———, C. Guillemin, F. Permingeat, and J. P. de Roever (1961) *Bull. Soc. Fr. Mineral. Crystallogr.* **84**, 96–104.
Kennard, O., J. C. Speakman, and J. D. H. Donnay (1967) *Acta Crystallogr.* **22**, 445–449.
Russian Commission on New Minerals (1957) *Zapiski Vses. Mineral. Obshch.* **86**, 315–316.
——— (1958) *Zapiski Vses. Mineral. Obshch.* **87**, 203–205.

THE AMERICAN MINERALOGIST, VOL. 55, MAY–JUNE, 1970

NATIVE ZINC AND α-Cu,Zn FROM MINA DULCINEA DE LLAMPOS, COPIAPÓ, CHILE

A. H. Clark, *Department of Geological Sciences, Queen's University, Kingston, Ontario, Canada*

AND

R. H. Sillitoe, *Instituto de Investigaciones Geológicas, Casilla 10465, Santiago de Chile*

Abstract

Native zinc (Cu, 0.12 ± 0.05 percent by microprobe analysis; Pb, Sn, Cd n.d.) and α-Cu,Zn (Zn, $\leq 9.5 \pm 0.5$ percent) occur as oxidation products of sphalerite and djurleite in the Dulcinea copper deposit.

Although the existence of native zinc has been established in recent years (*e.g.* Goncharova, 1959; Boyle, 1961; Bartikyan, 1966), its mode of occurrence in nonplacer environments requires further documentation. Microscope and electron-microprobe studies of ores from the Dulcinea de Llampos copper mine (Lat. 27°8.9′S; Long. 69°57.7′W), near Copiapó, northern Chile, have revealed minor amounts of metallic zinc and a copper-rich, Cu-Zn alloy.

These phases occur in association with native copper, and represent products of the oxidation of sphalerite intergrown with supergene djurleite. Specimens were taken from the 180-fathom level of the mine; the native metals antedate mining and are definitely not artifacts. The djurleite at this depth formed by the replacement of chalcopyrite and pyrite during the later of the two major episodes of supergene sulfide enrichment which affected the Dulcinea vein during the Tertiary (Sillitoe, 1969; Sillitoe, Mortimer and Clark, 1968). Rims of native copper, intergrown with cuprite, developed locally through replacement *in situ* of djurleite in the course of subsequent oxidation, and now surround masses of hypogene and supergene sulfides.

The sphalerite, which forms narrow veins and irregular patches in hypogene chalcopyrite and pyrite, exhibits microscopically sharp contacts with the djurleite, lacking the development of the (Cu, Zn) S solid solutions observed at mines a short distance to the north (Clark and Sillitoe, 1970), and has been replaced only to a minor extent by djurleite. The zinc-bearing alloys are restricted to the vicinity (*i.e.* within 200 μm) of sphalerite which extends to the outer boundaries of the djurleite zones, and are greatly subordinate to the native copper.

Aggregates of ovoid or platy grains of anisotropic, bluish-gray native zinc, not exceeding 15 μm in diameter, are surrounded, successively, by narrow discontinuous rims of an isotropic, pale yellowish-pink Cu, Zn alloy, and by pinkish native copper. The Zn—Cu, Zn contacts are sharp, whereas the two copper-bearing phases characteristically grade into one another.

Microprobe analysis of the three metallic phases, using pure copper and zinc as standards, has shown that: (i) the native zinc contains only 0.12 ± 0.05 weight percent Cu; (ii) the Cu, Zn alloy has a *maximum* zinc content of 9.5 ± 0.5 percent, and is strongly zoned, with a Cu:Zn ratio increasing away from contacts with native zinc, grading to zinc-free copper; (iii) native copper not directly associated with the zinc alloys shows no solid solution of that metal (*i.e.* Zn <0.01 percent), but contains minor amounts of iron (up to ~ 2 percent).

The Cu-Zn alloys are apparently free from additional metals; Pb, Sn, and Cd, recorded in native zinc by Goncharova (1959), Boyle (1961), and Bartikyan (1966), were sought, but not detected. The low copper content of the native zinc conforms to the equilibrium phase relations in the system Cu-Zn at low temperatures (Hansen, 1958). The composition of the Cu, Zn alloy falls well within the stability field of the cubic α-brass phase, however, and the association of these alloys represents disequilibrium (Hansen, 1958; Elliot, 1965).

The α-Cu,Zn areas have the appearance of reaction rims formed by the partial equilibration of the essentially contemporaneous native copper and zinc, but there is no textural evidence for the breakdown of the latter metal. The variations in Cu:Zn ratio may merely reflect changes in the relative concentrations of these metals released in the course of desulfurization of the sphalerite-djurleite assemblage.

This occurrence of native zinc resembles that described by Boyle (1961) in that the metal has formed as an oxidation product of sphalerite, but the zinc from Keno Hill differs in being clearly a transported phase. The zinc alloys in the assemblages from Dulcinea probably owe their preservation to insulation from supergene solutions and oxidate phases by the surrounding native copper. This is the first recorded natural occurrence of a brass.

References

Bartikyan, P. M. (1966) Native lead and zinc in the rocks of Armenia. *Zap. Vses. Mineral. Obshch.*, **95**, 99–102 [in Russian; *Mineral. Abstr.* **18**, 200].

Boyle, R. W. (1961) Native zinc at Keno Hill. *Can. Mineral.*, **6**, *pt. 5*, 692–694.

Clark, A. H. and R. H. Sillitoe (1970) Cuprian sphalerite and a probable copper-zinc. sulfide, Cachiyuyo de Llampos, Copiapó, Chile. *Amer. Mineral.* **55**, 1021–1025.

Elliot, R. P. (1965) *Constitution of Binary Alloys.* McGraw-Hill Book Co., Inc., New York, 877 p.

Goncharova, T. Ya. (1959) On native metallic zinc. *Zap. Vses. Mineral. Obschch.*, **88**, 458–459 (in Russian).

Hansen, M. (1958) *Constitution of Binary Alloys (in cooperation with K. Anderko).* McGraw-Hill Book Co., Inc., New York, 1305 p.

Sillitoe, R. H. (1969) *Studies on the Controls and Mineralogy of the Supergene Alteration of Copper Deposits, Northern Chile.* Ph.D. thesis, Univ. London, 498 p.

———, C. Mortimer and A. H. Clark (1968) A chronology of landform evolution and supergene mineral alteration, southern Atacama Desert, Chile. *Inst. Min. Met. Trans.*, **77**, B166–169.

THE AMERICAN MINERALOGIST, VOL. 55, MAY–JUNE, 1970

CUPRIAN SPHALERITE AND A PROBABLE COPPER-ZINC SULFIDE, CACHIYUYO DE LLAMPOS, COPIAPÓ, CHILE

A. H. Clark, *Department of Geological Sciences, Queen's University, Kingston Ontario, Canada*

AND

R. H. Sillitoe, *Instituto de Investigaciones Geológicas, Casilla 10456, Santiago de Chile.*

Abstract

Preliminary data are reported for two supergene sulfides from northern Chile. One, apparently a cuprian sphalerite (*nil* to 15 ± 2 percent Cu.), formed as an intermediate stage in the replacement of sphalerite by djurleite. The second, with a composition close to Cu_3ZnS_4, was a product of the breakdown of the first phase during a subsequent oxidation episode.

Introduction

Although few natural mineral assemblages conform strictly to the ternary system, Cu—Zn—S, phase relations in this system could have a significant influence on the inter-relationships between ferroan sphaler-