PETROGRAPHY AND MINERAL CHEMISTRY OF A NEWLY DISCOVERED Ag AND Cd ORE MINERALS IN THE Zn-Pb-BARITE OCCURRENCE IN ALANISH AREA, ZAKHO, NORTHERN IRAQ

Salih M. Awadh

Received: 03/12/2017, Accepted: 18/01/2018

Key words: Acanthite, Greenockite, Mineral chemistry, Zn-Pb-barite, Alanish, Zakho, Iraq

ABSTRACT

The Alanish locality, situated along the northern passive margin of the Arabian Plate, is one of several Zn-Pb-Barite occurrences widespread in northern Iraq (north of Zakho City). The mineralization was emplaced in the Late Permian dolostone of the Chia Zairi Formation and can be seen at the superficial exposures. A scanning electron microprobe coupled with an X-ray energy-dispersive spectrometer (SEM-EDX) was used for the identification of mineral phases. Acanthite (Ag\textsubscript{2}S) and greenockite (CdS) are reported here as their first occurrence in Iraq within a strata-bound polymetallic sulfide ores of Zn, Pb, Fe, Cu, Ag, and Cd. It is a Mississippi Valley Type (MVT) deposit formed at 120 °C as inferred from Cd fractionation in sphalerite and galena. The metals and sulfur sources are derived from the brines originated from the sedimentary basin rich in evaporate. The average composition of acanthite is 83.9 wt.% Ag and 12.5 wt.% S equivalent to 96.4% acanthite as tiny inclusions of lenticular shape inside galena and smithsonite grains. The remobilization of Cd from the sphalerite lattice resulted in the formation of greenockite with an average composition of 68.9 wt.% Cd and 21.2 wt.% S. The mineralization is dominated by sphalerite and galena with minor amounts of chalcopyrite, pyrite, marcasite, and fewer amounts of acanthite and greenockite associated with dolomite, calcite, barite, and siderite as gangue minerals. The common features of the mineralization are replacement, veins, veinlets, and cavity filling of small paleo-karsts. The fault plane and the secondary permeability formed pathways for the movement of metals-bearing solution into dolostone in which the ore body was accommodated.
Petrography and Mineral Chemistry of a Newly Discovered Ag and Cd ore Minerals in the Zn-Pb-Barite Occurrence in Alanish Area, Salih M. Awadh

INTRODUCTION

The northern and northwestern Iraq is a metallogenic provenance (Al-Bassam, 1986 and Awadh and Nejbert, 2016) in which the metallic ore deposits are widely distributed, but they have not yet been economically evaluated to be mined. The mineral deposits in north and northeastern Iraq have been studied by many workers (e.g., McCarthy and Smit, 1954; Al-Bassam, 1986; Al-Qaraguhli and Lange, 1978; Hak, et al., 1983; Awadh et al., 2008a; 2008b; Awadh, 2009; Awadh and Nejbert, 2016; Mirza et al., 2016). These deposits include zinc-lead-barite, copper, chromium, nickel and iron.

Acanthite (Ag ore mineral) and greenockite (Cd ore mineral) are reported in this paper for the first time in Iraq. They are associated with the polymetallic sulfide ore minerals of Zn, Pb, Fe, Cu, Ag, and Cd situated in Alanish locality, northern Iraq. The mineralization is hosted by the Late Permian dolostone of the Chia Zairi Formation (McCarthy and Smit, 1954).

The aim of this study is to report for the first time the presence of acanthite and greenockite as scientifically interesting ore minerals in the Alanish Pb-Zn-barite occurrence. The study included detailed mineral and chemical analysis of these two minerals together with suggestions for their mode of formation. However, these metallic ore occurrences need more detailed studies to evaluate their economic viability.

GEOLOGICAL SETTING

The study area is just one site of the metallogenic province in northern and northeastern Iraq. The mineralization is situated in the Late Permian dolostone of the Chia Zairi Formation, on an anticlinal limb E – W strike and dipping 60° – 70° N, with 100 m long parallel to the bedding plane. The Chia Zairi Formation is mainly composed of limestone shelf facies at the bottom and top with dolomite and limestone mixed with deep fine clastic facies in the middle (Fig.2). Rugged Permian to Triassic-aged mountainous terrains of about 1000 m (a.s.l) elevation is exposed in the study area. The total thickness of the late Middle Permian – Triassic succession in Iraq is 2500 m (Dunnington et al., 1959 cited in Aqrawi et al., 2013). Most of the sulfide metallic ore deposits and occurrences in northern Iraq have been classified
as Mississippi Valley Type (MVT) (Awadh et al., 2008a and b). The MVT deposits have accounted for 24% of the global resources of Pb and Zn in sediment and volcanic-hosted deposits (Leach et al., 2010). The sulfide ores occur mainly in platform carbonate sequences and commonly found in foreland thrust belts of wide age ranges that extended from the Upper Paleozoic to the Upper Cretaceous.

