The Canadian Mineralogist
Vol. 31, pp. 945-956 (1993)

THE FORMATION OF ATACAMITE DURING WEATHERING OF SULFIDES ON THE MODERN SEAFLOOR*

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ABSTRACT

Atacamite [$Cu_2Cl(OH)_3$] is a common secondary mineral in the oxidized portions of black smoker deposits on the modern mid-ocean ridges. Weathered seafloor sulfides from the TAG Hydrothermal Field (Mid-Atlantic Ridge) contain abundant Fe oxyhydroxides, jarosite, and secondary copper minerals. All three polymorphs of $Cu_2Cl(OH)_3$, atacamite, paratacamite and the rare mineral botallackite, have been identified in samples recovered from the seafloor gossans at TAG. Atacamite forms when cuprous chloride complexes and Cu^{2+} ions are released from sulfides during corrosion by acidic pore-fluids. The copper ions migrate in solution through the gossans and reprecipitate as basic cupric salts in contact with the surrounding seawater. The atacamite and paratacamite occur as colloform masses, crystalline aggregates, or disseminations within amorphous Fe oxyhydroxides, goethite, jarosite, and secondary Cu sulfides. Botallackite is present as sparse corroded crystals. Gibbs free-energy data for atacamite and paratacamite indicate that $Cu_2Cl(OH)_3$ is the most stable salt of copper in the seafloor weathering profile, and solubility calculations show that it is only sparingly soluble in seawater. Observations at TAG suggest that the atacamite in gossans overlying the deposits may have been present on the seafloor for as long as 20,000 years and possibly 40,000–50,000 years. Contrary to recent suggestions in the literature, atacamite does not form on the modern seafloor under hydrothermal conditions. The susceptibility of atacamite to hydration and dissolution in fresh water accounts for its absence in most surficial environments and precludes its long-term preservation in the geological record.

Keywords: atacamite, paratacamite, botallackite, Fe oxyhydroxides, seafloor weathering, sulfide gossans, TAG hydrothermal field, Mid-Atlantic Ridge.

SOMMAIRE

L'atacamite [$Cu_2Cl(OH)_3$] est un minéral secondaire répandu dans les parties oxydées des gisements associés aux fumeurs noirs le long des dorsales médio-océaniques modernes. L'altération des sulfures des fonds marins du champ hydrothermal de TAG (dorsale médio-Atlantique) contient une abondance d'oxydes de fer, de jarosite, et des minéraux secondaires du cuivre. Les trois polymorphes de $Cu_2Cl(OH)_3$, atacamite, paratacamite, et même botallackite, espèce rare, ont été identifiés dans les échantillons prélevés des chapeaux de fer. L'atacamite se forme quand les complexes chlorurés de cuivre (cupreux) et les ions Cu^{2+} sont libérés des sulfures pendant leur corrosion par une phase fluide à caractère acide. Les ions de cuivre se propagent en solution à travers des chapeaux de fer et forment un précipité de sels basiques cupriques au contact avec l'eau de mer ambiante. L'atacamite et la paratacamite se présentent en masses colloformes, en agrégats cristallins, ou en disséminations au sein de masses d'oxydes amorphes de fer, de goethite, de jarosite, et de sulfures secondaires de cuivre. La botallackite se présente sous forme de cristaux épars corrodés. Les données sur l'énergie libre de formation de l'atacamite et de la paratacamite montrent que $Cu_2Cl(OH)_3$ est la forme la plus stable de cuivre dans le milieu sous-marin près des zones d'altération. Des calculs de solubilité démontrent que ces phases sont très peu solubles dans l'eau de mer. Les observations à TAG font penser que l'atacamite des chapeaux de fer qui recouvrent les gisements pourraient avoir été formés il y a au moins 20,000 ans, et peut-être même 40,000–50,000 ans. Contrairement à une opinion émise récemment dans la littérature, l'atacamite n'est pas précipitée directement sous conditions hydrothermales dans les fonds océaniques modernes. Sa susceptibilité à être hydratée et dissoute dans l'eau fraîche rend compte de son absence dans la plupart des milieux de surface, et explique son absence dans les roches plus anciennes.

(Traduit par la Rédaction)

Mots-clés: atacamite, paratacamite, botallackite, oxydes de fer, lessivage sous-marin, chapeau de fer, sulfures, champ hydrothermal de TAG, dorsale médio-Atlantique.

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* Geological Survey of Canada contribution number 44492.

INTRODUCTION

In its type locality, the Atacama Desert in the high Andes of northern Chile, the basic cupric chloride, atacamite [$Cu_2Cl(OH)_3$], occurs in the oxidized zones of exposed porphyry copper deposits (*e.g.*, Bandy 1938). The rapid descent of the water table through these deposits and the onset of a sustained, hyperarid climate in the Miocene have resulted in the preservation of abundant secondary copper sulfide, sulfate, and chloride minerals within a thick weathering profile (Mortimer 1973, Alpers & Brimhall 1988, 1989). The Atacama Desert is now one of the driest places on the surface of the earth. In stark contrast to this environment, atacamite also is commonly found as a secondary mineral in the weathered portions of massive sulfide deposits on the modern seafloor. This paradox owes itself to the unique physical and chemical behavior of atacamite in natural environments.

Atacamite was first reported from the modern seafloor by Bonatti *et al.* (1976). They noted the occurrence of secondary atacamite in disseminated and stockwork-type veinlets of chalcopyrite exposed in basaltic crust uplifted along fracture zones on the Mid-Atlantic Ridge. A similar occurrence was noted by Scott *et al.* (1982). The atacamite in both cases occurs with other secondary Cu oxide, Cu sulfide and Fe oxide minerals, and was interpreted to be a product of seafloor weathering of the chalcopyrite veins. Atacamite has since been described in weathered sulfides from most of the known black smoker deposits forming on the mid-ocean ridges, and it is especially abundant at fossil hydrothermal sites, where sulfides have experienced a long history of submarine weathering (*e.g.*, Hekinian & Fouquet 1985, Alt *et al.* 1987, Alt 1988a, b, Embley *et al.* 1988, Scott *et al.* 1990, Vanko *et al.* 1991). Despite the numerous documented occurrences of atacamite on the modern ocean floor, few studies have addressed the physical and chemical conditions under which it forms. This paper examines the mineralogy, chemistry, and paragenesis of atacamite in samples recovered from the TAG Hydrothermal Field on the Mid-Atlantic Ridge (26°N). The samples were collected by dredging of a large sulfide mound in 1985 and during submersible operations with ALVIN in 1986 and 1990.

