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Diagenetic pyrite in the El Soldado stratabound copper deposit: a link with the petroleum system of the Cretaceous basin of central Chile

Zentilli, M.¹, Collins, P.G.², Boric P., R.³, Wilson, N.S.F.⁴

- (1) Dept. Earth Sciences, Dalhousie University, Halifax, Nova Scotia, B3H 3J5, Canada.
- (2) Dept. Earth Sciences, Memorial University of Newfoundland, St. John's, NL, Canada.
- (3) Codelco Norte, Calle 11 Norte 1291, Villa Exótica, Calama, II Región, Chile.
- (4) Murphy Oil Corp., 1700 555 4th Ave NW, Calgary AB T2P 3E7, Canada.

zentilli@dal.ca

Introduction

El Soldado, located in Central Chile (32°38'S; 71°04W) 120 km northwest of Santiago, is the largest (>200 Mt @ 1.4 % Cu) of the known copper manto-type deposits in central Chile [1, 2]. Although structurally controlled and discordant at the scale of the mine, it is regionally strata-bound within shallow marine, bimodal calc-alkaline basalt - rhyodacite (extrusive- intrusive) rocks of the Lower Cretaceous Lo Prado Formation, which also contains marine carbonaceous shale and volcaniclastic sandstones. It is generally acknowledged that hydrothermal sulphide base metal deposits in the Andes obtained their metals and sulfur from calc-alkaline magmatic systems. However, it has been proposed [3] that El Soldado sulphides originated by hydrothermal enrichment of copper replacing pre-existing diagenetic pyrite. This early formed pyrite displays framboidal and colloform textures and developed at low temperatures, probably in the presence of bacteria [4], within degraded reservoirs of petroleum, locally preserved as pyrobitumen [3]. Hydrothermal, chloride-rich basinal fluids brought copper during an event ca. 20 My later than the formation of diagenetic pyrite [5]. Sulfur isotope characteristics in chalcopyrite, bornite and chalcocite that were formed by replacement of pyrite, were inherited from the diagenetic pyrite [4]. The above model implies that pre-existing organic carbon in petroleum source rocks or degraded petroleum accumulations are favorable loci for concentrations of copper of any source [6], and that the hydrothermal fluids may contribute little sulfur to some of these deposits. Although the model is published in the scientific literature, some geologists are not convinced that all the pyrite is of low-temperature or diagenetic origin; they hypothesize that massive pyrite and pyrite-chalcopyrite assemblages in veins and halos of the deeper parts of the deposit (Fig. 1) are of higher tempera-





ture, hydrothermal, origin. To test this proposition we selected samples of massive pyrite and chalcopyrite-pyrite assemblages [1] in the deepest parts of the El Soldado orebodies, and studied their ore mineralogy and geochemistry, including sulfur isotope composition [7].

Geology

Several structurally-controlled orebody clusters occur within an area of ca. 2000 x 800 m, 600 m vertical, in a dilational fault jog within a large NS orogen parallel (sinistral) strikeslip shear fault system that was active in the Cretaceous [1, 2]. The orebodies are zoned (Fig. 1) with pyrite in outer halos or envelopes, followed inwards by zones with abundant pyrite-chalcopyrite, chalcopyrite-bornite and a bornite-chalcocite core with minor hematite in the higher levels and the chalcocite cores; pyrite is relatively more abundant at depth and in the northern half of the deposit [1, 2]. El Soldado was generated in two main phases [3,1,2]: During the first stage (Stage I), petroleum, generated from underlying carbonaceous shales and heated by active volcanism, migrated upwards through normal faults and accumulated under seals of reduced permeability, such as tuffs in the upper Lo Prado Fm (Fig. 1). Pyrite (plus marcasite and other Fe-S phases) formed within and close to petroleum in colloidal, spheroidal (e.g. framboidal) textures, probably assisted by reduction of pore-water sulfate by sulfate-reducing bacteria, thus at temperatures below 100°C [3, 6]. The basin continued to subside; petroleum was solidified to bitumen [6] before the strata were tilted to the east [3]. The second stage (Stage 2) occurred during regional metamorphism and the intrusion of the Cretaceous batholith [5]. Incoming Cu-rich chloride solutions [3] at ca. 300°C [2], channeled by fractures in a dilational jog [1, 2], replaced pre-existing pyrite forming chalcopyrite, bornite and chalcocite, that to a great extent inherited diagenetic textures [3]. All Fe-S phases recrystallized as pyrite and some euhedral pyrite cubes grew at the expense of framboids. Bitumen was locally graphitized by the hot solutions; acting as active carbon, was enriched in copper and chlorine [3, 8].

Mineralogical Study

Samples of massive pyrite and associated chalcopyrite and bornite, devoid of visible bitumen, were selected from the Valdivia Sur, Arauco Norte, Catedral and Morro orebody clusters, most from the pyrite-chalcopyrite halos such as those shown in Fig. 1, or veins. Under close inspection under the reflected microscope and the microprobe [7], even the most massive pyrite assemblages show remnants of colloidal or framboidal textures (Fig. 2). Some pyrite crystals are tabular and probably grew as marcasite, but since this mineral is unstable above ca. 160°C [e.g. 9] it recrystallized as pyrite. As temperature rose, framboidal structures recrystallized as cubes, yet (at high magnification) their cores preserve the diagenetic framboidal structures (Fig. 2). Partial or total replacement of pyrite by chalcopyrite and bornite did not totally destroy the original diagenetic textures (Fig. 2C)





[3, 7]. Pyrite contains some Cu, As (up to 2.78%), Ni, Mn, Co, Pb, and Mo. The highest As values are consistently spatially associated with framboidal pyrite [7, 3].