Fig. 1: Simplified tectonic map showing the zinc-lead deposits scatter along the major thrust zone in Turkey, Iraq, and Iran. The upper left figure is an enlarged view the zinc-lead deposits district in the studied Alanish area. The upper right figure shows a detailed geological map of Alanish locality displaying mineralization within the upper Permian dolomite of Chia Zairi Formation (Awadh and Nejbrt, 2016)
Fig.2: Stratigraphic section in the studied locality (Awadh and Nejbert, 2016)

MATERIALS AND METHODS

Ore minerals have been investigated in fifty ore-bearing carbonate rock samples collected from the mineralized country rocks through an extensive fieldwork. All analytical methods and measurements were performed at the Institute of Mineralogy, Petrology, and Geochemistry at the Geological Faculty of Warsaw University with the exception of polished and thin sections, which were mostly prepared in the workshop of the Department of Geology at the University of Baghdad, Iraq. One hundred and twenty polished sections, as well as
300 thin sections were microscopically investigated. A Nikon Eclipse E600 polarized microscope equipped with reflected light and transmitted light was used for the mineralogical identification. Photomicrographs of thin and polished sections are taken using the Nikon digital camera attached to the microscope. A JEOL JSM-6380LA scanning electron microscope coupled with an X-ray energy-dispersive spectrometer (SEM-EDX) were used for the identification of mineral phases. The investigated samples were carbon-coated for microprobe analysis. Analytical EDX settings were 20 KV beam voltage and count time of 60 s (peaks). The sulfide ores were analysed for Zn, Pb, Fe, Cd, Ag, Cu, Ni, Co, As, Sb, Se, and S; the carbonates were analysed for Zn, Fe, Ca, Ba, Mn, Mg, Sr, Si, Pb, S, C, and O, while the sulfates (barite) were analysed for Ba, Ca, Sr, Zn, Fe, Mn, Mg, V, U, K, Si, S, and O using standard electron microprobe (EPMA-Cameca SX100).

RESULTS AND DISCUSSION

- Mineralization of the country rocks

The poly-metallic, strata-bound type sulfide ore occurrence at the Alanish locality, comprised of Zn, Pb, Fe, Cu, Ag, and Cd, are situated in the Late Permian dolostone of the Chia Zairi Formation. The mineralization seems to be of hydrothermal origin indicated by more than 1 Km long and several meters thick lithogeochemical halo around it. Dissolution and open-space filling features in the host dolostone are evidently characteristic of this mineralization. The fresh dolostones are characterized by the mosaic texture which consists typically of rhombic shaped crystals with an undulatory extinction (Fig.3-1).

![Fig.3: Ore minerals hosted in dolostone country rocks; Rhombic dolomite with undulotary extinction (1); Dissolved dolomite resulted in anhedral hosed galena along the irregular boundaries (2); Fractured dolomite grains enclosed by ore minerals (brown is sphalerite and smithsonite, dark is galena) (3); sphalerite, cerussite, and smithsonite-cemented dolomite epigentically (4)](image-url)
The porous dolostones allowed the circulation of the ore-bearing fluids to pass and then dissolved the outer surface of dolomite forming anhedral shaped crystals with irregular intercrystalline boundaries (Fig.3-2). The intergranular ore minerals replaced by small dolomite rhombs, indicates a contemporaneous precipitation during early dolomitization. The irregular-shaped euhedral grains enclosed by ore minerals are the result of the ore-bearing fluid passing through brecciated zone (Fig.3-3). Sphalerite and galena mainly replace dolomite and fill the pore spaces, resulting in a cement-like dolomite (Fig.3-2 and 3-4). The supergene oxidizing solutions led to the formation of ores represented by cerussite and smithsonite following the formation of galena and sphalerite (Fig.3-2 and 3-4). Pyrite and marcasite represent the iron-sulfide mineral phases, whereas some of the small pyrite cubes, replaced by goethite, are wholly enclosed by barite. Barite commonly occurs as veins, veinlets, and rosette-like space fillings.

