The First Report of Rosasite Mineral in Qaleh-Zari Copper Mine, East of Iran
(Based on SEM and AAS Analysis)

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Abstract
The Rosasite group is a family of rare secondary minerals occurring in oxidized zones in Cu-Zn ore deposits. This group includes seven minerals (zincrosasite, for instance) that are formed by a chemical reaction between Zn bearing solutions and Cu minerals. The Qaleh-Zari mine, which is a well-known copper mine in Eastern Iran, is located in South Khorasan province. This mine is a polymetallic deposit of Copper, Zinc, Iron and Lead sulfides, carbonates and oxides. Limitedly, there is a mineral which appears in globular and compact mammillary to botryoidal crusts on hemimorphite in oxidation zones. The analyses conducted in this study determined that this mineral belongs to the rosasite group. Up to now, the presence of rosasite group minerals and mineralogical studies on them have never been reported in this deposit. Scanning Electron Microscope (SEM), Atomic Absorption Spectroscopy (AAS), and other mineralogical results suggested that the blue mammillary mineral is zincrosasite with Zn= 9.1 % and Cu=3.42%.

Keywords
Rosasite, Zincrosasite, SEM, AAS, Raman, Qaleh-Zari, Iran.

Introduction
Rosasite group is a collection of rare known secondary minerals that occur in the oxidized zone in Cu-Zn ore deposits formed by action between Zn bearing solutions and cupric minerals. Their general formula is A2(CO3) (OH)2 or AB(CO3) (OH)2. A and B may have been filled by Co, Cu, Mg, Ni and Zn (Mandarino, 1999), to make seven rare minerals (Frost, 2006). The minerals, their formula and references are listed in table 1.
Rosasite was first reported in 1908 at the Rosas mine in Sardinia, Italy. After that, subsequent examinations were carried out on many mines around the world but zincrosasite was unknown till 1959. Unfortunately, the available chemical analyses for zincrosasite are very few (Fehér et al., 2015). It was first introduced from the Tsunem mine in Namibia by Strunz (1959). Strunz descriptions are very short (only six sentences), in which there is no additional explanation for mineralogical data (Anthony et al., 2003). Pauliš et al. (2005) issued the formula (Zn1.53Cu0.43)(CO3)(OH)2 for the mineral from Herlíkovice in the Czech Republic and Fehér et al. (2008) presented the result of the microprobe analysis of the zincrosasite from Andrássy-1 mine, Rudabínya in Hungary with chemical formula (Zn1.35Cu0.65Fe0.05)(CO3)(OH)2.
Braithwaite and Ryback (1963) studied the properties of rosasite that have been found in Rutland Cavern using infrared spectroscopy. Hudson-Edwards et al. (1996) described the formation of rosasite in the process of substitution of carbonate in sulfate minerals. Also, rosasite was reported from skarn-hosted caves in Bihor country Romania by Onac (2002). Frost (2006) and Frost et al. (2007) issued the results of Raman spectroscopy study of minerals of rosasite group. Moldovan et al. (2013) contributed to secondary minerals, including rosasite, in the Guisi cave in SW Sardinia. Also Clark-Arnold (1964), Nickel (1985), Reddy et al. (2004), Hancock et al. (2007), Trajanova and Zamago (2013), are the other researchers who have worked and published on rosasite. In Iran Zincrosasite was reported from Kali Kafi mine, Anarak, central Iran (fig.1) (www.mindat.org).
Rosasite and zincrosasite are more likely to be found with hydrozincite, auricalcite, hemimorphite, cerussite, smithsonite, malachite and goethite (Fehér et al., 2008). Their colors are various from a hue of light blue (like turquoise) to very pale blue, green and rarely colorless with crusts and botryoidal masses or nodules aggregates up to 3 mm (Anthony et al, 2003; Frost, 2006; Frost et al., 2007), the hardness of 4.5, glassy and silky luster, and transparent to translucent. The minerals of rosasite group are triclinic (Frost, 2006). Hancock et al. (2007) has reported rosasite as a light blue botryoidal crust on hemimorphite in the polymetallic vein deposit from Australian Ragged Hills Mine. Onac (2002), believed that it can be also produced in hypogenous processes or under hydrothermal surface conditions during the metamorphism or at the final stages of skarn. Undoubtedly, the examination of chemical processes and mineralization that occurred in ore deposits requires further information and more sampling. The secondary mineral study discloses...
information on the chemical conditions in the oxidized zone during the weathering of the ore bodies. But the purpose of this article is just to introduce one of the secondary minerals formed in the Qaleh-Zari mine, which has not been investigated and reported before. The deposits of the Qaleh Zari mine have been studied from various perspectives and many of master's and doctoral papers and thesis have been written about it (Suzuki et al., 1976; Sadaghyani-Avval, 1976; Moore and HassanNezhad, 1994; Khatib, 1999; Karimpour and Zaw, 2000), but none have indicated the existence of rosasite or zincrosasite.