OCCURRENCE OF ATACAMITE IN THE TAG HYDROTHERMAL FIELD

The TAG hydrothermal field comprises three large sulfide mounds, one active and two inactive. The active mound occurs on the floor of the rift valley and is a large, steep-sided deposit measuring 200–250 m in diameter and 20–40 m in height, with a vigorous central black smoker complex and an apron of oxidizing sulfide talus and metalliferous oxide sediments (Rona *et al.* 1986, Thompson *et al.* 1988, Metz *et al.* 1988). Two additional inactive sulfide deposits occur on the east wall of the rift valley and are currently undergoing extensive erosion and mass-wasting (Rona *et al.* 1990, 1993). The largest sulfide deposits have been exposed to seawater possibly for as long as 40,000–50,000 years (Lalou *et al.* 1990), and parts are now covered by extensive deposits of Fe oxyhydroxides (up to several tens of centimeters thick). These *gossans* resemble the weathered caps on many ancient sulfide deposits now exposed on land, and are apparently a product of similar processes of oxidation taking place on the seafloor (*e.g.*, Herzig *et al.* 1991).

Pyrite, marcasite, and chalcopyrite have been altered extensively to secondary mineral assemblages consisting mainly of amorphous Fe oxyhydroxides, together with abundant secondary Cu sulfides, jarosite, atacamite, and traces of native copper and native gold. The oxidizing sulfide mound contains acidic pore-

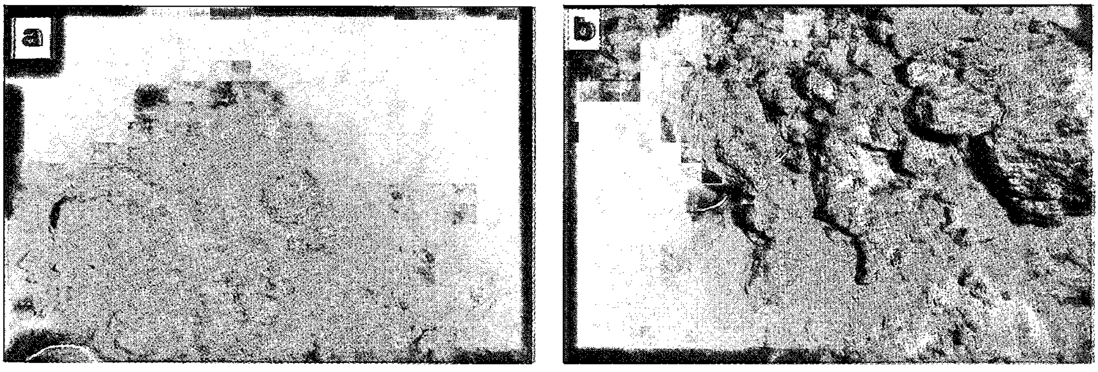

FIG. 1. Bottom photographs taken from the submersible ALVIN showing the weathered and oxidized surface of the TAG Mound. The greenish color of the outcrop is due to the presence of abundant atacamite, for which this part of the deposit has been labeled the "green cliffs". Approximate field of view is 3 meters in photo (a) and 1 meter in photo (b).