The textural features, represented by the dog-teeth (comb structure) in marcasite and rosette and space-filling texture in barite, are indication of low-temperature ore-forming solution. Deposition from epithermal solutions in open fissures can result in comb structures (Craig and Vaughan, 1981). Impurities of organic matter are also found in association with large bladed barite grains. The MVT deposits have a lot of organic matters in some deposits (e.g., Polaris, Pine Point, Robb Lake, Jubilee, Walton), but not necessarily present in significant amounts in others.

**Ore petrography and genetic implications**

The cataclastics texture is predominant in sphalerite, galena, and pyrite. Sphalerite, the most common mineral in the mineralization has pre- and distinctive post-tectonic phases of mineralization. The post-tectonic brecciated sphalerite grains are filled by barite (Fig.4-1). Fractures cross-cutting galena indicate late tectonic activity (Fig.4-1), whereas, galena has been sequentially grown after sphalerite. Galena typically post-dated sphalerite in close association, displaying an irregular masses (Fig.4-2) and disseminated replacement bodies in dolomite. The curvature triangle-shaped cleavage in galena, indicate a post-tectonic deformation (Fig.4-3). Galena is converted into cerussite due to the supergene alteration (Fig.4-3). The post-tectonic idiomorphic cubes of disseminated pyrite, formed as a result of the replacement of dolomite groundmass and sometimes exist as inclusions in sphalerite and galena, displays crushed texture (Fig.4-2). Marcasite fills the open spaces forming a dog-tooth texture. The dog-teeth texture, which is also named a comb structure provides evidence of low-temperature solution.

Pyrite and marcasite, which are genetically formed earlier than sphalerite and galena, are weathered to goethite as a normal product of oxidation (Fig.4-2). Goethite enclosed barite, forming a skeletal texture (Fig.4-4). The sphalerite grains were more affected by solutions than galena grains, and consequently the sphalerite was totally altered to smithsonite, whereas galena was partially altered to cerussite (Awadh and Nejbert, 2016) (Fig.4-5). Copper-rich fluids reacted with sphalerite forming chalcopyrite disease texture (Fig.4-6).

Acanthite is found in the studied samples only as tiny lenticular plebs or in larger galena and smithsonite grains (Fig.4-7). It is a low-temperature silver-sulfide phase, stable below 177 °C (Bruhwiler et al., 1999). Greenockite is identified as a small skeletal-shaped grains enclosed in smithsonite (Fig.4-8). Paragenetically, acanthite was coevally deposited with sphalerite, whereas greenockite was deposited later as a secondary remobilization product. Textural relations indicated that acanthite was primarily deposited during the early mineralization phase, while greenockite was deposited at the last phase of the supergene mineralization.
Fig. 4: Reflected light micrograph: barite fills fractures of the post-tectonic decomposed sphalerite (1); irregular mass of galena in association with sphalerite and enclosed pyrite that was altered to goethite, (2); The post-tectonic galena alters to cerussite (3); skeletal texture composed of spaced filling goethite around barite (4). Irregular mass of smithsonite after sphalerite-enclosed galena respond slightly to the weathering and partially altered to cerussite (5). Veinlet in siderite shows a chalcopyrite disease texture between sphalerite and chalcopyrite (6). Tiny grain of acanthite in smithsonite (7). Well crystalline greenockite in smithsonite (8).
Acanthite has a similar chemical composition as argentite (Ag$_2$S), but it has different structure. Argentite has a cubic structure and is only stable at temperatures above 173 °C; during cooling to below 173 °C, argentite is converted into monoclinic structure forming acanthite (Craig and Vaughan, 1981). So, acanthite represents the lower temperature phase of (Ag$_2$S). Transformation sometimes distorts the crystals forming pseudomorphs where they are actually acanthite crystals in the shape of argentite crystals. Acanthite and greenockite occur as tiny grains associated with the polymetallic sulfides which consist mainly of sphalerite, galena, chalcopyrite, pyrite, and marcasite. On the other hand, smithsonite, cerussite, and goethite are the weathering products resulted from the supergene solution action. Barite is commonly associated with the polymetallic sulfide deposits as a sulfate mineral (Abbott and Turner, 1990).