Geological Setting

Qaleh-Zari mine is the biggest polymetallic vein deposit in the east of Iran. It is located 180 kilometers away from the city of Birjand in the South Khorasan province, the center of Lut block (fig.1). The Lut block is about 900 km long and 200 km wide, and lies between the Nayband fault in the west and the Nehbandan fault in the east. The Darouneh fault is located on the northern border, and the Jazmourian depression defines the southern boundary, which is the fore-arc basin of the Makran subduction zone. The extensive Tertiary and Quaternary volcanic activity, the recent

Table 1. Minerals of rosasite group.

<table>
<thead>
<tr>
<th>Name</th>
<th>Formulae</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rosasite</td>
<td>(Cu,Zn)2(CO3)2(OH)2</td>
<td>Lovisato, 1910 – Perrier, 1921</td>
</tr>
<tr>
<td>Zincrosasite</td>
<td>(Zn,Cu)2(CO3)2(OH)2</td>
<td>Strunz, 1959 – Feher et al., 2008</td>
</tr>
<tr>
<td>Glaukospaerite</td>
<td>(Cu,Ni)2(CO3)(OH)2</td>
<td>Prye and Just, 1974</td>
</tr>
<tr>
<td>Kolwezite</td>
<td>(Cu,Co)2(CO3)(OH)2</td>
<td>Deliens and Piret, 1980</td>
</tr>
<tr>
<td>Mcguinnessite</td>
<td>(Mg,Cu)2(CO3)(OH)2</td>
<td>Read, 1984 – Erd et al., 1981</td>
</tr>
<tr>
<td>Nullaginite</td>
<td>Ni2(CO3)(OH)2</td>
<td>Nickel et al., 1979</td>
</tr>
<tr>
<td>Pokrovskite</td>
<td>Mg2(CO3)(OH)2:1/2H2O</td>
<td>White, 1987</td>
</tr>
</tbody>
</table>
earthquakes along with the faults in Quaternary sediments indicate the active dynamics of this block (Agha-nabati, 2004). Sedimentary rocks are the oldest formations in the Qaleh-Zari region and consist of Jurassic shales and sandstones overlain unconformably by Upper Cretaceous red conglomerates (Day-Mehvar, 1996). Sadaghyani-Avval (1976) also reports localized Jurassic radiolarian cherts and Maastrichtian carbonates. The Paleogene volcanic rocks comprise of potassium rich calc-alkaline andesites (subduction zone shoshonites), andesitic basalts, dacites and rhyolites, andesitic and dacitic tuffs and pyroxene-bearing andesites (Sadaghyani-Avval, 1976; Suzuki et al., 1976; Hassan-Nezhad, 1994, Hassan-Nezhad and Moore, 2006). The geological map of Qaleh-Zari area is illustrated in Fig.2. The Qaleh-Zari deposit is a fissure-filling polymetallic vein system formed by hydrothermal solutions circulating through the fault planes and breccia zones (Sadaghyani-Avval, 1976; Suzuki et al., 1976; Karimpour and Zaw, 2000; Hassan-Nezhad and Moore, 2006). Mineralization in this area occurs in a NW–SE directed trans tensional fault system (Khatib, 1999, Ghazbanee, 2010). The textures in the ore minerals show evidence of repeated faulting, fracturing and ore deposition (Hassan-Nezhad and Moore, 2006). The main mineralization, formed in veins contain two mineral complexes that were identified in three main zones (Fig. 2). From NW to SE these zones are numbered as No.1 through No.3 deposits (Karimpour et al., 2005). The first complex has several mineralization zones including Cu, Ag, Pb and Zn in minerals of quartz, specularite, chalcopyrite, sulfosalt minerals, chlorite, pyrite, sphalerite and galena (Mohammadi, 2005). The thickness of the veins varies from a few millimeters to more than one meter. Most of the second complex consists of quartz and contains gold mineralization (Mohammadi, 2005). To access to the deposits, seven shafts have been drilled. The samples, examined in this research, were collected from shaft number 6 (figs. 2 and 3).

