Sedimentary and epigenetic copper mineral assemblages in the Cambrian Timna Formation, southern Israel

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ABSTRACT


Copper mineralization in the Timna Formation occurs in the dolomitic, sandy, and shaly lithofacies of the Upper Sasgon Member. Scanning electron microscope, chemical, and isotopic studies of the copper mineral parageneses indicate an evolution from diagenetic, neutral reducing conditions through stages of epigenetic alteration at oxidizing and progressively more acid conditions. Primary copper sulfide minerals are djurleite (Cu_{1.93}S) and covellite (CuS) with minor chalcocite (Cu_{2–1.93}S), digenite (Cu_{1.8}S), and anilite (Cu_{1.75}S) randomly dispersed in the dolomitic lithofacies. δ^{34}S values of –14‰ are consistent with their formation by reduction of marine sulfate. Subsequent evolution of the ores involves their replacement by malachite (Cu_{2} (OH)_{2}CO_{3}), which armors and replaces the sulfide minerals, followed by the development of paratacamite (Cu_{2}(OH)Cl) as veins emanating from the altered sulfides. The malachite alteration stage represents a change to oxidizing conditions; paratacamite develops with a decrease in pH and in the presence of chloride ion, which allows the development of stable aqueous copper chloride complexes. The first copper mineral to form in the sandy and shaly lithofacies is chrysocolla (Cu_{2}–XSiO_{5}(OH)_{3}·yH_{2}O), which forms by the dissolution of precursor silicate minerals (quartz, clays, feldspars). The chrysocolla subsequently evolves into plancheite (Cu_{8}(Si_{4}O_{11})_{2}(OH)_{4}·yH_{2}O), pseudomalachite (Cu_{x}(OH)_{2}PO_{4}), and dioptase (CuSiO_{3}·H_{2}O). Thermodynamic calculation indicates that copper silicate formation was brought about by a decrease in pH and/or increase in aCu and is thus consistent with the evidence for epigenesis in the dolomitic lithofacies.

INTRODUCTION

Copper mineralization occurs in the Early/Middle Cambrian (~525 Ma) Timna Formation, Timna Valley, southern Israel, ~25 km north of Elat (Fig. 1). Due to the economic potential of the copper mineralization, the Timna Formation was the subject of a significant amount of research from the 1960s (e.g., Bentor, 1952; McLoad, 1959; Bartura, 1966; Milton, 1966; Bartura and Würzburger 1974; Ayalon et al., 1983, 1985; Bar-Matthews, 1986, 1987; Segev, 1986; Segev and Sass, 1989a,b; Bar-Matthews and Matthews, 1990; Segev, 1992; Shlomovitch, 1995). The copper was mined during this period and until the 1980s. The Timna Formation is exposed in several locali-
ties in Israel and adjacent lands: Timna Valley, Amram Mountain, Shehoret and Roded Valley; Ras en Naqb, Sinai (Fig. 1) (Blake, 1936; Bentor, 1952; Garfunkel, 1970; Segev, 1986). An equivalent section was also described from Feinan in the south of Jordan to the northern part of the Dead Sea (e.g., Blanckenhorn, 1912; King, 1923; Bender, 1968, 1974; Bigot, 1981).

The best-studied exposure is in the Timna Valley, where the Timna Formation was previously divided into four units (Bentor, 1952), which Bartura (1966) defined as (lower to upper): Hakhlil, Nimra, Nehushtan, and Mikhrot formations. Segev (1986) united the three upper units into one Sasgon Member, composed of 3 different lithofacies: dolomites, sands, and shales (Fig. 2). Thus, whereas Bartura (1966) considered that the four members were deposited at different times, Segev (1986) and Segev and Sass (1989b) argued that the sandy lithofacies is the insoluble residue of the dolomite rocks left after epigenetic dissolution processes.

The main copper ore concentrations in the Timna Formation occur within the sandy and the shaly lithofacies (Segev, 1986; Segev and Sass, 1989b) or...
the previously Nehushtan and Mikhrot formations (e.g., Bartura and Würzburger, 1974; Bar-Matthews, 1986, 1987; Bar-Matthews and Matthews, 1990). High copper ore concentrations were also found within the sandstones of the Early Cretaceous Avrona Formation. This copper was extracted during the Chalcolithic, early Bronze, Roman, and Nabatean periods (Rothenberg, 1998; Segal et al., 1998).