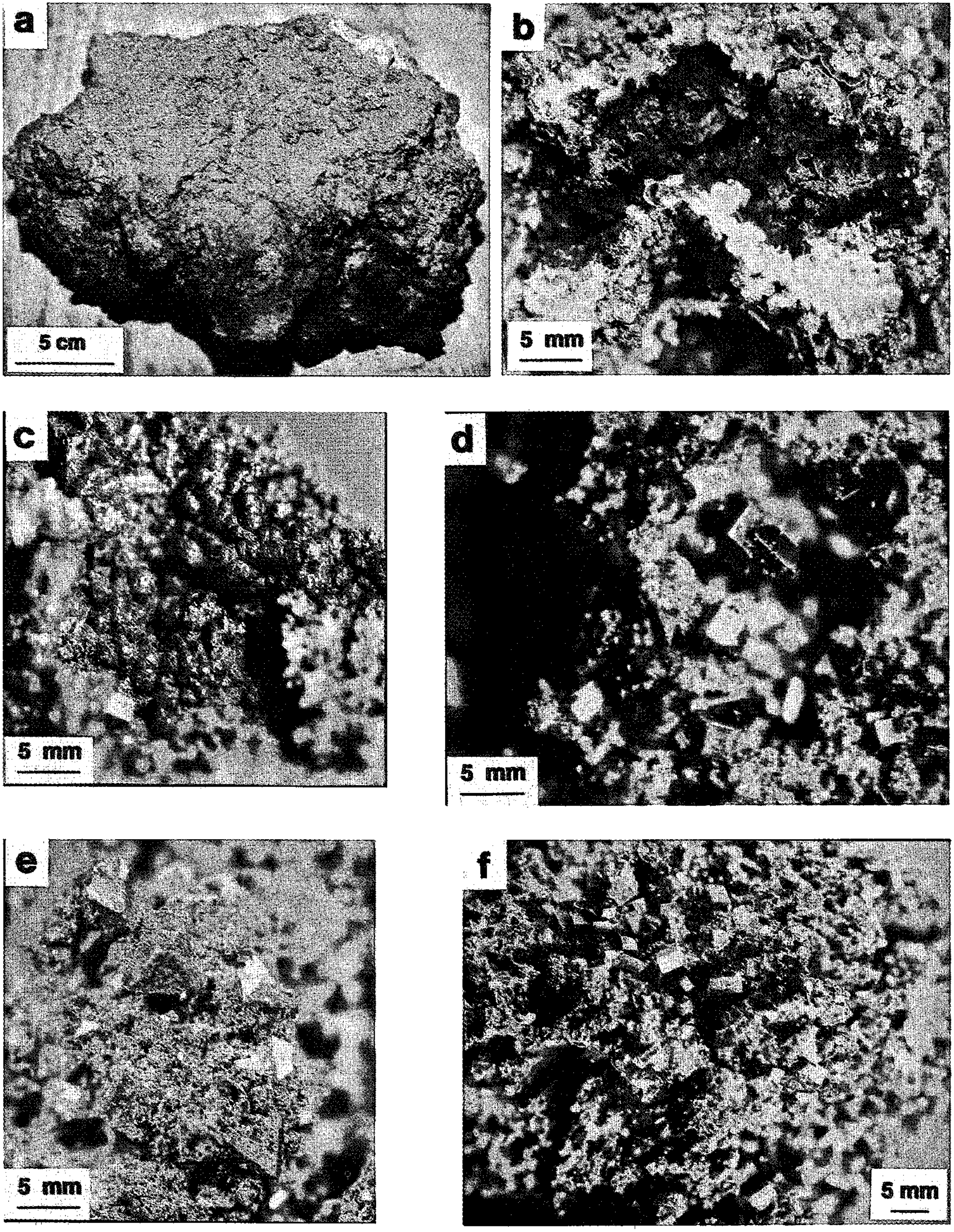

FIG. 2. a) Large block of massive sulfide from the TAG Mound, with an encrustation of emerald-green atacamite. b) Crust of colloform atacamite with central cavity lined by a thin film of amorphous Fe oxyhydroxides. c) Cryptocrystalline, colloform masses of atacamite. d) Euhedral rhombic prisms of atacamite on the corroded surface of massive chalcopyrite. e) Intergrowth of atacamite and paratacamite (dipyramids) dusted with Fe oxyhydroxides. f) Large, blocky crystals of botallackite.

fluids, having pH values between 3.6 and 5.5, produced by the reaction of exposed pyrite and chalcopyrite with seawater (Hannington *et al.* 1990). Measurements of pH and redox potential indicate that conditions within the oxidation profile are similar to those encountered in areas of acid mine-drainage. This modified seawater is sufficiently acid and oxidized to become saturated with atacamite during weathering of the exposed sulfides. Thompson *et al.* (1988) first noted the occurrence of atacamite on the weathered surfaces of the active TAG mound, and its distribution on oxidized surfaces of the deposit was widely noted during subsequent cruises (Lisitsyn *et al.* 1989, 1990, Rona *et al.* 1990, Tivey *et al.* 1990). Hannington *et al.* (1988, 1991) briefly described the mineralogy and chemistry of the Fe-oxide gossans and the relationship of atacamite to the secondary sulfide assemblages.

Samples of gossanous material were collected from all three deposits by dredging and using the submersible. Cu chlorides in most of the samples are intergrown with amorphous Fe oxyhydroxides, lesser amounts of goethite and lepidocrocite, jarosite, and secondary Cu sulfides. Most of the atacamite occurs as (1) patchy (1–2 cm thick) encrustations or colloform masses on the outer surfaces of weathered sulfide blocks, (2) as crystalline aggregates that fill open spaces in massive Fe-oxide crusts, and (3) as disseminated crystals intergrown with fine-grained Fe oxyhydroxides or that fill open spaces within corroded sulfides. Atacamite is most common in the wholly oxidized remnants of massive sulfide blocks and locally constitutes up to 50 vol.% of the gossanous material. The presence of abundant brightly colored atacamite in the gossans is a useful indicator of weathered Cu sulfides in the substrate. The widespread crusts of atacamite coating weathered sulfide surfaces on talus slopes at the edge of the active mound has led a number of observers to describe these steep scarps as "green cliffs" (Fig. 1). Atacamite also is a common detrital constituent of metalliferous sediments that surround the TAG mound (Hannington *et al.* 1991). These sediments are composed of the weathered debris deposited on the flanks of the mound by mass-wasting.

Nodular crusts, colloform masses, and *blisters* of atacamite on the surfaces of large, oxidized sulfide blocks (Fig. 2a) are apparently precipitated from Cu^{2+} ions leached during corrosion of the sulfides by sea-

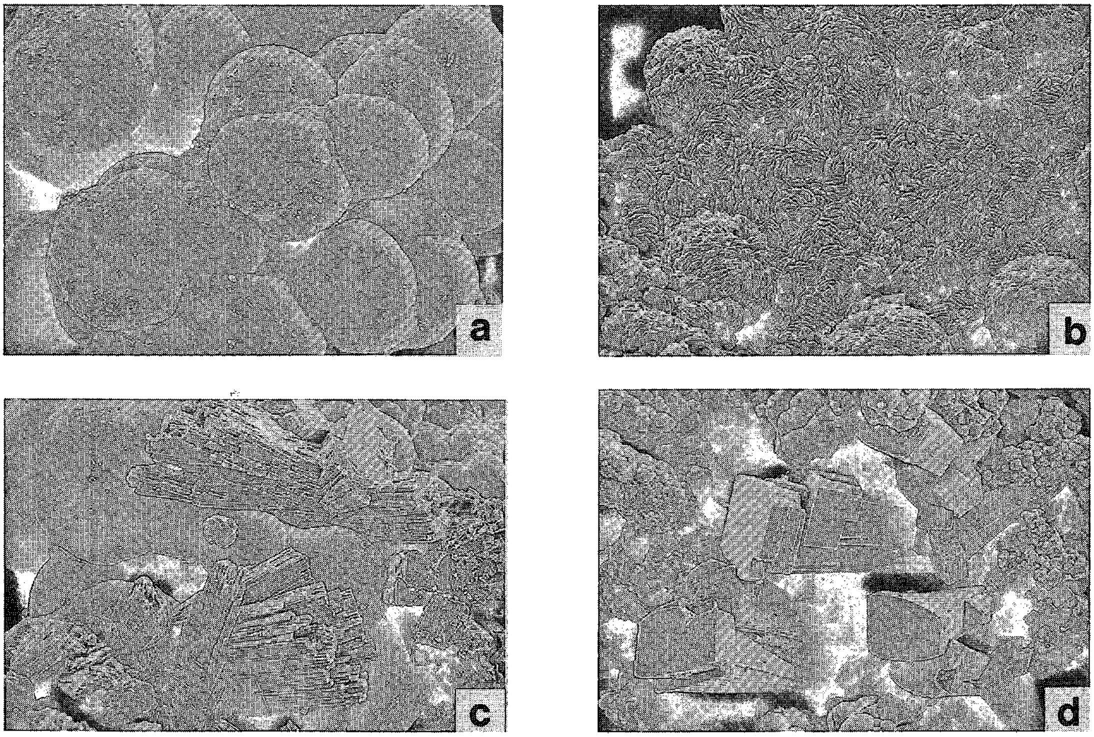

FIG. 3. SEM photographs of cryptocrystalline and coarser atacamite. a) Cryptocrystalline atacamite in colloform masses. b) Sheath-like masses of atacamite. c) Slender prismatic crystals or needles of atacamite as overgrowths of cryptocrystalline globular masses. d) Slender prismatic crystals of atacamite with blunt terminations. Photographs by L.K. Radburn (Geological Survey of Canada).

