# Mineralogy of the near-surface expression of Au-As-Cu mineralization in an arid environment

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# Abstract

In the arid, Late Precambrian terrain of southern Israel, a complex suite of minerals and amorphous species were deposited in host gneiss from fluids under near-neutral conditions within 1 m of the surface. The morphology of secondary gold appears to relate to its host mineral (skeletal-dendritic with quartz; multi-faceted crystals with arsenates; spherical droplets with iron oxide). The gold is very fine-grained, and was most likely complexed as a thiosulphate.

Three amorphous phases are present (iron oxide, chrysocolla, Cu-Mn-(Fe-As) silicate). At least in part, gold and baryte appear to have crystallized out of a metal–Fe-oxide gel. Other minerals, including apatite, anglesite, and conichalcite, may have grown from appropriate crystallites present in the gel.

The conichalcite occurs mainly as bladed to acicular radial spherulites. In the presence of lead, a solid solution phase between duftite and conichalcite ('Pb-conichalcite') was formed.

KEYWORDS: secondary Au-As-Cu minerals, conichalcite, gold, arid environment

#### Introduction

An Au-As ephemeral stream sediment anomaly in the Late Precambrian terrain in southern Israel (Bogoch *et al.*, 1993) led to the discovery of *in situ*, gneiss-hosted gold-bearing mineralization. The latter was sampled from exposures close to the surface and consists of a suite of arsenate, sulphate, phosphate, oxide and silicate minerals (partly as amorphous species), together with gold. Sulphide minerals are absent.

The close spatial association of all species in this complex mineral suite within the very limited (examined) vertical depth interval of 0-1 m, and the consistently arid conditions in an open weathering environment, suggests that depositing fluids were neutral to mildly acidic (Mann, 1984), and well oxygenated.

Morphological and chemical data are presented and these are used in an attempt to constrain the nature of mineral growth and of the depositing fluids in the near-surface environment.

Mineralogical Magazine, June 1994, Vol. 58, pp. 315–323 © Copyright the Mineralogical Society

#### Methods

Powders of mineral concentrates were analysed using a Philips PW1730/1710 X-ray diffractometer with Cu-K $\alpha$  radiation. Mineral analyses were made using a JEOL 840 scanning electron microscope with an attached Link 10,000 energy dispersive spectrometer (EDS) using the ZAF4 program for polished sections (comparison with standard block files). The accuracy is better than  $\pm$  5%.

# **Field description**

The Au-As-Cu mineralization is located some 5 km NW of the town of Elat (northern extremity of the Red Sea, Fig. 1). The area is topographically rugged and the climate arid (rainfall of <30 mm/yr).

The Precambrian terrain of southern Israel is part of the Proterozoic Arabo-Nubian Shield. The mineralization is hosted within strongly foliated

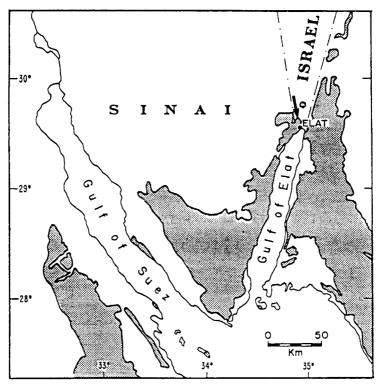


FIG. 1. Outline of northern part of Arabo-Nubian Shield (dark) showing location of study area (arrow).

	а	b	с	d	e
CuO	31.6	30.8	28.6-32.2	1.42	24.9
CaO	22.8	23.1	21.8-25.8	1.33	16.9
As <sub>2</sub> O <sub>5</sub>	42.6	42.2	39.6-44.6	1.66	42.4
PbŌ	-	-	-	-	12.7
ZnO	-	-	*	-	-
Total	95.0				96.9

TABLE 1. Analyses of conichalcite (wt.%).

a – Conichalcite, representative analysis

- b Average of 12 analyses
- c Range
- d Standard Deviation
- e Plumbian conochalcite

\* – One sample contained 1.1% ZnO

and fissile gneiss of quartz-dioritic composition. It is composed of plagioclase, quartz, and biotite with minor hornblende, magnetite, chlorite, and epidote. Rhyolitic and lesser intermediate dykes are present. Soils are absent.