McLoad (1959), Milton (1966), and Bartura and Gross (1966) were the first to describe and identify the mineralogy of the modern exploited copper deposit in Timna, comprised mainly of copper silicate assemblages. Most of the early studies suggested that the source for the copper was the erosion of adjacent Precambrian rocks, and that deposition within the clastic rocks occurred through stratiform syngenetic sedi-
mentation in lagoons (Bentor, 1956; Wurzberger, 1970; Bartura and Wurzberger, 1974). Veins cutting through the strata were considered to have formed by epigenetic processes. However, Segev and Sass (1989a) proposed that both the stratiform and the veins within the clastic sediments are epigenetic in origin. Segev (1986) found sulfides which altered to paratacamite within the dolomite lithofacies and argued for a syngenetic origin having significant quantities of copper (Segev, 1992). Bar-Matthews (1986, 1987) and Bar-Matthews and Matthews (1990) suggested that the manganese and copper mineralization occurred within the dolomitic lithofacies under early diagenetic reducing conditions, whereas the stratiform copper and manganese ores were deposited under oxidizing conditions during diagenesis.

Electron microscopy and microanalysis study combined with stable isotope and thermodynamic calculations applied in the present study enable a better understanding of the processes and the geochemical conditions under which the different copper minerals were formed and will be discussed in this paper.

GEOLOGICAL BACKGROUND

The Timna Valley, 9 × 10 km² in size, is a semi-crater-shaped valley, truncated in the east by the Dead Sea Rift and surrounded by a 500-m-high sedimentary sequence of Cambrian and Cretaceous age. Garfunkel (1970) and Segev and Beyth (1983, 1986) studied the geology and mapped the Timna Valley (Fig. 3).

Within the Timna Valley, calc-alkaline to alkaline igneous rocks of late Precambrian age comprise the high structural block of Mt. Timna and they define the northernmost tip of the Arabian–Nubian shield (Garfunkel, 1980; Beyth, 1987; Shpitzer et al., 1991; Beyth et al., 1994). Uplift and peneplaination during the Early Cambrian marked the cessation of the Precambrian Pan-African orogeny. Early Cambrian sedimentation began with fluviatile subarkoses of the Amudei Shlomo Formation, which is overlain by dolostones, sandstones, and siltstones of the Timna Formation, representing a marine ingress of the late Early/Middle Cambrian age. The continental, Middle Cambrian subarkoses and siltstones of the Shehoret Formation (Fig. 2) overlie this marine unit.

Lower Cretaceous quartz-arenites of the Amir, Avrona, and Samar formations are conformably overlying the Cambrian sequence (Weissbrod, 1981). In the northern Timna Valley the Cambrian Formation and the Lower Cretaceous Amir and Avrona formations are cut by a basaltic plug and funnel-shaped vents with volcanioclastic fill (Weissbrod et al., 1990) of Lower Cretaceous age (Segev and Beyth, 1983). The Lower Cretaceous clastic units are covered by a thick series of platform carbonates (Judea Group), which build the upper part of the escarpment surrounding the Timna Valley (Figs. 2,3).

The Tertiary–Recent Dead Sea transform, a sinistral strike-slip fault system of about 100 km (e.g., Freund et al., 1970; Garfunkel, 1981) was formed by the breakup of the once-continuous Arabian–African continent. East from the Timna Valley it formed a deep basin fill by approximately 1700 m of clastic sediments (Segev et al., 1999, fig. 7, this issue). An intensive network of faults and joints, whose dominant direction is NW–SE, crosses the studied area.

METHODS

The geology of the Timna Valley and the sample locations are shown in Fig. 3. Samples were collected from the dolomitic, sandy, and shaly lithofacies. Copper minerals were separated mechanically and using heavy liquid methods. Clay minerals were separated after dissolution of carbonate with HCl 1:10 and then separated using decantation. The identification of Cu²⁺ within the clay minerals was determined using Nicolet FTIR spectroscopy. Mineral identification was done by Philips-PW 1820 XRD using Cu-Kα radiation. Clays were prepared using a back-pack method on a glass slide to enhance the basal reflection, and identified at room temperature without special preparation, after heating to 500 °C for 2 h and after treatment with glycol at 60 °C for 24 h (Moore and Reynolds, 1989). The determination of the degree of crystallinity of minerals from the chrysocolla group was made using Scherrer’s equation (Klug and Alexander, 1974).