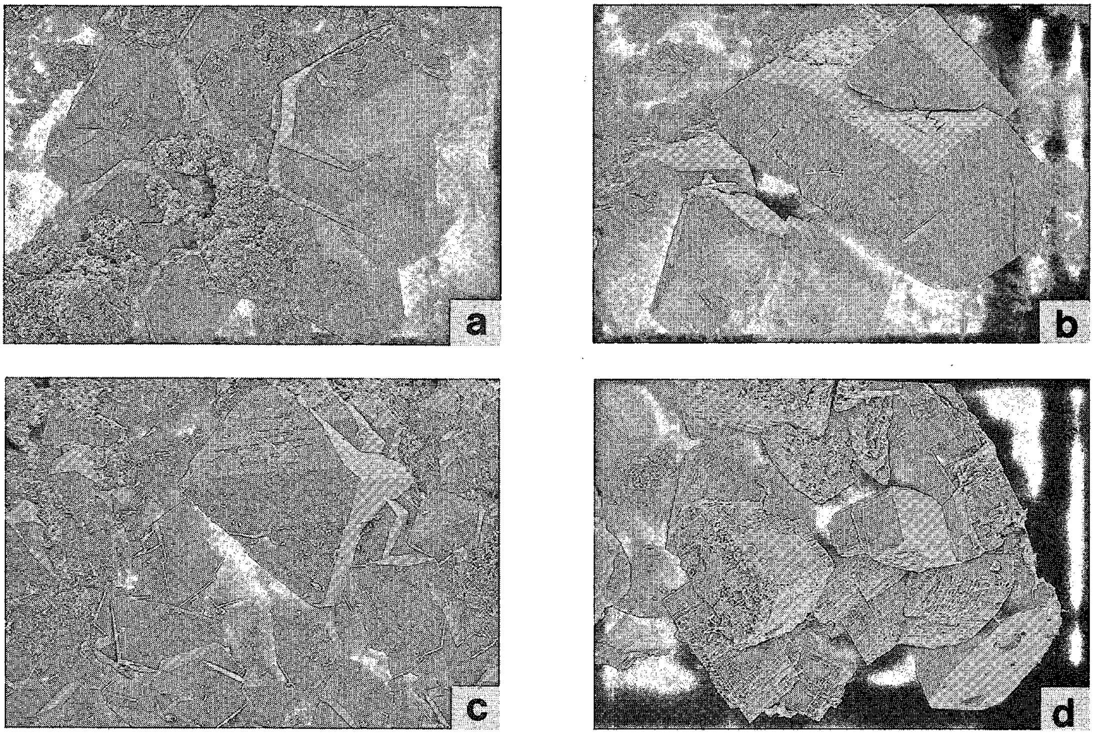

FIG. 4. SEM photographs showing dominant habits of crystals of atacamite, paratacamite, and botallackite. a) Prismatic crystals of atacamite with corroded chalcopyrite (see also Fig. 2d). b) Prismatic crystals of atacamite with well-developed twin. c) Intergrowth of atacamite and paratacamite (dipyramids). d) Corroded, blocky crystals of botallackite. Photographs by L.K. Radburn (Geological Survey of Canada).

water. In a number of samples, atacamite occurs along fractures leading to the outer surfaces of the blocks, and these fractures appear to have been paths for migrating Cu ions. The *blisters* of atacamite are commonly hollow, and some interiors are lined by euhedral crystals of atacamite or a thin film of amorphous Fe oxyhydroxides (Fig. 2b). The more massive nodular crusts of atacamite consist mainly of anhedral masses (Fig. 2c). In some cases, crystals of atacamite have grown directly on the exposed surfaces of primary chalcopyrite and infill pore spaces within the corroded sulfides (Fig. 2d).

MINERALOGY AND CHEMISTRY OF ATACAMITE

All three naturally occurring polymorphs of $Cu_2Cl(OH)_3$ have been identified in the gossans from TAG using single-crystal X-ray diffractometry. Atacamite is most common, followed by paratacamite and rare botallackite. The crystalline habits of atacamite (orthorhombic) observed in the gossans include slender prismatic crystals and equant, rhombic prisms that exhibit the $\{110\}$, $\{011\}$ and $\{010\}$ forms. Individual euhedra range in size from a few tens of micrometers up to about 2 mm, but are typically less than 500 μm in size (Fig. 2d). Paratacamite commonly occurs together with atacamite and forms characteristic hexagonal dipyramids up to 2 mm in size (Fig. 2e). Botallackite (monoclinic) was identified in one sample, lining the hollow interior of an atacamite crust, where it forms blocky crystals up to 2 mm across (Fig. 2f). The crystal structures of the three polymorphs have been described in detail by Wells (1949), Frondel (1950), Fleet (1975) and Hawthorne (1985). Figures 3 and 4 show the common habits of atacamite and its polymorphs in the TAG gossans. In detail, the colloform masses of atacamite consist of cryptocrystalline material (Fig. 3a) and sheath-like aggregates (Fig. 3b). These are commonly overgrown by characteristic slender, prismatic crystals (Figs. 3c,d). Figure 4a shows typical fine-grained crystalline atacamite, with well-developed $\{010\}$ forms, present in cavities and pore spaces within the oxidizing sulfides. Some of these crystals are twinned (Fig. 4b). Atacamite and paratacamite are usually complexly intergrown (Fig. 4c), but can be distin-