- **Chemistry of ore minerals**

The results of ore-mineral chemistry are listed in Table 1 together with main statistical parameters. Galena in some deposits often contains small amounts of impurities, including Ag and Se. As a common Ag-carrier (Dorfmann, 1974) galena can incorporate variable amounts of Cu and Ag (Pring and Etschmann, 2002). In the Alanish locality, the veinlets of galena occurring within sphalerite show very little variation in Pb content. The Pb and S contents range from 85.5 to 87.5 wt.% (86.2 wt.% ± 0.5) and 12.3 to 13.6 wt.% (13.1 wt.% ± 0.46) respectively. They are indicating a nonargentiferous galena, which is already free of As, Se, Sb, Cu, Fe, Co, Ni, and Zn. An electron microprobe analysis confirmed that the Ag in galena is below detection limit.

The general empirical formula of sphalerite is Zn$_{0.95}$Fe$_{0.05}^2+$S accounting for 64.06 wt.% Zn, 2.88 wt.% Fe and 33.06 wt.% S. Sphalerite is sometimes an argentiferous or auriferous mineral, and it can host Fe, Cd, Mn, Hg, and rarely Pb, Sn, In, Ga, and Ti in its lattice (Zhang et al., 2008). The considerable variations of both Zn (40.3 – 55.5 wt.%; mean = 49.4 wt.%) and Fe (1 – 14.9 wt.%; mean = 6.2 wt.%) are characteristic of sphalerite and may be attributed to tectonic events, where pre and post tectonic phases are identified (Awadh and Nejbert, 2016). Cadmium is fractionated between the coexisting phases of galena and sphalerite (Table 3) which can be used as a geothermal indicator (Bethke and Barton, 1971). The ratio of Cd: Cd in sphalerite and galena ranged from 2302 to 18,197. The temperature of crystallization is computed from two equilibrated pair minerals (Table 2), based on the equation below Bethke and Barton (1971):

$$\log K_{Cd}^{sph-gn} = \frac{2080 + 0.0246 p}{T \circ K} - 1.08$$

Where

$$K = \frac{\text{wt.\% cadmium in sphalerite}}{\text{wt.\% of cadmium in galena}}$$

$p$ = pressure in atmosphere

$T \circ K$ temperature in Kelvin

Pure phases of acanthite (Ag$_2$S) and greenockite (CdS) are identified (Fig.4-7 and 8, respectively). The average crystallization temperature of Alanish ore minerals is 120 °C under which acanthite is a stable phase. Acanthite contains much more Cd (0.43 wt.%) than galena (0.0007 wt.%), and the computed value, as 614 times, indicates a primary phase. The average
content of Ag (83.9 wt.%) is equal to 96.4% acanthite-end member, and the highest acanthite component is 97.6%, suggesting that there is no solid solution between Pb and Ag. Meanwhile, Greenockite is differently formed than acanthite, where Cd is released from sphalerite lattice and moved away, in response to supergene action, to link, eventually, with S forming greenockite. The Cd-end member contains from 68.7 to 69.2 wt.% Cd, equivalent to 88.3 – 88.9 wt.% greenockite. Zinc replaces Cd in greenockite with a range of 7.7 – 8.3 wt.% Zn. Greenockite is therefore identified as a sphalerite weathering product. Chalcopryte may have originated from hydrothermal solution, indicated by the collapsed brecciation, recrystallization, dissolution, dolomitization, and silicification. Collapsed breccia is a hydrothermal feature resulting from the dissolution of underlying carbonate beds (Leach and Sangster, 1993). Chalcopryte with mineral chemistry of 33.3 wt.% Cu, 29.5 wt.% Fe, and 34 wt.% S has been proven as primary mineralization (Awadh and Nejbert, 2016). Pyrite, with a composition of 46.3 wt.% Fe and 53.3% S, contains up to 0.6 wt.% Zn and 0.16 wt.% Pb within its lattice. The pseudomorphic goethite was formed after pyrite by supergene oxidation.