The identification and distinguishing of the different copper phases within a sample was done using scanning electron microscope (SEM) JEOL-840 equipped with a back-scattered electron detector (BSE) and an energy-dispersive (EDS) Link 10000 system, and with an electron probe microanalyzer (EPMA) JEOL-8600 equipped with four wavelength-dispersive spectrometers (WDS). Most of the chemical analyses were done with the EDS using a correction for atomic number, absorption, and fluorescence known as the ZAF program (Goldstein et al., 1984).

The δ¹⁸O values of quartz and various copper silicate minerals were determined using conventional nickel bomb techniques (Clayton and Mayeda, 1963).
Fig. 4. (a) Field occurrence showing two copper sulfide spherules in the massive dolomite. Spherule A is a metallic copper sulfide surrounded by a green envelope of paratacamite. The contact with the host dolomite is sharp. The green spherule B is composed mainly of malachite and paratacamite, which replaced the original copper sulfide. (b) Irregular, metallic copper sulfide surrounded by a green envelope of paratacamite, which sends small veins into the host dolomite. Black spots are manganese dendrites. (c) Green laminae of paratacamite within the laminar dolomite alternating with darker clays rich-laminae. (d) Optical microscope image of several rounded green spherules of malachite and paratacamite within a network of thin laminae of paratacamite. (e) Round and elliptic-shaped dark, ocean- and midnight-blue-colored plancheite surrounded by pale-to-sky-blue chrysocolla in the sandy lithofacies. (f) Optical microscope image of veins of chrysocolla (light green) cutting through quartz (Q) grains, and in places, entirely replacing the quartz, forming round grains of chrysocolla (Chr) that mimic the original quartz texture. Scale as in Fig. 4d.
Isotope ratios were measured on a SIRA-II mass spectrometer. All analyses are reported as $\delta^{18}O$ (‰ SMOW) values. Isotopic analyses of sulfides were done after the sulfide minerals were hand-separated using a 0.5 to 2-mm driller. After washing the sulfide minerals with distilled water to remove any possible contamination with gypsum, they were chemically deposited as barite, and the extraction of the sulfur was done according to the method described by Coleman and Moore (1978). Further details of the analytical methods can be found in Shlomovitch (1995).

**COPPER MINERALIZATION WITHIN THE DOLOMITIC LITHOFACIES**

**Petrography and mineralogy of the sulfide minerals**

The sedimentological character of the Hakhlil Member and the Sason Member with its three lithofacies (dolomitic, sandy, and shaly) is described in detail by Segev (1986, 1992) and Segev and Sass (1989 a,b). The dolomitic lithofacies occurs mainly as massive coarse-grained dolomite, but the base of the section is composed of laminar dolomite. This lithofacies contains 0.06% copper on average, and at the base of this unit the copper concentration is higher and ranges from 0.68 to 1.77% (Segev, 1986, 1992). These dolomites are also enriched in manganese (1.7 to 2.8%) within the dolomite lattice (Bar-Matthews, 1986, 1987; Segev, 1986, 1992).

The copper ore within the dolomite occurs rarely as copper sulfides and dominantly as hydrated copper chlorides and carbonates (Segev, 1986; Shlomovitch, 1995). The mineralization in the massive dolomite occurs as small, one-tenth to a few millimeters, metallic-to-green-colored rounded spherules of copper sulfides (Fig. 4a), surrounded by a green envelope and having a sharp contact with the host dolomite. In places, the metallic sulfides have irregular shapes surrounded by a green envelope that sends small veins into the host (Fig. 4b). Within the laminated dolomite, the mineralization occurs as greenish thin (a few millimeters) laminae composed mainly of paratacamite (Cu$_2$(OH)$_3$Cl), alternating with clay and mica-rich laminae (Fig. 4c).