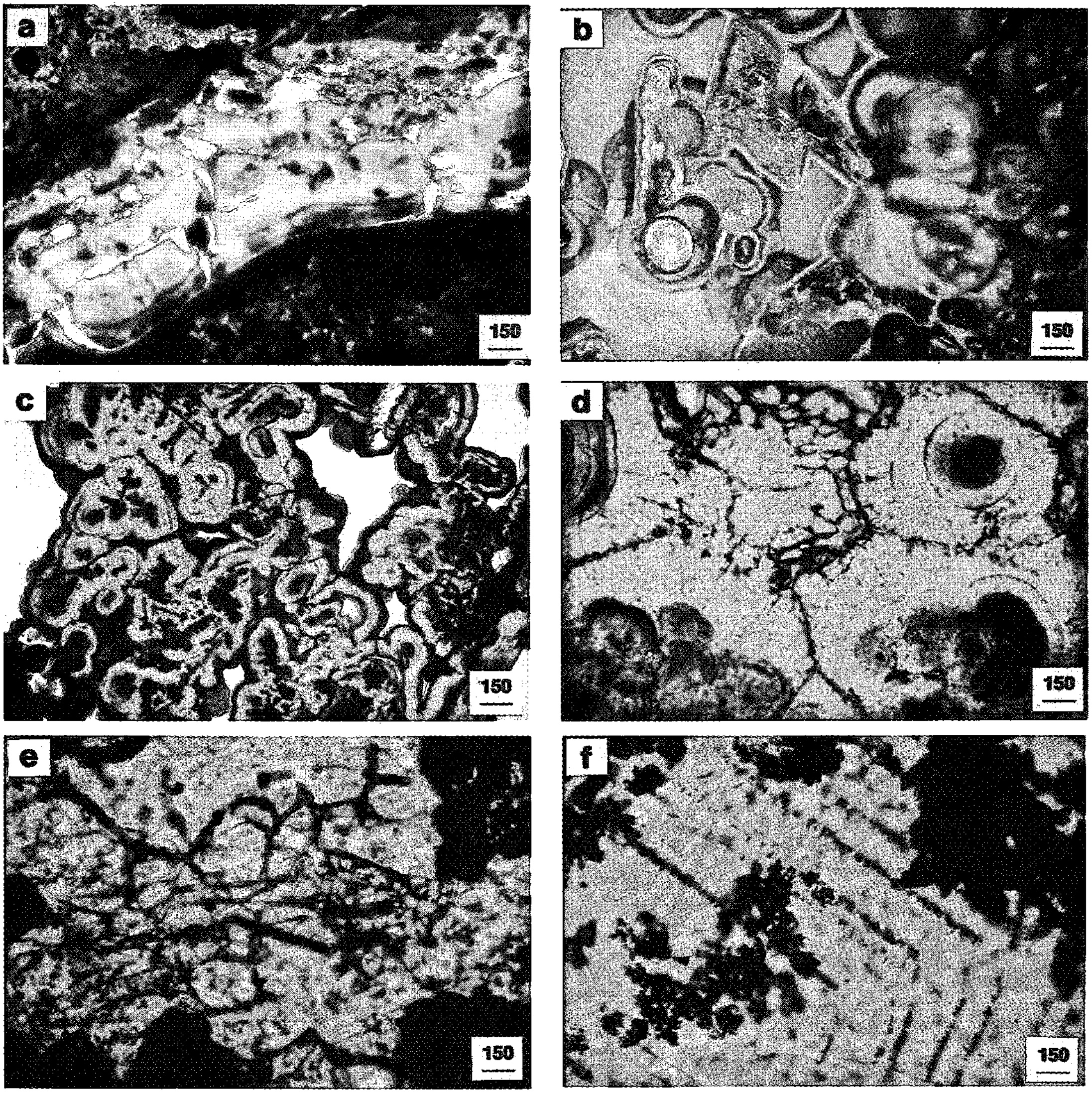

FIG. 5. Photomicrographs of atacamite textures in reflected and transmitted light. a) Fine-grained atacamite within desiccation cracks in massive Fe oxyhydroxides (transmitted light). b) Colloform encrustation of atacamite coated by a film of amorphous Fe oxyhydroxides (reflected light). c) Colloform masses of atacamite that appear to have nucleated on fine-grained Fe oxyhydroxide particles and bacterial filaments (transmitted light). d) Colloform atacamite overgrown by coarse crystals (transmitted light). e) Microscopic, biogenic filaments trapped within atacamite (transmitted light). Individual filaments are typically <20 μm in length and only a few micrometers in thickness. f) Microscopic fluid inclusions (<2 μm) trapped on growth planes within crystalline atacamite (transmitted light). The inclusions may represent healed etch-pits on former crystal faces that were exposed to dissolution by seawater. Individual inclusions are too small to be useful for microthermometric measurements. Black patches are inclusions of amorphous Fe oxyhydroxides. Scale bars are in micrometers.

guished by their optical properties (see below) and in X-ray powder patterns. Rare crystals of botallackite observed in the scanning electron microscope are strongly etched and corroded (Fig. 4d), and therefore do not appear to have been in equilibrium with the pore fluids in the gossan.

In transmitted light, atacamite is bright to dark emerald-green, with strong pale to yellow-green pleochroism. Paratacamite also is dark green in transmitted light, but is not pleochroic. Botallackite was not observed in thin section, but has a slight blue-green tint in ordinary light (Fig. 2f). In thin section, crystalline forms of atacamite are commonly observed within late-stage cavities in the massive Fe oxides, filling open spaces between colloform bands of Fe oxides, or in desiccation cracks that form during the incipient crystallization of goethite from amorphous Fe oxyhydroxides (Fig. 5a). More massive colloform atacamite on the surfaces of oxidized sulfides shows concentric growth-zones typical of open-space filling (Figs. 5b,c). Discrete botryoidal forms, rimmed by crystalline atacamite, appear to have nucleated on particles of Fe oxides (Fig. 5d). Most of the atacamite samples that were collected are dusted with fine inclusions of oxide particles (see Fig. 2e). In most published experimental work on these phases, the presence of such foreign nuclei appears to have encouraged crystal growth. Fossilized remnants of filamentous bacteria are present throughout the massive Fe oxide gossan and also are locally preserved within atacamite (Fig. 5e). The filamentous threads closely resemble the bacteria found in low-temperature iron-rich deposits elsewhere on the seafloor (*e.g.*, Juniper & Fouquet 1988), and they may have played an important role in the oxidation of sulfides and the release of Cu^{2+} ions to seawater (*cf. Thiobacillus ferrooxidans*: Alt 1988b, Holm 1987, Hannington & Jonasson 1992). Crystalline forms of atacamite also show distinct zoning, commonly with abundant microscopic fluid inclusions along the growth planes (Fig. 5f). These inclusions are generally too small to be used for microthermometric measurements.