Sulfur Isotopes Study.

Characteristically, a value of $\delta^{34}S$ close to 0 ‰ is interpreted to indicate a magmatic source. In an earlier study in El Soldado [10], a mean (average) value near 0 ‰ for sulphur in Cu sulfides was so interpreted; an observed range in $\delta^{34}S$ values was ascribed to variations in temperature and oxygen fugacity; two $\delta^{34}S$ values of 7.3 ‰ and 28 ‰ found in framboidal pyrite were interpreted to reflect biogenic reduction of seawater sulfur [10]. A more recent study [4] analyzed chalcopyrite, bornite, chalcocite as well as pyrite obtaining $\delta^{34}S$ from –13 ‰ to +29 ‰, attributing the great divergence from 0 ‰ to bacterial fractionation [4]. In this study [7] $\delta^{34}S$ values from analysis of pure pyrite have a range of 24.5‰, from –7.4‰ to + 17.1‰. The lowest $\delta^{34}S$ values, closest to a magmatic signature are found adjacent to a gabbro intrusive deep in the Arauco orebody cluster [1, 7]. These results are consistent with a little homogenization by recrystallization of widely variable sulphur composition inherited from diagenetic pyrite, and perhaps a minor external contribution during the hydrothermal stage of mineralization. Degraded hydrocarbon accumulations can thus represent chemically reducing reservoirs of sulphur that serve to precipitate copper from circulating hydrothermal solutions of any source.

References

- [1] Boric, R. (2002). Unpubl. M.Sc. Thesis, Dalhousie Univ., Halifax, Canada, 378p.
- [2] Boric, R., Holmgren, C., Wilson, N.S.F., Zentilli, M. (2002) The geology of the El Soldado manto type Cu (Ag) deposit, Central Chile. *In Porter*, *T.M.* (*Ed*), *Hydrothermal Iron Oxide Copper-Gold & Related Deposits.*.. Vol. 2, PGC Publ., Adelaide, 163-184.
- [3] Wilson, N.S.F., Zentilli, M. (1999) The role of organic matter in the genesis of the El Soldado. *Economic Geology*, Vol. 94, 1115-1136.
- [4] Wilson, N.S.F., Zentilli, M., Spiro, B. (2003) Scientific Communication, *Economic Geology*, Vol. 98, 163-174.
- [5] Wilson, N.S.F, Zentilli, M., Reynolds, P.H., Boric, R. (2003) ⁴⁰Ar/³⁹Ar geochronology of K-feldspar from the El Soldado manto-type copper deposit, Chile. *Chemical Geology, Isotope Geoscience.*, Vol. 197, 161-176.
- [6] Zentilli, M., F.Munizaga, M.C.Graves, R.Boric, N.Wilson, P.Mukhopadhyay, L.Snowdon (1997) *International Geology Review*, Vol. 39, 1-21.
- [7] Collins, P.G. (2002) Unp. B.Sc (Hon) Thesis, Dalhousie Univ., Halifax, Canada, 144p.
- [8] Wilson, N.S.F. (2000) International Journal of Coal Geology, Vol. 43, 53-82.
- [9] Lennie, A.R., Vaughan, D.J (1992) American Mineralogist, Vol. 77, 1166-1171.





[10] Klohn, E., Holmgren, C., Ruge, H. (1990) El Soldado, a stratabound copper deposit associated with alkaline volcanism in the central Chilean coastal range. *In Fontboté, L. et al. (Editors) Stratabound Ore Deposits in the Andes:* Springer Verlag, Berlin, 435-448.

Fig. 1. Cross section through Filo and Valdivia Sur orebody clusters, El Soldado deposit, showing sulfide zonation by Boric [1, 2]. Samples for this study were collected in the deepest pyrite-chalcopyrite (py-cpy) zones.

Fig. 2. Massive pyrite samples from lower levels of Valdivia Sur. A. Electron probe micrograph of banded aggregate. B. Electron probe micrograph of colloform pyrite; black is calcite. C. Reflected light photomicrograph of (tarnished) chalcopyrite replacing framboidal pyrite (white); framboidal pyrite centers are preferentially replaced, leading to *atoll* structures. D. Chalcopyrite (Cpy) replaces framboidal pyrite (Py). From Collins [7].

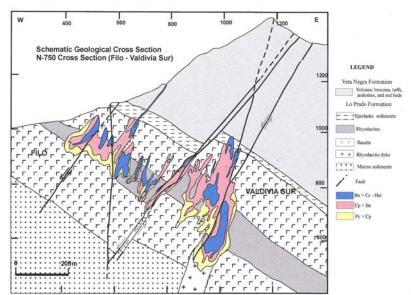


Fig. 1





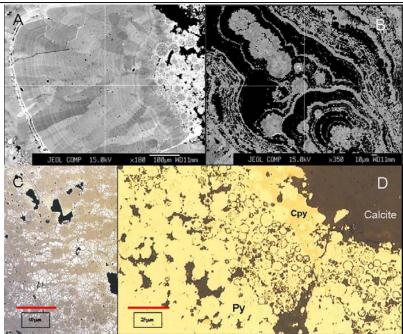


Fig. 2