The visible mineralization in the field consists of rust-coloured yellowish brown iron oxide, light green minerals (determined as arsenate, see below), and iron oxide-stained quartz. The most common features are iron-oxide zones mainly in the form of fracture fillings and veins (from <1 to c. 20 cm in width), and replacement or alteration zones, occassionally several metres in length. The disposition of these linear features is largely controlled by the NE-SW trending foliation, although cross-cutting veinlets are present. Between these zones, the country rock is relatively fresh.

Quartz veins and pods from < 1 cm to c. 20 cm are present and tend to be disconformable to the trend of the metamorphic host rock. Some of these contain iron-oxides within internal fracture surfaces, and green arsenate is present locally as fracture coatings and vug linings.

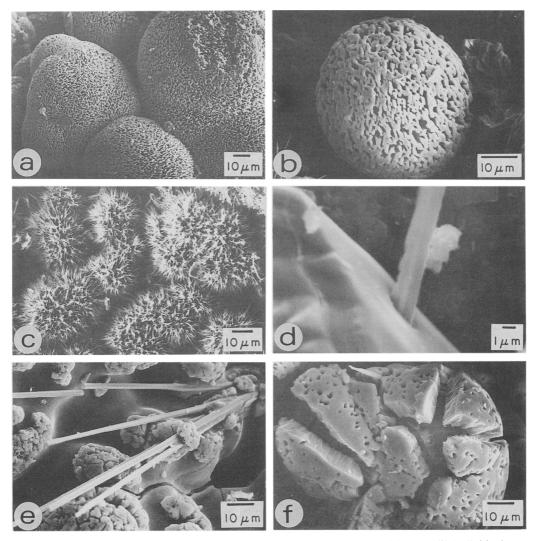


FIG. 2(a-f). SEM micrographs of: (a) Aggregates of radial-spherulites of conichalcite; (b) Individual, near perfect sphere consisting of conichalcite blades; (c) Acicular conichalcite spherulites; (d) Single conichalcite blade rooted in gypsum; (e) Cauliflower-like protuberances of conichalcite (on chrysocolla) with later conichalcite blades; (f) Individual cauliflower-like conichalcite showing septarian-like cracks. Note fibrous appearence (arrow) and 'holes' which may have contained acicular or bladed crystals.

Although sulphides were not noted in this mineralized showing, a single quartz vein occurring some 500 m to the southwest contains gold, minor arsenate, and traces of arsenopyrite, chalcopyrite and galena.

# Secondary minerals

With the possible exception of vein quartz, all the minerals observed in the occurrence are considered

to have a secondary origin in the sense that they either (1) precipitated from fluids containing cations and anions derived from the dissolution of primary ore-, gangue- and country rock minerals, or (2) formed by direct replacement. Certain of the species are amorphous without visible crystalline features.

Arsenates Two arsenates are present, the relatively abundant conichalcite (Cu-Ca arsenate) and very rare plumbian conichalcite (Cu-Ca-Pb arsenate). Their chemical analyses are given in Table 1.

Conichalcite occurs mainly in two forms: (1) aggregates of sub-spherical shapes (Fig. 2a), or in places as isolated, near perfect spheres (Fig. 2b), generally varying in diameter between 10 and 50  $\mu$ m. These are built of radiating acicular (Fig. 2c) to blade-like crystals, with pointed to rhombohedral terminations. The bladed forms also occur in isolation (Fig. 2d); (2) cauliflower-like protruberances with an amorphous appearence, but apparently formed from very fine, dense, radiating fibres (Fig. 2e-f). In places, these have radial-outward cracks, not unlike septarian (dessication) cracks in certain concretions. Accicular crystals, also of conichalcite, locally grow outward from the cauliflower-like forms; in one case, long ( $c.100 \mu m$ ) needles of conichalcite are rooted in one, and enveloped by another cauliflower-like form (Fig. 2e). The Cu-Ca-Pb arsenate occurs as euhedral, rhomboform to bladed crystals,  $1-2 \mu m$  in width.