Table 1: Statistical summary of mineral chemistry results (wt.%); N, is the number of microprobe spot analyses

<table>
<thead>
<tr>
<th>Minerals</th>
<th>N</th>
<th>Stat</th>
<th>Zn</th>
<th>Fe</th>
<th>S</th>
<th>Cd</th>
<th>Cu</th>
<th>Co</th>
<th>Ni</th>
<th>As</th>
<th>Se</th>
<th>Sb</th>
<th>Pb</th>
<th>Ag</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sphalerite</td>
<td>54</td>
<td>Min</td>
<td>40.0</td>
<td>1.0</td>
<td>30.7</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.03</td>
<td>0.04</td>
<td>0.03</td>
<td>0.04</td>
<td>0.04</td>
<td>0.03</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Av</td>
<td>49.4</td>
<td>6.2</td>
<td>33.5</td>
<td>11.8</td>
<td>0.07</td>
<td>0.04</td>
<td>0.03</td>
<td>0.04</td>
<td>0.04</td>
<td>0.03</td>
<td>0.21</td>
<td>0.45</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Max</td>
<td>55.5</td>
<td>14.9</td>
<td>34.6</td>
<td>17.9</td>
<td>0.14</td>
<td>0.08</td>
<td>0.07</td>
<td>0.08</td>
<td>0.08</td>
<td>0.06</td>
<td>0.43</td>
<td>0.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SD</td>
<td>7.2</td>
<td>4.3</td>
<td>0.56</td>
<td>2.7</td>
<td>0.07</td>
<td>0.04</td>
<td>0.03</td>
<td>0.04</td>
<td>0.04</td>
<td>0.03</td>
<td>0.21</td>
<td>0.45</td>
</tr>
<tr>
<td>Galena</td>
<td>18</td>
<td>Min</td>
<td>0</td>
<td>0</td>
<td>12.3</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Av</td>
<td>0.01</td>
<td>0.01</td>
<td>0.0007</td>
<td>0.07</td>
<td>0.01</td>
<td>0.005</td>
<td>0.003</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>86.2</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Max</td>
<td>0.11</td>
<td>0.06</td>
<td>13.6</td>
<td>0.11</td>
<td>0.7</td>
<td>0.11</td>
<td>0.04</td>
<td>0.03</td>
<td>0.02</td>
<td>0.05</td>
<td>87.1</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SD</td>
<td>0.03</td>
<td>0.02</td>
<td>0.46</td>
<td>0.06</td>
<td>0.16</td>
<td>0.02</td>
<td>0.01</td>
<td>0.007</td>
<td>0.01</td>
<td>0.02</td>
<td>0.48</td>
<td>0</td>
</tr>
<tr>
<td>Greenockite</td>
<td>2</td>
<td>Min</td>
<td>7.6</td>
<td>1.17</td>
<td>21.1</td>
<td>68.7</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1.6</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Av</td>
<td>7.9</td>
<td>1.18</td>
<td>21.2</td>
<td>68.9</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1.6</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Max</td>
<td>8.3</td>
<td>1.2</td>
<td>21.3</td>
<td>69.2</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1.7</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SD</td>
<td>0.5</td>
<td>0.02</td>
<td>0.14</td>
<td>0.35</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.02 --- 0.07</td>
</tr>
<tr>
<td>Pyrite</td>
<td>5</td>
<td>Min</td>
<td>0.2</td>
<td>46.3</td>
<td>53.3</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.005</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.16</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Av</td>
<td>0.6</td>
<td>46.3</td>
<td>53.3</td>
<td>0.03</td>
<td>0.01</td>
<td>0.03</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Max</td>
<td>0.9</td>
<td>46.4</td>
<td>53.4</td>
<td>0.06</td>
<td>0.03</td>
<td>0.06</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.03</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SD</td>
<td>0.5</td>
<td>0.02</td>
<td>0.02</td>
<td>0.04</td>
<td>0.02</td>
<td>0.04</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.02</td>
</tr>
<tr>
<td>Acanthite</td>
<td>5</td>
<td>Min</td>
<td>2.3</td>
<td>1.0</td>
<td>12.3</td>
<td>0.41</td>
<td>0.1</td>
<td>0</td>
<td>0.04</td>
<td>0.005</td>
<td>0.003</td>
<td>0</td>
<td>0.05</td>
<td>82.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Av</td>
<td>2.35</td>
<td>1.1</td>
<td>12.5</td>
<td>0.43</td>
<td>0.2</td>
<td>0.1</td>
<td>0.01</td>
<td>0.006</td>
<td>0</td>
<td>0.07</td>
<td>83.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Max</td>
<td>2.4</td>
<td>1.1</td>
<td>12.7</td>
<td>0.48</td>
<td>0.4</td>
<td>0.2</td>
<td>0.3</td>
<td>0.1</td>
<td>0.09</td>
<td>0</td>
<td>0.09</td>
<td>85.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SD</td>
<td>0.5</td>
<td>0.03</td>
<td>0.3</td>
<td>0.04</td>
<td>0.1</td>
<td>0.1</td>
<td>0.03</td>
<td>0.04</td>
<td>0.04</td>
<td>---</td>
<td>0.02</td>
<td>1.3</td>
</tr>
<tr>
<td>Chalcopryte</td>
<td>6</td>
<td>Min</td>
<td>1.0</td>
<td>28.9</td>
<td>33.4</td>
<td>0.2</td>
<td>32.6</td>
<td>0.03</td>
<td>0.2</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.05</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Av</td>
<td>1.4</td>
<td>28.5</td>
<td>34.0</td>
<td>0.2</td>
<td>33.3</td>
<td>0.02</td>
<td>0.2</td>
<td>0.02</td>
<td>0.02</td>
<td>0</td>
<td>0.03</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Max</td>
<td>1.6</td>
<td>30.2</td>
<td>34.7</td>
<td>0.2</td>
<td>34.5</td>
<td>0.04</td>
<td>0.21</td>
<td>0.03</td>
<td>0</td>
<td>0</td>
<td>0.1</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SD</td>
<td>1.4</td>
<td>1.85</td>
<td>0.97</td>
<td>0</td>
<td>1.2</td>
<td>0.2</td>
<td>0.05</td>
<td>0.01</td>
<td>0</td>
<td>---</td>
<td>0.02</td>
<td>---</td>
</tr>
<tr>
<td>Zn Fe U Ca Ba Mn Mg Sr Si V S O</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Barite</td>
<td>11</td>
<td>Min</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>54.9</td>
<td>0</td>
<td>0</td>
<td>0.03</td>
<td>0</td>
<td>0</td>
<td>13.0</td>
<td>26.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Av</td>
<td>0.02</td>
<td>0.02</td>
<td>0.1</td>
<td>0.003</td>
<td>57.1</td>
<td>0.004</td>
<td>0</td>
<td>0.83</td>
<td>0.004</td>
<td>0.01</td>
<td>13.5</td>
<td>27.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Max</td>
<td>0.09</td>
<td>0.1</td>
<td>0.3</td>
<td>0.02</td>
<td>57.6</td>
<td>0.013</td>
<td>0</td>
<td>2.7</td>
<td>0.02</td>
<td>0.02</td>
<td>13.7</td>
<td>27.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SD</td>
<td>0.04</td>
<td>0.04</td>
<td>0.14</td>
<td>0.006</td>
<td>1.41</td>
<td>0.005</td>
<td>0</td>
<td>0.77</td>
<td>0.01</td>
<td>0.01</td>
<td>0.17</td>
<td>0.28</td>
</tr>
</tbody>
</table>