The copper sulfide minerals within the dolomite are mainly composed of djurleite (Cu$_{1.93}$S) and covellite (CuS), but also solid-solution varieties are common, mainly chalcocite (Cu$_{2-1.93}$S), digenite (Cu$_{1.8}$S), and anilite (Cu$_{1.75}$S). Djurleite forms the major part of the sulfide, with covellite occurring mainly as needles in sharp contact with the djurleite towards the outer part of the spherules and along cleavage surfaces (Fig. 5a,b). This textural relationship supports a solid-solution transition from djurleite to covellite, as was also described by Frueh (1954), Djurle (1958), Morimoto et al. (1969), and Morimoto and Koto (1970). All the sulfide minerals contain high concentrations of Ag (~0.13 to ~2.65 wt%), which increase with the decrease of Cu/S ratio. This relation suggests that Ag replaces Cu in the sulfide lattice as the acentite (Ag$_2$S) component, which is as a discrete mineral observed by SEM as thin veins and small inclusions (Fig. 5a,b). The acentite occurs usually with the covellite suggesting that they are genetically related. Voids can be seen when the surface of the copper sulfides is smooth and well preserved (Fig. 5c). These voids occasionally are filled with gypsum, quartz, K-feldspar, calcite, and native copper (Fig. 5c). This mineral assemblage suggests that they are trapped inclusions of the original sediment.

Copper carbonate, copper chlorides, and copper silicates within the sulfides

The metallic sulfides are almost always surrounded by a green envelope (Figs. 4a,b, 5a). This envelope is composed of copper hydroxides, usually malachite (Cu$_2$(OH)$_2$CO$_3$) and paratacamite (Cu$_2$(OH)$_3$Cl). Commonly, the malachite and the paratacamite completely replace the sulfide minerals (Fig. 5d) giving a green color (Fig. 4a, spherule b). Whereas malachite replaces the sulfides and mimics their round shape, paratacamite develops as veins from the rim of the spherules into the host dolomite, forming horizontal laminae along layers rich in micas and clays (Figs. 4d, 5e). The secondary development of paratacamite relative to malachite is evident also from observations in which secondary malachite occurs within the laminae of paratacamite (Fig. 4d). When quartz and feldspars are present within the sulfide spherules, veins of chrysocolla (Cu$_{2-x}$SiO$_4$(OH)$_2$·yH$_2$O) can be seen cutting them (Fig. 5f). The chrysocolla within the sulfides is rare and only restricted to the occurrence of silicate minerals (as will be discussed later). In addition, sporadically, very small (micron-size) crystals of Zn-rich mottramite Pb(Cu, Zn)(VO$_4$)(OH) are present.

Layers of detrital (mainly kaolinite) and authigenic (mainly illite) clays occur within the laminated dolomite. Copper occurs only within the authigenic clays, with concentrations of 500 to 4000 ppm. Infrared analyses indicate that the copper occupies the octahedral sites within the illite.
Fig 5. (a) Scanning electron microscope (SEM) with back-scattered image (BSE) of the sulfide spherule within the dolomite (darkest gray). Most of the sulfide is composed of djurleite (Dj). Covellite (Co) occurs along cleavage planes and at the outer surface of the spherule. Tiny white spots of acentite (Ac) are also observed. The darker envelope around the sulfide is malachite (Ma). (b) Close-up of 5a, showing the needles of covellite (Co) penetrating the djurleite (Dj). A thin vein of acentite (Ac) is observed. The sulfide is embedded within the host dolomite (Do). (c) SEM image of the surface of a sulfide spherule, showing micron-size pits. In places, the pits are filled with gypsum (Gy). (d) SEM-BSE image of a sulfide spherule within the dolomite (Do) which is almost entirely replaced by secondary malachite (Ma)—dark gray and paratacamite (Par)—lighter gray. (e) SEM-BSE image of several spherules composed of malachite (darker) and paratacamite (brighter) with a network of subhorizontal laminae of paratacamite veins within the dolomite (dark background). (f) SEM-BSE image of a sulfide spherule with djurleite (Dj) being the main mineral. Within the djurleite an ~50 µm quartz grain (Q) cut by a vein of chrysocolla (Chr) can be observed.
Fig. 6. Phase diagram of the system Cu$_{2-x}$S showing that the solid-solution copper sulfides assemblage of djurleite–covellite is typical of low-temperature conditions (after Morimoto and Koto, 1970). The shaded area represents the probable temperature of the growth of the sulfide minerals (see text for explanation).

Conditions for the formation of the copper sulfides and their oxidized products

The assemblage of the covellite, dignite, and anilite series is typical of a low-temperature assemblage (25–75 °C), as can be seen in the phase diagram in Fig. 6 (Morimoto and Koto, 1970). However, Bar-Matthews and Matthews (1990) showed that the upper temperature limit of 50 °C could have prevailed during dolomitization. On an Eh–pH diagram (Fig. 7) and at pH ~8 (corresponding to marine conditions), copper sulfides are only stable at lower Eh (reducing) conditions.