**Materials and Methods**

Two samples of Geoscience Museum of Mashhad (GMM) were selected to be analyzed by X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Atomic Absorption Spectroscopy (AAS) and Raman microprobe. At first, samples powder was examined by XRD. The instrument is a Brucker D4 with Cu lamp andKa radiation at 40 kV/30 mA, between 4 and 70° (20) at the step size of 0.02° at the laboratory of Geological Survey and Mineral Exploration of Iran (GSI). Then, they were examined by SEM [LEO 1450vp SEM and equipped with a link analytical backscattered electron detector (EDS)] in the central laboratory of Ferdowsi University of Mashhad. The operating conditions for SEM were 35 kV maximum voltages with a resolution of 2.5 µm and EDS (7353) with a resolution of 133 ev.

![Fig. 2. The Geological map of Qaleh-Zari area (modified from Karimpour, 2005)](image)

The samples were first coated with gold-palladium for 120 seconds by the SC7620's coater spotter and then placed on the camera for shooting. In order to prevent the presence of gold that causes changes in the percentage of the elements, the samples required for analysis were covered by a thickness of carbon and EDS analysis was performed. The obtained results show the presence of copper-zinc carbonate hydroxide phase, as well as zinc permeation compared with copper, but the accurate concentration of Cu and Zn is not reliable due to the fact that the device was semi-quantitative. Thus, copper and zinc were accurately measured by AAS method in the laboratory of Geological survey of Iran, North East territory. For this purpose, some of the powder used in XRD method was tested to determine the amount of copper and zinc. The instrument was a Varian-AA240 model and to determine the amount of silica a Shimadzu UV-3100S Spectrophotometer was used. Based on the amount of SiO₂ in the sample, the amount of zinc required for the formation of hemimorphite was isolated. Thus, the residual Zn content was considered for use in the construction of a rosasite.
mineral. Because of the lack of efficient information about this mineral on the one hand and collecting more data on the other, we did Raman microprobe too. Raman Spectroscopy is one of the minerals’ determination methods. It has different applications for investigating materials, but for studying minerals the microprobe method is more common. In this method, a beam of laser with its known power hits the target points of sample. The results give us spectra that are identical for each mineral. Zirconiasite’s Raman spectrum was examined in Ferdowsi Central Lab Raman department. The instrument is Ava-Raman-PRB-78. The analysis performed in these conditions has its features such as intensity 35000, AV-5- P 600 and P 800 (There was no difference between the two powers). Raman raw spectra of zirconiasite at P600 in two regions were acquired: the 1210 to 800 cm\(^{-1}\) region (The main pick is shown at 921.33 cm\(^{-1}\)) and 750 to 100 cm\(^{-1}\) region (The main picks were shown at 177.97 cm\(^{-1}\), 323.93 cm\(^{-1}\), 388.35 cm\(^{-1}\), 438.16 cm\(^{-1}\), 674.35 cm\(^{-1}\)). The results are following in fig. 4a and 4b respectively. Selected samples are housed in Geological Survey of Iran, Northeast Territory, Mashhad, Iran under the repository numbers with prefix GMM (Geoscience Museum of Mashhad) collection at code 95.MS.155 and 95.MN.492 (Fig.5).