Table 2: Fractionation of cadmium (wt.%) and crystallization temperature calculated from the distribution constant of Bethke and Barton (1971)

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Mean</th>
<th>Cd_{sp}/Cd_{gan}</th>
<th>logK_{Cd}^{sp-gan}</th>
<th>Temperature °C</th>
<th>Pressure Bar</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sphalerite</td>
<td>11.8</td>
<td>0.0007</td>
<td>18197</td>
<td>4.26</td>
<td>120</td>
</tr>
</tbody>
</table>
Petrography and Mineral Chemistry of a Newly Discovered Ag and Cd ore Minerals in the Zn-Pb-Barite Occurrence in Alanish Area, Salih M. Awadh

- **Ore genesis**

  Precious ore minerals are well known to occur in the zinc-lead-barite deposits. Regardless of the Zn, Pb, Cu, and Fe; the presence of Ag and Cd gives special importance to these deposits, particularly if they exist in economic quantities. The mineralization features in the Alanish area indicate an MVT deposit characterized by simple mineralogy of sphalerite, galena, pyrite, marcasite, chalcopyrite, acanthite, greenockite and barite; similar in this respect to global MVT ore deposits (Leach and Sangster 1993; Sangster 1995; Misra 1999; Leach *et al*., 2001). It is well known that the MVT ore deposits are epigenetically deposited under low-temperature conditions (50 – 200 °C, usually 100 – 150 °C) in restricted dolostone or limestone strata away from the igneous activity (Sverjensky, 1986). The 60 to 250 °C is a temperature range characteristic the MVT fluids (Gregg and Kevin, 2012). The geothermometric evidence computed in this study from Cd, as a minor element fractionated in sphalerite and galena, indicate a formation temperature of 120 °C, where acanthite is a stable phase. The mineralized dolostone is exclusively attributed to the easy penetrating of ore-bearing fluids as compared to limestone (Leach *et al*., 2005). Accordingly, the most suitable name of the host rock in the Alanish occurrence is ore-bearing dolomite.