The stable isotope composition $\delta^{34}$S (CDT) of five well-preserved sulfide minerals from different spherules range from −13.7 to −14‰, indicating that they were all formed under similar conditions. If we assume a $\delta^{34}$S (CDT) of ~30‰ for the isotopic composition of the original sulfate from which the sulfide minerals were reduced (similar to Cambrian sulfates from elsewhere; Claypool et al., 1980), the fractionation between the sulfate to sulfide was ~44‰. At temperatures of 25–50 °C, the sulfate CuS (covellite) fractionation is $10^3 \times \ln \alpha = 75$ to 64 (data of Sakai, 1968 and Ohmoto and Rye, 1979) and complete oxidation of this sulfate would therefore lead to $\delta^{34}$S (CDT) values of ca. −45 to −34‰. The higher $\delta^{34}$S (CDT) values found for the covellite thus indicate that only partial reduction of sulfate occurred in the early diagenetic stages in the Cambrian Sea.

Whereas copper sulfide minerals in most occurrences in the world are associated with iron sulfides such as pyrite and chalcopyrite, in the Timna Formation these minerals are absent. This indicates that either iron was not present in the marine Cambrian environment (as was also observed for the primary manganese ore, Bar-Matthews, 1986, 1987), or that the conditions allowing copper sulfide to form with iron sulfides and copper-iron-sulfides were not developed.

The transition from reducing to oxidizing conditions that caused replacement of the sulfide spherules by malachite (Cu$_2$(OH)$_2$CO$_3$) clearly occurred in the presence of carbonate ion in solution. The Eh–pH diagram for the system Cu–H$_2$O–O$_2$–S–CO$_2$ indicates that this process requires an increase in Eh (see arrow, Fig. 8). In contrast, the replacement to paratacamite (atacamite in figure) requires the presence of chloride ion, but also the lowering of the pH (see arrow, Fig. 9). This suggests that the replacement of sulfide minerals
first occurred during changes in the conditions from reducing to oxidizing in the presence of carbonate solution species. Later on, a drop in the pH occurred in the presence of chloride solution causing the formation of paratacamite (Fig. 9). Whereas the oxidation of the sulfides to malachite was restricted to the original sulfide spherules, the paratacamite laminae developed far beyond into the dolomite, especially along layers rich in mica and clays, and clearly indicates higher mobility of the Cl—bearing solutions. Dissolution of primary clays and the formation of secondary authigenic clays within the dolomite were followed by adsorption of copper into the authigenic illite lattice. As pH continued to decrease, mottramite was formed (Gross and Bartura, 1984; Bar-Matthews, 1986, 1987; Shlomovitch, 1995).

**COPPER MINERALIZATION IN THE SANDY AND SHALY LITHOFACIES**

**Petrography and mineralogy of the copper silicate minerals**

The main copper mineralization, and the one that has been studied most intensively, is that occurring within the sandstones and the shales (Bentor, 1952, 1956; Milton, 1966; Wurzburger, 1970; Bartura and Wurzburger, 1974; Charrach et al., 1976; Lazar, 1982; Segev, 1986; Segev and Sass 1989a; Shlomovitch, 1995). Most of the earlier studies dealt with the description of the ore; here, we extend these studies into a detailed description of the paragenetic relationships among the various minerals and their stability fields at different Eh–pH conditions.

Most of the copper minerals in the sandy and shaly assemblages occur as copper silicates: chrysocolla and plancheite. Both minerals belong to a larger group of minerals with variable composition and color. Chrysocolla group minerals (usually light blue, Fig. 4e): Cu$_2$SeO$_4$(OH)$_4$yH$_2$O (Van-Oosterwyck-Gastuch, 1970) are poorly structured and contain 2 to 8 molecules of water (Hindman, 1985). Plancheite group minerals (turquoise and deep blue-purple color, Fig. 4e): Cu$_8$(Si$_4$O$_{11}$)$_2$(OH)$_4$yH$_2$O are more highly structured relative to the chrysocolla group minerals. Based on EDS analyses and X-ray diffraction, we found that the deeper blue color is associated with a reduction in number of water molecules and increase in the crystallinity, while the Cu/Si ratio remains almost constant, as shown in Fig. 10. Their field occurrence is of highly variable color, irregular shape, and discordant relation to the stratification throughout the clastic units (Fig. 4e). They occur mainly as cement to the sandstones (usually chrysocolla with dark blue color), and along fracture planes (light blue...
chrysocolla). Deep blue-turquoise plancheite occurs as elliptic bodies, from a few millimeters to a few centimeters in size, within the chrysocolla (Fig. 4e), from which smaller veins emanate, cutting through the sandy lithofacies into the dolomitic lithofacies. Petrographically, the copper silicate minerals replace clays, quartz, and feldspars (Figs. 4f, 11a). The replacement causes the etching of the surface of the silicate minerals (Fig. 11b), followed by precipitation of chrysocolla and plancheite. A secondary occurrence of chrysocolla with the lightest color and the highest amount of water occurs along fracture planes.