**Results and Discussion**

Due to the tectonic activations of the Lut zone as well as the fragile nature of the volcanic rocks, many fractures have been formed on the host rocks and the ore veins of the Qaleh-Zari deposit. The performance of tectonic forces and the occurrence of the abundant faults and fractures after the formation of the ore caused the creation of influential channels; atmospheric waters have a significant effect on the ore deposits in the veins, causing vertical zonation. The influence of atmospheric oxidant fluids through these channels, leads to the reaction and as a result, the dissolution of sulfide minerals is deeply equivalent to the underlying underground water, and creates the stable minerals in the oxidant conditions. Agharezaei et al. (2018) emphasize that the penetration of surface water flows to deeper parts through the fractures and their impact on sulfide minerals have resulted in the formation of oxide minerals in the Qaleh-Zari mine. Oxidized zone is located in different areas with various depths in the Qaleh-Zari mine, especially in shaft No. 6 range (Fig. 3). According to Hassan-Nezhad

![Fig. 4. Raman raw spectra of zirconiasite at P600: a) Scan area is 1210 to 800 cm\(^{-1}\) region and the main pick is shown at 921.33 cm\(^{-1}\), b) Scan area is 750 to 100 cm\(^{-1}\) region and the main picks are shown at 177.97 cm\(^{-1}\), 323.93 cm\(^{-1}\), 388.35 cm\(^{-1}\), 438.16 cm\(^{-1}\), 674.35 cm\(^{-1}\).](image-url)
and Moore (2006) in some veins oxidation minerals are found extending from the surface to a depth of 70 m. The most common minerals are limonite, goethite, malachite, azurite, hemimorphite and smithsonite, but there are blue globular and compact mammillary to botryoidal crusts overlying hemimorphite that never studied before in Qaleh-Zari deposits. At the first glance, the minerals were suspected of being rosasite, but for more accurate diagnosis, further studies are required. Figure 5 shows two specimens from the Qaleh-Zari mine which are hosted in GMM collection and used in this research. Strunz (1959) and Fehér et al. (2008) showed the concentration ratio of copper and zinc is different in the rosasite group minerals. For rosasite and zincrosasite this ratio is: Cu>Zn in rosasite and Cu<Zn in zincrosasite. Based on AAS results, this ratio for samples taken from Qaleh-Zari deposits is Cu<Zn. The minerals have not been studied by single crystal because most of the crystals are composed of thin fibers, overlaying hemimorphites. One of our samples contained other minerals, so we can’t access accurate result of the ratio of Cu and Zn. The XRD result of the other sample suggests the mineral is only rosasite and hemimorphite as expected. Therefore, this sample has been selected for further analyses. EDS also showed Cu-Zn carbonate hydrate phases in the mineral. In addition, the copper and zinc values expressed the superiority of zinc in the composition. Table 2 shows the processing option; figure 6 shows the EDS spectra, and figure 7 is SEM back scattered image of zincrosasite from Qaleh-Zari mine.

As previously stated, due to EDS device semi-quantitative, the exact amount of zinc and copper was measured by AAS method. After the removal of zinc from hemimorphite, the zinc and copper levels required for rosasite were obtained: Zn=9.1% and Cu=3.42%. According to the results, samples collected from the Qaleh-Zari mine should be zincrosasite. In Table 3, copper-zinc ratios of the Qaleh-Zari samples are compared with Namibia and England mines samples. Braithwaite and Ryback (1963) considered the formation of rosasite in England Masson Hill mine to be occurred at direct action of solutions containing Zn on dispersed grains of chalcopyrite at normal temperatures. Of course, the temperature and the concentration of these solutions have a direct effect on the reaction intensity and the rate of the formation of residual. The remaining iron of these minerals remains in the form of brown spots in the environment. This reaction occurs under the high pH/pCO₂ conditions.
Hancock et al. (2007) explained that the high CO₂ pressure in the groundwater of the region has created a malachite-beresite-smithsonite complex in the Ragged Hills Mine. Then, this complex can be affected by the active Zn ions in excess of Cu and Pb in the supergene zone. With zinc replacing copper in malachite, zinc bearing malachite or rosasite can be formed (Williams, 1990; Hancock et al., 2007).