  Highly saline brines play an important role in the precipitation of MVT ore deposits under stratigraphic and structural controls (Leach and Sangster 1993; Sangster 1995; Misra 1999; Leach *et al*., 2001). Typically, the MVT deposits are emplaced in platform carbonate sequences, located either in relatively undeformed rocks bordering foredeeps or in foreland thrust belts (Misra, 1999). Recent studies have suggested a relationship to the major tectonic events that may supply a driving force for these hydrologic systems, although this is still an issue of some debate (Leach *et al*., 2001; Bradley and Leach 2003; Kesler *et al*., 2004; Bradley *et al*., 2004). The Alanish mineralization is preferentially developed in the Late Permian dolostone, within one of the most important periods of global formation of MVT deposits; identified by Leach *et al*. (2001) as Devonian-Permian and Cretaceous-Tertiary.

  The brines and evaporates are the potential sources of the Alanish ore mineralization supplying base metals and sulfur respectively (Awadh and Nejbert, 2016). The ore-forming metals were generated from the dense brines influxes from the sedimentary basin. The MVT mineralization is believed to result from a complex mixing and/ or cooling of saline fluids expelled from sedimentary basins (Craig and Vaughan, 1981). The sulfates in the metalliferous fluids are locally reduced into sulfides by reductants, such as organic matter (Leach *et al*., 2010) which are available in the studied sequence. The ultimate source of sulfur is most likely evaporates existing nearby the mineralization site where sulfur was reduced by one or more processes. The tectonic activity of the Laramide Orogeny (Late Cretaceous) was likely the driving force that squeezed and moved the ore-bearing solutions towards areas of low pressure. The Larmaide Orogeny, marked by uplift and folding, may have caused the rise of isotherms and regional metamorphism in the Zagros Fold Belt (Jassim *et al*., 1982).

**CONCLUSIONS**

The Alanish locality represents an important geological site for polymetallic sulfide mineralization of base metals, including silver and cadmium beside the most common metals already reported in this locality represented by zinc, lead, iron, copper and barium. The mineralization is emplaced in dolostone beds of the Chia Zairi Formation. Silver and cadmium ore minerals, represented by acanthite and greenockite respectively, are found as tiny grains associated with the zinc-lead mineralization. The ore-bearing solutions are believed to be dense brines of 120 °C influxes from the sedimentary basin, which were expelled by
tectonic activity. The brecciated zones and inter-connected joints in dolostone, in addition to the permeable dolomitic strata, actively accommodated the ore-bearing solution and participated in the formation of an epigenetic strata-bound MVT deposit.

REFERENCES
Petrography and Mineral Chemistry of a Newly Discovered Ag and Cd ore Minerals in the Zn-Pb-Barite Occurrence in Alanish Area, 

Salih M. Awadh


Zhang, M., Zhou, Z., Xiong S., Gong Y., Yao Sh. and Li, H., 2008. Enrichment of the dispersed elements Cd, Ge and Ga in the Huize lead-zinc deposit, Yunnan [J]; Sedimentary Geology and Tethyan Geology; 04.

About the author

Dr. Salih M. Awadh: A geochemist professor graduated from the University of Baghdad in 1986 with B.Sc. Degree in Geology; M.Sc. (1992) in Geochemistry; Ph.D. (2006) in Geochemistry and Economic Geology; and Post Doctorate degree (2014) from Warsaw University – Poland. He has an experience of over 24 years in Geochemistry, Petroleum Geochemistry, Ore Geology and Environmental Studies, and over 22 years as an academician. He currently works at the Department of Geology, University of Baghdad. He is an editor-in-chief of the Iraqi Geological Journal, and a member of the editorial board of both of the Iraqi Bulletin of Geology and Mining, and International Journal of Earth Sciences and Engineering. (Scopus Elsevier indexing). He supervised more than 20 theses (M. Sc. and Ph. D) and his publications are more than sixty papers with five academic books.

e-mail: salihauad2000@yahoo.com; salihauad2000@scbaghdad.edu.iq