experiments, no inferences can be made from the absolute abundances in Table 1. Furthermore, the calcium contents of the leach solutions, especially in the fluorite samples (No.1 to 5), were undoubtedly contaminated by the solution of fluorite, and possibly minor amounts of calcite in the crushed materials. However the results indicate that all leachates contain sodium, magnesium and large amounts of calcium, which is compatible with the dolomitic nature of the host rock at the Komshechek deposit. The low values of metals, especially for Cu along with low Na/K ratios in the solutions, suggest that the mineralizing fluids are characteristic of basinal waters [17].

Table 1. Chemical composition of fluid inclusion leachates in fluorite (No. 1-5) and barite (No. 6 and 7) from Komshechek deposit (in ppm)

	Ca ²⁺	Na ⁺	K ⁺	Li ⁺	Mn ²⁺	Mg ²⁺	Cu ²⁺	Fe ²⁺	Na ⁺ /K ⁺	Na ⁺ /Mg ²⁺
1	31.64	13.22	2.46	N.D.	0.29	16.4	0.04	0.18	5.37	0.8
2	59.52	16.45	2.52	N.D.	0.38	4.66	N.D.	0.002	6.52	3.53
3	44.18	19.73	1.97	N.D.	0.14	1.76	N.D.	0.98	10.1	11.2
4	22.47	4.65	1.07	N.D.	0.24	6	N.D.	0.19	4.34	0.77
5	10.1	17.28	1.28	N.D.	0.09	1.5	N.D.	0.051	13.5	11.52
6	47.3	22.31	1.95	N.D.	0.08	1.8	0.04	0.42	11.44	12.4
7	12.96	12.35	1.04	N.D.	0.08	2.7	0.02	0.15	11.87	4.6

8. STABLE SULFUR ISOTOPES

Three barites from the major ore zones were examined for sulfur isotopes. Approximately twenty grams of each sample were crushed and passed through 0.5 and 0.25 mm sieves. The remains on the 0.25 mm sieve were washed with pure HCl to remove impurities. The samples were analyzed by Therimon Quadropol Mass Spectrometry (THQ) in the geochemical research center of Gottingen University, Germany. The results are expressed as $\delta^{34}\text{S}$ values in parts per mil, where the standard is the troilite sulfur from the Canon Diablo meteorite [18]. The isotopic values from the Komshechek deposit plot in the sedimentary-evaporative environments. The $\delta^{34}\text{S}$ values are 22.6, 23.4 and 26.7 per mil. (Fig. 12). There is only a slight variation in the $\delta^{34}\text{S}$ values, reflecting almost identical genetic conditions.

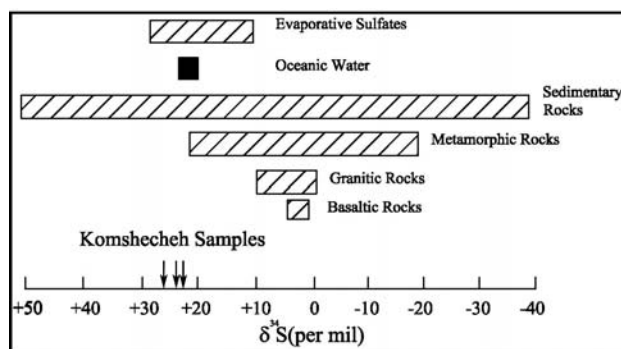


Fig. 12. Isotopic composition of barites from Komshechek deposit as compared with some geologically important materials (note text from Hoefs 1997)

9. DISCUSSION

The fluid inclusion study of Komshechek mineralization puts constraints on the origin and evolution of the ore-forming fluids. All primary and pseudosecondary fluid inclusions in fluorite homogenize to the liquid phase with the relatively constant filling degrees, indicating that the original fluid in the inclusions was an homogenous liquid [19, 20]. The broad range of homogenization temperatures shows that fluorite deposition took place continuously throughout this range and no evidence of boiling was observed. The measured densities for the fluids in fluorite vary from 1 to 1.1 gr/cm³, which show that the mineralizing fluids are basinal saline brines (Fig. 13). Some of the inclusions are hydrocarbon-bearing types. In contrast to fluorites, highly variable liquid-vapor ratios in primary fluid inclusions hosted by barite with two modes at 150°C and 250°C indicate that barite was deposited from the more heated fluids under boiling condition. Igneous heat sources in basement rocks may still prove integral to MVT formation. The similarities between the secondary fluid inclusions in fluorite and the primary fluid inclusions in barite suggest that the barite deposition occurred after fluorite precipitation, a conclusion that is confirmed by the field and petrographic observations. The compositions of the brines in the two minerals are similar, and both show a wide similarity to salinity. It seems likely that the ore solutions arrived in pulses and the episodic nature of the hydrothermal processes is supported by paragenetic evidence.