Mohammadi (2005) has studied mineralization stages in all seven shafts in the Qaleh-zari deposits for her doctoral thesis. According to Mohammadi (2005), sphalerite is only seen in shaft No. 6. Interestingly, the GMM zincrosasite has been found only in the same place. The presence of sulfide minerals such as sphalerite needs oxidation zone and Zn²⁺ ion which is oxidized, and also Zn²⁺ is required to react with carbonate minerals such as malachite and chalcopyrite, which can provide zincrosasite. These reactions have been reported in similar deposits which are summarized in the following equations (Hudson-Edwards et al., 1996): 

\[ \text{ZnS} + 2\text{O}_2 = \text{Zn}^{2+} + \text{SO}_4^{2-} \]
\[ \text{CuFeS}_2 + \text{H}_2\text{CO}_3 + \text{H}_2\text{O} + 9/2\text{O}_2 + \text{Zn}^{2+} = (\text{Cu},\text{Zn})_2\text{CO}_3(\text{OH})_2 + 2\text{H}^+ + 2\text{SO}_4^{2-} + \text{Fe}^{2+} \]

### Table 2. Processing option of EDS (wt.% of Qaleh-Zari samples

<table>
<thead>
<tr>
<th>Spectrum</th>
<th>C</th>
<th>O</th>
<th>Cu</th>
<th>Zn</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spectrum1</td>
<td>10.21</td>
<td>47.46</td>
<td>14.44</td>
<td>27.89</td>
<td>100.00</td>
</tr>
<tr>
<td>Spectrum2</td>
<td>10.05</td>
<td>49.82</td>
<td>14.83</td>
<td>25.31</td>
<td>100.00</td>
</tr>
</tbody>
</table>

### Table 3. Rosasite and zincrosasite, their origin and Cu/Zn ratio

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Color</th>
<th>Locality of origin</th>
<th>Cu:Zn (atoms)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rosasite</td>
<td>Light green</td>
<td>Rutland cavern (England)</td>
<td>1.34</td>
<td>Braithwaite and Ryback, 1963</td>
</tr>
<tr>
<td>Rosasite</td>
<td>Dark green</td>
<td>Rutland cavern (England)</td>
<td>1.21</td>
<td>Braithwaite and Ryback, 1963</td>
</tr>
<tr>
<td>Rosasite</td>
<td>Blue</td>
<td>Tsumeb (Namibia)</td>
<td>1.93</td>
<td><a href="http://www.mindat.org">www.mindat.org</a></td>
</tr>
<tr>
<td>Rosasite</td>
<td>Blue</td>
<td>Tsumeb (Namibia)</td>
<td>0.97</td>
<td><a href="http://www.mindat.org">www.mindat.org</a></td>
</tr>
<tr>
<td>Zincrosasite</td>
<td>Light blue</td>
<td>Tsumeb (Namibia)</td>
<td>0.58</td>
<td><a href="http://www.mindat.org">www.mindat.org</a></td>
</tr>
<tr>
<td>Zincrosasite</td>
<td>Light blue</td>
<td>Andrássy-1 (hungary)</td>
<td>0.31</td>
<td>Fehér et al., 2008</td>
</tr>
<tr>
<td>Zincrosasite</td>
<td>Light blue</td>
<td>Qaleh-Zari copper mine</td>
<td>0.37</td>
<td>This study</td>
</tr>
</tbody>
</table>

### Conclusion

In this study, several analytical techniques have been implemented on some unknown minerals having globular and compact mammillary aggregates with botryoidal crusts formed on hemimorphite in Shaft Number six in Qaleh-zari, revealing that the samples contain the rosasite group minerals. SEM and AAS analyses have been executed on the samples to determine the rosasite type. A comparison of the results with those of rosasite samples from other well-known mines has revealed that the zinc content in these minerals is higher than that of copper (Zn=9.1% vs. Cu=3.42%). The results suggest that the type of mineral is zincrosasite. The paragenesis of sphalerite and hemimorphite (with high zinc contents) in the oxidized zone shows a suitable environment for the formation of zincrosasite. A Raman microprobe analysis has been conducted on zincrosasite as well.

### References


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(in Persian).