Conichalcite is a member of the isostructural adelite group of arsenates (Palache et al., 1951). The chemical analyses obtained here are similar to those reported for end-member conichalcite (Palache et al., 1951; Radcliffe and Simmons, 1971) and for its theoretical composition (Qurashi and Barnes, 1963). Jambor et al. (1980) have shown that extensive binary solid solutions (Cu-Zn and Pb-Ca substitutions) are present among conichalcite (CaCuAsO<sub>4</sub>OH), austinite (CaZnAsO<sub>4</sub>OH) and duftite (PbCuAsO<sub>4</sub>OH) and all of the adelite group. The composition of the (zinc-free) Cu-Ca-Pb arsenate noted in the present study lies close to the range of values for 'plumbian conichalcite' (Jambor et al., 1980), and thus represents a solid solution between duftite and conichalcite.

Sulphates One hydrous and three anhydrous sulphate minerals were recognized. In order of decreasing abundance, these are gypsum (moderate), baryte (moderate), anglesite and celestite (both rare).

Gypsum occurs as idiomorphic, somewhat flattened rhombs up to several mm in size. Celestite, which was noted in only one sample, has a similar habit, but exhibits pyramidal terminations. Baryte veinlets in conichalcite consist of tabular crystals,  $<5 \mu$ m in width, and as flat platelets (parallel to 001, with well developed 100 and 210 faces), in iron oxide (Fig. 3a). Intergrown baryte crystals with acicular to bladed conichalcite were also recorded (Fig. 3b).

Anglesite occurs in both elongated and stubby prismatic forms, the latter with partially preserved pyramidal terminations. (Fig. 3c-d).

*Phosphates* Apatite occurs in most samples but in minor amounts. It is consistently idiomorphic as short, prismatic crystals (Fig. 3*e*).

Oxides. The abundant iron-species in the mineralization (field-termed limonite) is amorphous to XRD. Most occurrences consist of varying amounts of iron oxide and water, although up to 1% Cu is present locally. It appears either with a 'smooth' (amorphous) surface, or commonly with 'botryoidal' protruberances (Fig. 3/). In both cases, apparent dessication cracks are present.

Silicates. Chrysocolla is reasonably common, occurring in two modes: smooth surface, or as concretionary- or mushroom-like forms consisting of outward radiating fibres  $< 1 \mu m$  in width (Fig. 4a). It should be noted that one analysis of material with an appearance similar to the amorphous variety of chrysocolla yielded c. 9 wt.% total Fe oxide (Table 3). This is considerably higher than the maximum value (2%) reported by Dana (1911) and may indicate an admixture.

One amorphous compound with a consistent chemical composition is present in small amounts (Cu-Mn-(Fe-As) silicate) (Table 2). This exhibits a smooth surface with dessication cracks (Fig. 4b). Secondary quartz is rare, occurring as small clusters or single, tiny, idiomorphic crystals. Kaolinite is sporadic but widespread.

TABLE 2. Analyses of silicates (wt.%)

	а	b	с	d
	37.4	29.1	25.9	22.5-33.1
SiO <sub>2</sub> Al <sub>2</sub> O <sub>3</sub>	2.7	3.7	6.9	6.0-9.0
FeO	0.8	9.1	4.9	3.2-8.9
CaO	3.6	-	2.4	1.5-3.8
CuO	39.7	35.7	32.2	24.6-36.2
As <sub>2</sub> O <sub>5</sub>	-	-	1.4	<-2.2
MnO	0.2	0.4	21.3	14.3-23.3
TiO <sub>2</sub>	-	1.9	0.3	<-1.1
MgŌ	0.1	-	2.2	1.5-3.8

a – Chrysocolla

b - Fe-bearing chrysocolla

c - Cu-Mn-(Fe-As) silicate, average of 6 analyses

d – Range

< - not detected

Gold. The crystal habit of the gold appears to relate to its host mineral association. In quartz it was found as flattened, paint-like, dendritic grains, rarely up to 20  $\mu$ m in maximum length (Fig. 4c). In the arsenates, it occurs as somewhat flattened