Other secondary minerals are: pseudomalachite (Cu₅(OH)₄PO₄) and diopside (CuSiO₃·H₂O) together with authigenic fluorapatite (Bartura and Gross, 1966). Paratacamite and malachite, which are common in the dolomitic lithofacies, are relatively rare in the sandy and silty lithofacies.

Thus, on the basis of the petrographic and field occurrence, three main stages operated during development of the copper ore in the sandy and shaly lithofacies. During the first stage, amorphous chrysocolla replaced clays, feldspars, and quartz. This stage was followed by the transition from an amorphous phase to a better crystallized phase, i.e., the formation of plancheite concretions and veins from chrysocolla. The third stage was the formation of chrysocolla along fracture planes.

**Thermodynamic conditions for the formation of chrysocolla**

The reactions involving the formation of chrysocolla during dissolution of silicate minerals are schematically described by the equations:

1. 2KAlSi₃O₈ + 2H⁺ + 9H₂O = H₄Al₂Si₂O₇ + 2K⁺ + 4H₄SiO₄
   
   K-feldspar

   and

   SiO₂ + H₂O = H₄SiO₄
   
   Quartz dissolved Silica

   and

   K₅(Al₃Si₃O₁₀)(OH)₂ + 3H₂O = H₄Al₂Si₂O₇ + K⁺ + Al₂O₃ + H₄SiO₄
   
   Illite

2. Cu⁺⁺ + H₄SiO₄ = 2H⁺ + CuSiO₃·H₂O
   
   Newberg (1967) crystallized chrysocolla under 25 °C at 1 atm and calculated the free energy of the idealized chrysocolla-forming reaction:

   \[ \Delta G^0(R) = -31.11 \text{ kJ/mol.} \]
is described by a straight line parallel to the log$\text{H}_2\text{SiO}_4$ axis, cutting the intersection of the lines for 1 and 2 (Fig. 12). The stability field of chrysocolla is bordered by those of quartz and solution, and shows that chrysocolla can be formed by reaction between quartz solution (either by decrease in $a\text{H}^+$ or increase in $a\text{Cu}^{++}$). This process is consistent with the petrographic evidence for dissolution and etched pits on quartz.

The isotopic composition ($\delta^{18}$O) of quartz, silica (chert), chrysocolla, and plancheite and their mode of occurrence are given in Table 1. Five different groups can be recognized: quartz with $\delta^{18}$O (SMOW) values of 10 to 12‰, cherts with 22.9 to 25.9‰, plancheite concretions 12.3 to 15.2‰, chrysocolla as cement to sandstones 15.2 to 16.5‰, and chrysocolla along fracture planes 17.5 to 18.7‰. The quartz $\delta^{18}$O values are consistent with a detrital origin as igneous minerals, as found by Bar-Matthews and Matthews (1990). The isotopic composition of the chert, however, is lower than generally found in marine cherts. This suggests that the chert origin may have been influenced by groundwater, as Kolodny et al. (1980) have also suggested for the Mishash cherts. A possibility is that the chert represents dissolved silica that has precipitated at $a\text{Cu}^{++}/a\text{H}^+$ ratio outside the chrysocolla field in Fig. 12. In this case, the lower $\delta^{18}$O values of the chrysocolla minerals possibly represent precipitation from the same ($\delta^{18}$O) water that formed the cherts. The highest $\delta^{18}$O values are of chrysocolla along fracture planes (~18‰) (about 2‰ higher than chrysocolla as cement to the sandstone), suggesting later precipitation of chrysocolla along fracture planes. Plancheite formation leads to a slight decrease in $\delta^{18}$O.