Results of electron-microprobe analyses of atacamite from the TAG gossans (Table 1) indicate average compositions of 56.2 wt.% Cu and 17.1 wt.% Cl. Two analyses of atacamite from sample 2190–6–1 correspond most closely to the stoichiometric composition of $Cu_2Cl(OH)_3$. However, most of the atacamite is slightly depleted in Cu, suggesting probable hydration of the outer surface.

TABLE 1. CHEMICAL COMPOSITION OF ATACAMITE FROM THE TAG MOUND*

Points	2183-6-1-3 (1)	2183-6-1-3 (2)	2190-6-1 (1)	2190-6-1 (2)	2183-6-2 (1)	Ideal $Cu_2(OH)_3Cl$
FeO wt.%	1.60	0.13	1.84	0.60	0.43	-
CuO	69.61	69.96	66.05	74.30	72.32	74.48
PbO	0.00	0.00	0.00	0.26	0.00	-
Ag_2O	0.07	0.00	0.00	0.05	0.00	-
HgO	0.04	0.00	0.00	0.03	0.03	-
SrO	0.01	0.17	0.00	0.20	0.10	-
Rb_2O	0.07	0.06	0.00	0.03	0.01	-
Na_2O	0.00	0.00	0.00	0.00	0.00	-
K_2O	0.00	0.02	0.00	0.01	0.00	-
Cl	17.26	17.80	16.35	17.12	17.13	16.60
SO_3	0.15	0.29	0.03	0.16	0.05	-
Total	88.81	88.42	84.27	92.74	90.06	91.08

*Electron microprobe analyses obtained on individual grains using a Cameca SX-50 microprobe (15 kV accelerating voltage, 10 nA beam current, and 20s counting time per element) with pure metal and mineral standards.

PARAGENESIS

Exposed surfaces of sulfide deposits on the modern mid-ocean ridges undergo rapid oxidation owing to the infiltration of cold seawater into the porous sulfide matrix. Seawater penetrates into cracks and along grain boundaries in the sulfides and reacts with the exposed surfaces of minerals to produce strongly acid pore-fluids. Acid conditions are generated by a series of sulfide-oxidation reactions, likely dominated by:

$$FeS_2 + 7/2\ O_2 + H_2O = Fe^{2+} + 2SO_4^{2-} + 2H^+$$

$$FeS_2 + 14Fe^{3+} + 8H_2O = 15Fe^{2+} + 2SO_4^{2-} + 16H^+$$

$$2Fe^{2+} + 1/2\ O_2 + 5H_2O = 2Fe(OH)_3 + 4H^+$$

as proposed by Nordstrom (1982).

Cuprous chloride complexes and Cu^{2+} ions are released by the dissolution of chalcopyrite and secondary Cu sulfides in the acidic, oxidizing solutions (*e.g.*, Rose 1976). The dissolved ions migrate outward through the gossans and are reprecipitated as basic copper salts upon contact with the surrounding seawater. The atacamite that fills veinlets or fractures in the gossans likely delineates the conduits through which seawater was able to penetrate the massive sulfides. Similar veinlets and fracture-fillings of atacamite have been described by Alt *et al.* (1987) in gossanous material from oxide deposits on the East Pacific Rise. The precipitation of the atacamite as crusts on the outer surfaces of the Fe-oxide gossans usually represents the last stage in the complete hydration of exposed sulfides.

The equilibria controlling the speciation of copper in seawater are well known, and the stability relations of atacamite and other basic copper salts have been examined by Barton & Bethke (1960), Bianchi & Longhi (1973), Rose (1976) and, most recently, by Woods & Garrels (1986). Stability diagrams based on early determinations of the Gibbs free energies for the basic copper salts indicated that tenorite should be the stable product of seafloor weathering of Cu sulfides (*e.g.*, Bianchi & Longhi 1973, Rose 1976). However, the free-energy data for atacamite and the cupric oxides published recently by Woods & Garrels (1986) indicate that atacamite is the more likely stable phase at the pH and Eh of normal seawater (Fig. 6). Because of the high Cl^-/SO_4^{2-} ratio of seawater, brochantite also is less favored than atacamite. The low pH of the pore fluids in contact with oxidizing sulfides may have prevented the formation of malachite, which otherwise might be the more stable copper salt in seawater (Fig. 6b). The free-energy data reported by Woods & Garrels (1986) indicate that atacamite and malachite are of nearly equal stability in surface seawater equilibrated with the atmosphere (*i.e.*, containing CO_2 at a constant partial pressure of $10^{-3.5}$ bar: Fig. 6b). However, because their stabilities are so close, the preferred species depends critically on the local $p(CO_2)$, which may be a function of temperature, depth, and

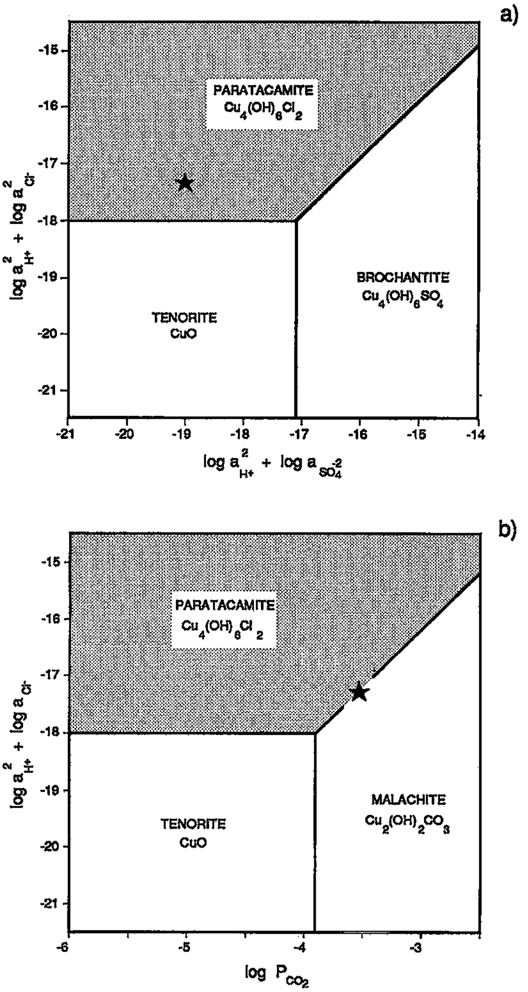

FIG. 6. Stability fields of paratacamite (atacamite), tenorite, brochantite, and malachite in seawater at 25°C. The approximate composition of seawater are shown by the star (modified after Woods & Garrels 1986).