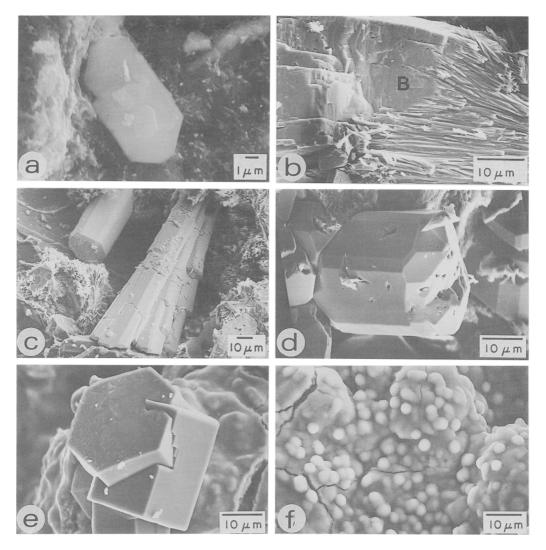


FIG. 3(a-f). SEM micrographs of: (a) Baryte platelet in amorphous iron oxide; (b) Intimately intergrown baryte (B) with conichalcite blades; (c) Elongated prisms of anglesite; (d) Partial pyramidal terminations of anglesite crystal; (e) Intergrown idiomorphic apatite crystals; (f) Amorphous, botryoidal iron oxide with dessication cracks.

(occasionally equant), multi-faceted crystals (tetrahedral faces?), less than 1  $\mu$ m in diameter (Fig. 4*d*-*e*). In botryoidal iron-oxide, the gold occurs as spherical 'droplets', < 1  $\mu$ m in size (Fig. 4*f*). Silver was not detected by EDS analyses.

### Relationships between the secondary minerals

Iron oxide and kaolinite are the only species noted to replace host gneiss minerals. The iron oxide, together with chrysocolla, the amorphous Cu-Mn-(Fe-As)-silicate, and quartz, all occur, at least locally, directly on the host rock. All of the arsenates, sulphates, phosphate and silicates are present in the iron oxide. The arsenates and iron oxide occur directly on vein quartz. Conichalcite also occurs on chrysocolla, and blades are locally rooted in gypsum. Baryte veinlets cross conichalcite, but apparent equilibrium textures between them are also present. Quartz is rarely present in

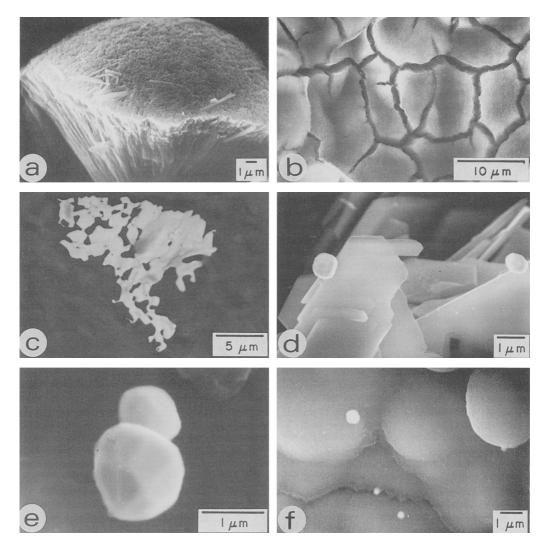


FIG. 4(a-f). SEM micrographs of: (a) Fibrous, mushroom-shaped chrysocolla; (b) Amorphous Cu-Mn-(Fe-As) silicate with dessication cracks; (c) Flat, dendritic gold (in vein quartz); (d) Multi-faceted, gold crystals on Cu-Ca-Pb arsenate (plumbian conichalcite); (e) Possible tetrahedral faces of near-equant gold crystal (from conichalcite concentrate); (f) Gold droplets (white) on botryoidal iron oxide.