<table>
<thead>
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<th>$\delta^{18}$O (‰ SMOW)</th>
<th>Mode of occurrence</th>
<th>Mineral</th>
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<tr>
<td>+10.00</td>
<td>detrital grains</td>
<td>quartz</td>
</tr>
<tr>
<td>+12.07</td>
<td>detrital grains</td>
<td>quartz</td>
</tr>
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<td>detrital grains</td>
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<tr>
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<tr>
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We assume the main component of Cu in solution is $\text{Cu}^{++}$ (aq), with $\text{H}_2\text{SiO}_4$(aq), $\text{SiO}_2$(s), and $\text{H}_2\text{O}$(l). $\text{Cu}^0$, $\text{Cu}_2\text{O}$, $\text{CuO}$, $\text{Cu(OH)}^+$, $\text{Cu(OH)}_0$, and $\text{Cu(OH)}_2$ usually either present in low concentrations or are not stable in natural environments (Hindman, 1985). From the value of $\Delta G^o(R)$, we have calculated the free energy of formation of chrysocolla ($\Delta G^f$ chrysocolla). $\Delta G^o$ values used in the following calculations are from: $\text{Cu}^{++}$(aq) (Handbook of Chemistry, 1990–91), $\text{H}_2\text{SiO}_4$(aq) and $\text{SiO}_2$(s) (Stumm and Morgan, 1981) and $\text{H}_2\text{O}$(l) (Garrels and Christ, 1965; Stumm and Morgan, 1981).

Thus:

$$\Delta G^o(R) = \Delta G^o(\text{chrysocolla}) - [\Delta G^o(\text{Cu}^{++}) + \Delta G^o(\text{H}_2\text{SiO}_4)]$$

$$-37.112 = \Delta G^o(\text{chrysocolla}) + 1251.18$$

$$\Delta G^o(\text{chrysocolla}) = 1288.29 \text{ kJ/mol}.$$
DISCUSSION AND CONCLUSIONS

The main copper ore body is located in the upper Sasgon Member of the Timna Formation. The dolomitic lithofacies of the Sasgon Member consists of early diagenetic assemblages that include copper sulfides and their hydroxide products. The sandy and shaly lithofacies host the late epigenetic assemblages, which include only oxidized copper minerals.

Spherical (0.1 to a few millimeters) copper sulfides are randomly distributed throughout the dolomitic lithofacies, with djurleite and covellite being the main sulfide minerals and with minor concentrations of chalcocite, digenite, and anilite. They contain silver as a significant minor element (0.13–2.65 wt %) and as an independent mineral, acentite. They also form a solid solution, typical of sedimentary low-temperature assemblages. The $\delta^{34}S$ values (−14‰ CDT) indicate bacterial reduction processes, which partially reduced marine sulfate to sulfide ($H_2S$), leading to copper sulfide deposition. The copper sulfides were deposited during early diagenetic stages in a shallow basin (reducing) environment.

Oxidation and hydration reactions during and post-dolomitization resulted in the development of secondary carbonate and hydroxy-chloride-copper minerals. The paragenetic order, in which malachite formed first and paratacamite later, was a function of changes in $Eh$, $pH$, and the solution chemistry (mainly carbonate to chloride). Unlike malachite, which armored sulfides, paratacamite formed veins that originated from altered sulfides and penetrated the dolomite host rock. Paratacamite mobilization was due to the presence of chloride-bearing solutions, which allowed high metal mobility due to the stability of copper-chloride aqueous complexes. The penetrative length of paratacamite veins depended on the character of the host dolomite. Mottramite marked the end of the epigenetic stages, characterized by the development of a low $pH$ (<4) microenvironment within the sulfides.

The main copper mineralization is concentrated within the sandy and shaly lithofacies and contains epigenetic secondary copper minerals in the following paragenetic order: chrysocolla, plancheite, pseudomalachite, and diopside. Chrysocolla was created as a result of reaction between copper-bearing minerals and silicate minerals in the host rock (clay, K-feldspar, and quartz). The copper minerals feature a range of several amorphous minerals with different water contents. Following deposition, the chrysocolla stabilized into plancheite. The last stage of mineralization was the remobilization and redistribution of copper-bearing solution and the precipitation of light blue chrysocolla on fracture planes and as fracture fillings.

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