local biological activity (*e.g.*, Bianchi & Longhi 1973). For the most part, a lower $p(CO_2)$ in the cold bottom-waters of the deep ocean (*i.e.*, undersaturated in calcium carbonate) compared to average surface-waters will inhibit the formation of malachite.

The free energies of formation for atacamite and paratacamite reported by Barton & Bethke (1960) and by Woods & Garrels (1986) imply only trivial differences in the predicted fields of stability of the two minerals. Apart from their thermodynamic properties, the kinetics of formation (nucleation and growth) play an important role in the crystallization of the various basic copper salts (Pollard *et al.* 1989). Woods & Garrels (1986) noted that under experimental conditions, the rate of crystallization (which is strongly dependent on the concentration of dissolved copper and the ratio of Cl^- to H^+ in solution) is apparently an important control on the particular species that forms. They found that paratacamite is the usual product in strongly acid solutions, whereas atacamite precipitates under more alkaline conditions (see also Sharkey & Lewin 1971). Pollard *et al.* (1989) confirmed the results of Sharkey & Lewin (1971) and noted that the first phase to crystallize in all experiments was botallackite, which rapidly recrystallized to atacamite or paratacamite, depending on the concentration of Cu^{2+} *(aq)*. Metastable botallackite was found to recrystallize to paratacamite at low concentrations of Cu^{2+} (*e.g.*, tens of ppm in solution) and to atacamite at intermediate concentrations (*e.g.*, hundreds of ppm Cu), with atacamite recrystallizing to paratacamite at even higher concentrations. On this basis, Pollard *et al.* (1989) suggested that paratacamite is the more stable trimorph at ambient temperatures and that crystallization of metastable atacamite and botallackite is largely a result of kinetic controls. The presence of high concentrations of Cl^- in the experiments (*i.e.*, close to those of typical seawater: 0.5 M NaCl) tended to inhibit the recrystallization of atacamite to paratacamite. This factor may account for the abundance of atacamite over paratacamite in seafloor gossans. Although botallackite has been reported at a number of localities where seawater is in direct contact with Cu minerals (*e.g.*, in old mine workings that extend below sea-level in the Botallack mine, Cornwall: Pollard *et al.* 1989), its metastable behavior accounts for its scarcity in nature. SEM photographs (Fig. 4d) of botallackite from the TAG gossans show clear evidence of etching and confirm that this phase is not stable.

Under acid, oxidizing conditions, Cu^+ and Cu^{2+} are carried in seawater solutions dominantly as cuprous chloride complexes ($CuCl_2^-$ and $CuCl_3^{2-}$) and Cu^{2+} ions, respectively (*e.g.*, Rose 1976). Figure 7 shows the stability fields of the basic copper salts, copper oxides, native copper, and chalcocite, and the solubility of copper in the acidic pore-fluids. The copper salts are quite soluble in the acid solutions that penetrate into the oxidizing portions of the sulfide mound. The release of Cu^{2+} and the stability of $CuCl_2^-$ and $CuCl_3^{2-}$ complexes under these conditions allow solubilities of the Cu-bearing phases in excess of 1,000 ppm. The solubility of copper is highest at a low pH and decreases sharply at slightly alkaline pH, resulting in the precipitation of atacamite where the oxidizing solutions come into contact with ambient seawater. Because of the high pH and high concentration of Cl^- in seawater, atacamite is only slightly soluble (*i.e.*, ≤10 ppb Cu) under normal conditions on the seafloor. This fact suggests that atacamite crusts forming on the surfaces of the gossans should persist the seafloor. This fact suggests that atacamite crusts forming on the surfaces of the gossans should persist for long periods, provided that the deposits remain submerged. In contrast, atacamite will dissolve readily in fresh water and therefore is rare in subaerial environments.

Several researchers have suggested that atacamite in seafloor sulfide deposits was precipitated directly from high-temperature hydrothermal fluids. For example, the occurrence of atacamite in veins or as fracture-fillings in some gossan samples from the TAG mound led Lisitsyn *et al.* (1989) to suggest that the mineral formed by hydrothermal venting. However, the presence of atacamite within the desiccation cracks in massive Fe oxyhydroxide crusts (*e.g.*, Fig. 5a) indicates that it formed late in the oxidation the massive sulfides, long after precipitation of hydrothermal phases had ceased. Sharas'kin *et al.* (1989), who observed atacamite within subseafloor stockwork-like veins in uplifted blocks of oceanic crust on the Mid-Atlantic Ridge, interpreted the atacamite to have formed from hydrothermal fluids at temperatures of 220–260°C (based on fluid inclusions in coexisting quartz). However, sulfides in these veins were strongly altered to goethite, and it seems likely that the observed atacamite formed during weathering of the sulfides following uplift and exposure to seawater along the fault scarps (*cf.* Bonatti *et al.* 1976, Scott *et al.* 1982). Mossman & Heffernan (1978) also observed atacamite in cores of metalliferous sediment from the Atlantis II Deep in the Red Sea. Because these sediments were deposited from hot sulfidic brines, they suggested that the atacamite might have formed from interstitial fluids under hydrothermal conditions. However, analyses of fluids from the Atlantis II Deep indicate that atacamite could not have formed at the low pH and Eh conditions prevailing at the bottom of the brine pool during accumulation of the metalliferous sediments (*e.g.*, temperatures of 61.5°C, pH = 5.5, Eh ≤ 310 mV: Bischoff 1969, Hartmann 1985). Rose (1976) also showed that extrapolation of the solubility product for atacamite to higher temperatures using available data on free energy and enthalpy indicates a dramatic increase in solubility with temperature such that the stability field of atacamite virtually disappears at temperatures much greater than 25°C. More recently, secondary Cu sulfides have been documented within sediments of the Atlantis II Deep, suggesting that *in situ* oxidation of the primary sulfide assemblage has occurred (*e.g.*, Pottorf & Barnes 1983). The formation of secondary gypsum in a number of the cores during storage also suggests that hydration of the assemblage of primary minerals in the sediments may have occurred since the time of collection (*e.g.*, Zierenberg & Shanks 1983). The presence of atacamite in samples of the Red Sea muds therefore is best explained in terms of sulfide oxidation, as observed elsewhere on the seafloor, and likely results from a late diagenetic reaction within the sediments at ambient bottom temperatures.