#### Discussion

conichalcite. Gold occurs with vein quartz, both arsenates, and iron oxide. A precise paragenetic sequence is thus difficult to establish. Nevertheless, of the main phases, a coarse depositional sequence may have been (1) iron oxide, (2) gypsum (3) chrysocolla, and (4) conichalcite and baryte. Gold precipitated together with the iron oxide and the arsenates.

Since country rock alteration (iron-oxide and, to a lesser extent, kaolinite) and secondary mineralization are spatially associated and confined to the same local sites (i.e. there is no alteration without mineralization, and vice versa), it is therefore probable that the secondary mineral suite developed close to the site of primary sulphides. Traces of arsenopyrite, chalcopyrite and galena in the distal quartz vein are the only possible hint of the nature of hypogene(?) sulphides. Such a suite (together with pyrite) within quartz veins and locally disseminated in the country rock could have been the source for all or part of the As, Cu, S, Au, and Fe (Au as either free gold in quartz or as inclusions within arsenopyrite). Alteration/ replacement of the host rock could yield additional Fe, plus the required Ca, Al, Mn, P and probably Ba and Sr. The relative localization of supergene minerals (after primary ore) was also noted by Bowell (1992).

The area has been under arid conditions since the Late Pleistocene (E. Zilberman, pers. comm.). Oxidation zones have been found to a depth of 80 m even in very arid areas (Cabello, 1985), and the mobility of gold and various metal ions in similar environments has been established (Mann, 1984; Andrade et al., 1991; Vasconcelos and Kyle, 1991). The stability of the arsenates in a carbonate-poor environment (Robins, 1981; Richardson and Vaughan, 1989), and the probable dissolution of sulphides in an arid environment, suggest neutral to mildly acidic, oxidizing conditions. Both conichalcite and duftite are stable under these conditions (Magalhaes and Pedrosa de Jesus, 1988), and a local increase in the activity of Pb could yield the plumbian-conichalcite in place of the Pb-free end member. The presence of apatite indicates that the solutions were above pH 5 (Nancollas, 1980).

The main varieties of ligand complexes for gold transport in supergene solutions are hydroxyl-, halide-, thiosulphate-, cyanide- and organic-Au complexes (Bowell, 1992). The essential lack of organic matter precludes the formation of cyanide- or organic-based complexes. Based on the relative abundance of sulphur-bearing species (high S activity), and the apparent absence of halides, thiosulphates (or other S-bearing ligands) appear to be the most likely metal complexing agents. Lakin et al. (1974) and Webster (1986) indicated that  $Au(S_2O_3)_2^{3-}$  is relatively stable in a natural environment, and Andrade et al. (1991) suggested that complexing by thiosulphate near oxidizing sulphide deposits would be a viable process in arid regions. The botryoidal and smooth (amorphous) surface texture of the iron oxide, which is the dominant secondary phase, is considered evidence for its precipitation from a fluid-Fe-oxide sol (Saunders, 1990).

Colloidal iron oxide will preferentially aggregate (gel or coagulate) at high concentrations and in the presence of an electrolyte which will promote bridging between the iron oxide colloidal particles (Tipping and Ohnstad, 1984). Many of the minute spherical droplets of gold associated with this iron oxide are in the range of colloidal particle size  $(0.05-0.5 \ \mu\text{m})$ . Tipping (1981) and Weiser (1933, quoted in Saunders, 1990) indicated that colloidal gold nucleates as spherical particles. Colloidal gold occurs in natural, near-surface environments (e.g.Bergeron and Harrison, 1989), and experimental studies by Enzweiler and Joekes (1991) have shown that colloidal gold adsorbs to a large extent on colloidal iron oxides at ambient temperatures. The destabilization of such an Au-Fe-oxide mutual coagulation would possibly result in the texture found herein (Fig. 4f).