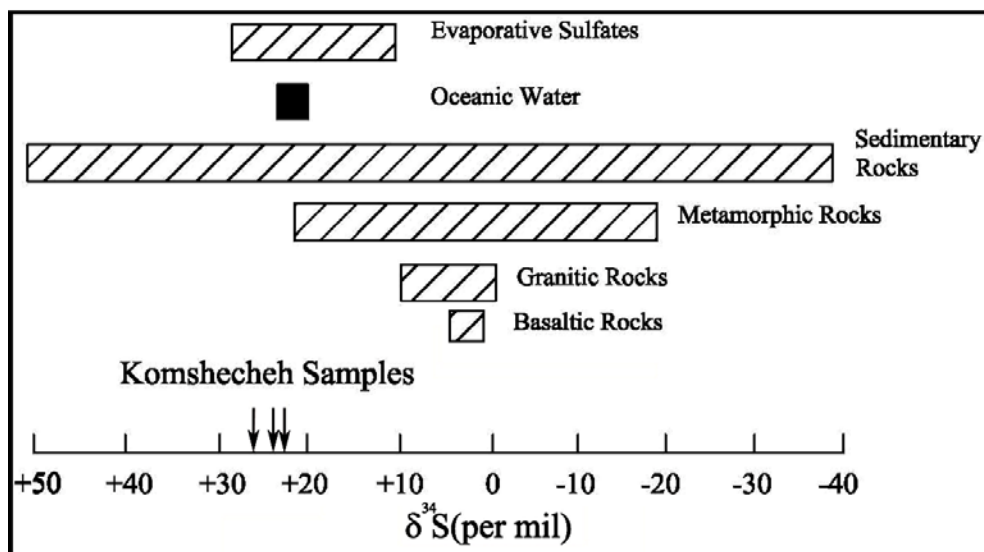


Fig. 13. Homogenization temperature versus salinity plot of fluid inclusions in fluorite from Komshechek deposit illustrate the range of fluid density

The source of barium and fluorine is important in developing a genetic model for the Komshechek deposit. It is proposed that the presence of 100-ppm Ba in the formational waters is enough for a large amount of barite deposition [21]. The albitization and diagenetic destruction of K-feldspar, mica and clay in the shale release sufficient amounts of Pb, Zn, F and Ba into the ore fluids of the MVT deposits [22]. Clay mineral maturation and dewatering of the shale also provide Mg for dolomitization [2, 10], and liberated Ca⁺² during dolomitization is consumed at fluorite formation. It should be noted that the basinal brines are not generally rich in fluorine, thus in most MVT deposits igneous activities can increase the fluorine concentration of basinal brines [23].

Based on the model presented here, a large-scale fluid flow through the sedimentary rocks occurred in the Komshechek area. Fluids migrating through deep portions of the sedimentary basin become heated and dissolve rock components and are then forced upward toward the basin margins [24]. At the deposit scale, mineralization tends to occur in breccias and solution-collapse features are formed during faulting.

The brecciation and faults permit the upward migration of the ore fluids. The ore solutions had a remarkable ability to dissolve carbonate rocks. In the study area, the NW-SE trending faults control the heat flux and act as channelways for hot fluids. Heat may have been locally generated from deep seated intrusions, forcing the overlying pore fluids to convect. The leaching of some elements from granodiorite by the alteration processes may increase the concentration of the elements in the ore fluids (Fig. 14). Granodiorite in the study area contains at least 500 ppm Ba [25]. It is very probable that some fluorine originated from the phlogopite and biotite in igneous rocks [26]. The ore fluids do not rule out the possibility of a small magmatic component, or a higher temperature exchange between ore fluids and igneous rocks, but if magmatic fluids were present, they were well mixed with the formational water before reaching the site of ore deposition. The wide range of salinity is explained by mixing with meteoric waters. The sulfur isotopic measurements on barite with high $\delta^{34}\text{S}$ values, along with fluid inclusion data, show that the fluids do not resemble magmatic fluids.

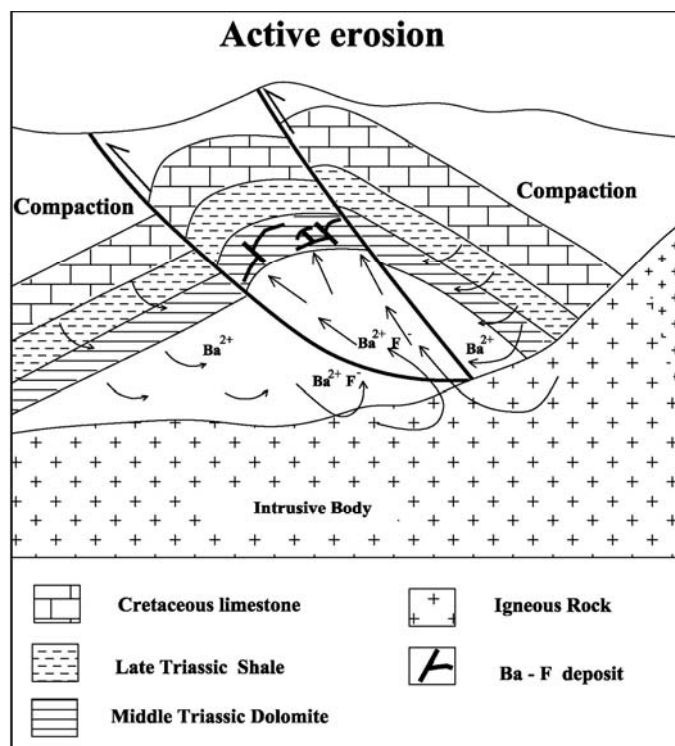
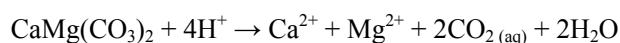