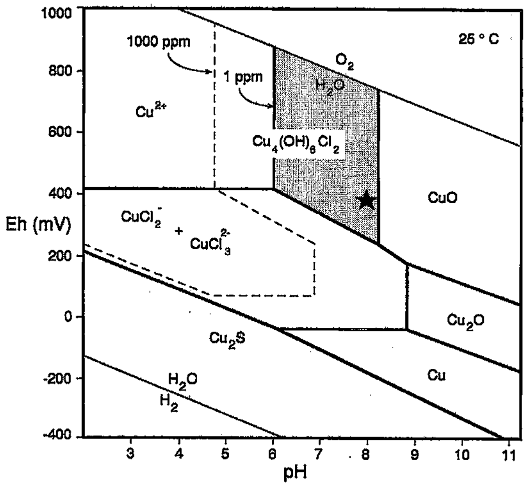

FIG. 7. Eh–pH diagram for the system Cu–O– H–S–Cl in seawater at 25°C ($\Sigma Cl = 0.5$ m, $\Sigma S = 0.03$ m). Stability fields are shown for the basic copper salts (paratacamite and atacamite), copper oxides (tenorite and cuprite), native copper, and chalcocite. The fields of the principal aqueous copper species (Cu^{2+}, $CuCl_2^-$, and $CuCl_3^{2-}$) in equilibrium with the solid phases are shown for $\Sigma Cu = 1$ ppm and 1000 ppm (dashed lines). Chloride complexes of Cu^{2+} are much weaker than the cuprous complexes $CuCl_2^-$ and $CuCl_3^{2-}$, and therefore are not considered. The approximate pH and Eh of seawater are shown by the star. Stability fields were calculated using standard Gibbs free energies of formation listed in Appendix 1.

CONCLUSIONS

Atacamite forms readily in modern seafloor environments through the oxidation of Cu sulfide minerals in contact with ambient seawater. Free-energy data on the formation of atacamite and paratacamite suggest that they are the stable copper salts in deep submarine gossans. Atacamite is only slightly soluble in seawater, and therefore should persist as components of the assemblage of secondary minerals following complete oxidation of the Cu sulfides. Radiometric dating of several atacamite-bearing gossan samples from the TAG mound indicates that they may be as old as 20,000 years and possibly as old as 40,000–50,000 years (Lalou *et al.* 1990). Atacamite also is present on the floor of the rift valley in sediments derived from the mass-wasting of relict sulfide deposits on the walls of the valley at least 13,000 years ago (Metz *et al.* 1988). However, the susceptibility of atacamite to hydration and dissolution in fresh water likely accounts for its absence in fossil submarine gossans

Conditions similar to those observed in modern seafloor gossans prevailed during the descent of the water table through exposed sulfide deposits in the Atacama Desert. Here, atacamite was precipitated by supersaturation during the evaporation of saline groundwaters, and the atacamite has since been preserved in this environment in the absence of fresh water to dissolve it.

ACKNOWLEDGEMENTS

The officers and crew of the NOAA ship *Researcher*, the *Atlantis II* and the ALVIN Group are thanked for their support in obtaining samples from the TAG Hydrothermal Field. The author is indebted to Peter Rona (NOAA) and Geoff Thompson (WHOI) for providing the opportunity to participate in this work. Meg Tivey, Susan Humphris, and Margaret Sulanowska (WHOI) kindly assisted in the handling, curation, and description of the samples. Special thanks are due to Robert Kelly (photography) and Laura Radburn (SEM imaging), who photographed the petrographic relationships discussed in this paper. X-ray diffractometry was carried out by A.C. Roberts, and electron-microprobe analyses were performed by J. Stirling in the Mineralogical Laboratories of the GSC. The paper has benefitted from the helpful comments and reviews of J. Jambor, P. Herzig, M. McNeil, G. Thompson, D. Mossman, and C. Alpers. This work was supported in part by grant #0552/88 from the NATO Scientific Affairs Division and by a special grant from the Alexander von Humboldt Foundation.

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Received February 9, 1993, revised manuscript accepted June 14, 1993.

APPENDIX I. STANDARD FREE ENERGIES OF FORMATION AND SELECTED THERMODYNAMIC DATA

Mineral or Species	Formula	G^o_f (kJ/mole)	Reference
Atacamite	$Cu_4(OH)_6Cl_2$	-1341.8	Woods & Garrels (1986)
Paratacamite	$Cu_4(OH)_6Cl_2$	-1341.8	Barton & Bethke (1960)
Tenorite	CuO	-125.9	Woods & Garrels (1986)
Cuprite	Cu_2O	-146.0	Wagman et al. (1982)
Chalcocite	Cu_2S	-85.6	Wagman et al. (1982)
Native Cu	Cu^o	0.0	
H^+ *(aq)*		0.0	
Cl^- *(aq)*		-131.3	Robie et al. (1978)
SO_4^{2-} *(aq)*		-744.5	Wagman et al. (1982)
OH^- *(aq)*		-157.3	Robie et al. (1978)
H_2O *(l)*		-237.2	Helgeson et al. (1978)
$CuCl_2^-$ *(aq)*		-243.1	Rose (1976)
$CuCl_3^{2-}$ *(aq)*		-376.9	Rose (1976)
Cu^{2+} *(aq)*		+65.5	Wagman et al. (1982)
Cu^+ *(aq)*		+50.0	Wagman et al. (1982)

The following activity coefficients from Bianchi and Longhi (1973) were used in all calculations: Cl^- (0.57), uncharged species (1.13), monovalent species (0.7) and divalent species (0.12).