Since the sulphate, phosphate and arsenate minerals are largely (or uniquely) rooted in the colloid-derived iron oxide, certain of these may also have crystallized out of a metal—Fe-oxide gel. Based on experimental data, the only evidence for this are the tiny baryte platelets (Fig. 3a) which are remarkably similar to those grown artificially in a silica gel medium from a supersaturated solution (Prieto *et al.*, 1992; see their Fig. 4). Other minerals such as apatite and anglesite may also, in part, have formed in a similar manner. They appear to have nucleated on or slightly below the iron oxide surface, possibly as colloidal expulsions; crystal growth could then have proceeded from this seed or crystallite.

The Cu-Mn-(Fe-As)-silicate, as well as the 'smooth surface' chrysocolla have a colloform texture and may also represent (very local) deposition from a gel or coagulate.

Chrysocolla and conichalcite occur as radiating spherulite forms. Grigor'ev (1965) described three modes for spherulite formation: (1) overgrowth of crystals on a pre-existing spherical body; (2) growth on accumulations of differently oriented crystallites (3) growth from a split crystal. Split crystal growth is considered to result in reniformlike aggregates in minerals such as malachite and hematite, suggesting a similar mechanism for the mushroom-like, fibrous chrysocolla, and for the cauliflower-like, fibrous protruberances of conichalcite. The blade-like and acicular crystal spherulites of conichalcite could have resulted from overgrowths on cauliflower-like forms, or from an accumulation of crystallites on, for example, 'spherically'-shaped botryoidal iron oxide.

In addition to the micro-spheres of colloidal gold in iron oxide, gold also exhibits 'crystalline' modes as dendritic grains in quartz, and multi-faceted crystals in the arsenates ( $< 1 \mu m$ ). Flat dendritic gold was considered by Vasconcelos and Kyle (1991) to be supergene in origin. The apparent high degree of fineness of the gold also

suggests that they were also deposited from supergene fluids (Webster and Mann, 1984). The shape of the somewhat flattened gold crystals may have been controlled by the crystallography of the arsenate substrate (Grigor'ev, 1965). The close spatial relationship between these gold crystals and the arsenates strongly suggests that they were precipitated simultaneously (largely onto the amorphous iron oxide substrate) from the same fluid phase which probably originated as meteoric water.

#### Summary and conclusions

(1) Neutral to mildly acidic water of probable meteoric origin in an arid environment resulted in the alteration/dissolution of highly localized, disseminated sulphide mineralization and host intermediate gneiss.

(2) The fluid became enriched in Fe, As, Cu, Au, Ca and S, with lesser Mn, Pb, P and Sr, and a complex suite of arsenates, sulphates, phosphate, oxide and silicates were deposited close to the site of the 'primary' sulphides.

(3) Three possible colloid-derived phases are present (iron oxide, chrysocolla, Cu-Mn-(Fe-As) silicate). At least in part, gold and baryte appear to have crystallized out of a metal-Fe-oxide gel, as suggested by recent experimental studies. Other minerals, including apatite, anglesite, and the abundant radial spherulites of conichalcite, are largely rooted in the iron oxide and may have grown from appropriate crystallites present in the gel.

(4) In the presence of lead, a solid-solution phase between duftite and conichalcite ('Pbconichalcite') was formed. Gold crystallized together with the arsenates.

(5) The morphology of the secondary gold appears to relate to its host mineral: skeletaldendritic with quartz; crystalline with the arsenates; 'exsolved' droplets with the iron oxide. The gold is fine-grained and may have complexed as a thiosulphate.

### Acknowledgements

We thank Ya'acov Raphael, Rami Madmon, Sa'adya Levy and Yehuda Peled for technical assistance. Michael Dvorachek is particularly thanked for assistance with SEM analyses and photographs. Comments on the text by Y. Nathan, A. Segev and the journal referees are gratefully acknowledged.

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[Manuscript received 20 April 1993: revised 15 July 1993]