Fig. 14. Schematic representation of the Komshechek mineralization. The basinal brine expulsion model and the deposition of barite-fluorite ores along faulted and brecciated zones by hot mineralizing solutions

Two main mechanisms have been proposed for barite deposition in large quantities [3, 27, 28]. The first is by the oxidation of barium and the sulfur-rich fluid that was proposed for the Central Kentucky and Southeast Missouri barite district. The other model, explaining the deposition of a large amount of barite by mixing barium-rich brine with sulfate-bearing fluids, is proposed for the northern Pennine Orefield in England and the Kentucky-Illinois fluorite district. In the first model, barite should be enriched in ^{32}S [2], whereas $\delta^{34}\text{S}$ values obtained for the barite samples of the Komshechek deposit show an enrichment in ^{34}S . The second model is consistent with the data presented in this study. Ba was likely transported in more reduced fluids with low S contents, with barite precipitation due to the reaction with more oxidized and S-rich formational water. If the initial reduced S was slightly heavy, then its oxidation, by mixing with oxidized surface waters, would yield the high values observed for the barium sulphate. It should be noted that a single fluid can not carry large amounts of barium and sulfur in the sulfate form [26, 29].

It is found that fluorite solubility in NaCl solutions increases with increasing temperature at all ionic strengths studied up to 100°C [30, 31]. A similar effect is seen with KCl, CaCl₂ and MgCl₂ solutions, and deviations from the Debye-Huckel theory suggest the presence of complexes such as NaF, CaF⁺, Na₂F⁺ and MgF⁺. It is suggested that no other complexes should be important in fluorite transport and deposition at temperatures below 300°C [30]. Fluorite deposition can occur when a Ca-F saturated fluid either 1) decreases in temperature and/or undergoes changes in chemistry, 2) mixes with another fluids, 3) changes in pressure or 4) interacts with wall rocks along the path of fluid flow [31-35]. In the case of saline fluids, such as the fluids at Komshecheh, the solubility of fluorite decreases with decreasing salinity. It is also suggested that one of the main controls of fluorite deposition is increasing pH. Dissolving of the carbonate host rock causes a rapid increase in fluid pH that leads to the instability of F-complexes and subsequent fluorite deposition [34]. This interaction supplies calcium to precipitate significant quantities of fluorite by the following reaction:



The circulation of Mg-rich hydrothermal fluids prior to the mineralization is evidenced by the epigenetic dolomitization of the Middle Triassic host carbonates. Saddle dolomite, which appears in all stages of mineralization, is regarded as the precipitant from hot, high-salinity solutions [36].

Sulfides occur in response to fluid dilution and destabilization of Pb and other metal complexes during the mixing of the fluids [16]. On the one hand, the magmatic origin for mineralizing fluids is rejected by the absence of high quantities of sulfides, while on other hand, the presence of ferrous dolomite and the lack of large quantities of pyrite in the paragenetic sequence indicate low S activity in the mineralizing solutions [2].

10. CONCLUSIONS

Mineralization at the Komshecheh deposit in the Ardestan region is hosted by Middle Triassic dolomitized limestone. The paragenetic sequence indicates that the mineralization is entirely epigenetic. Two episodes of deposition are identified as an early stage of fluorite precipitation and a later barite-fluorite mineralization event. The mineralizing fluids are forced from orogens and are squeezed out of the basin by crustal thickening and convergence during Cenozoic orogeny in the study area. Ba and F are leached from the sediments during the downward migration of brines through faults. Although questions remain concerning the age of the mineralization, it is considered most likely that mineralization takes place during post-Eocene, as the ore-forming fluids are significantly affected by heating and perhaps chemical exchange with intrusive bodies during downward migration. It seems likely that a deep seated intrusion is present beneath the study area. There is no doubt that the heated basinal brine formed within the sedimentary succession, but the fluorine, barium and possibly water contents might have been increased due to interaction with igneous rock. At the final step upon the rising updip into carbonate rocks, the brines tend to dissolve them. Cooling results in a host-rock solution with little change and in the deposition of the ores. Temperature, pH change and dilution effects may all be important. Based on these conclusions, it is suggested that the Komshecheh barite-fluorite deposit could be classified as an MVT deposit.

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