

Mineral features of Cu-Ag-Ba-Mn mineralisations of La Serena, Chile

J. Carrillo-Rosúa & S. Morales Ruano

Department of Mineralogy and Petrology, University of Granada, Avd. Fuentenueva s/n 18002 Granada, Spain.

D. Morata Céspedes

Department of Geology, University of Chile, P. Ercilla 803, Santiago de Chile, Chile.

Keywords: Silver, copper, manganese silicate, volcanogenic deposits, Andean Coastal Range

ABSTRACT:

Three kinds of mineralisation appear in Lower Cretaceous volcanic units in the La Serena area, which have undergone very low metamorphism (prehnite+pumpellyite, with albite, epidote and chlorite): a) Stratiform Mn mineralisation enclosed in sandstones interlayered with andesites. The ore mineralogy consists mainly of silicates composed of braunite, piemontite and minor pyrolusite. b) Stratabound Cu-(Ag) mineralisations ("Mantos tipo Chile"), associated with lappilli tuffs with bitumen. The major phases are bornite and chalcopyrite, with minor fahlore, sphalerite, galena, stromeyerite, cobaltite and hematite. Besides stromeyerite (AgCuS), there is Ag in minor quantities of Cu-bearing minerals, especially bornite (up to 0,33% at. Ag). c) Ba-Ag mineralisation in veins crosscutting volcanic rocks. The ore mineralogy consists of silver-bearing minerals (native Ag±Hg (87,4 - 93,4% at. Ag and 5,6 - 10,0 % at. Hg), Ag chloride (bromide), acanthite, and Ag-Cu sulphide ($Ag_{0,77-2,69}Cu_{0,90-1,44}S_1$)), and copper-bearing minerals (bornite, Cu sulphide, and fahlore). The systematic spatial relationship among the different kinds of mineralisations, the basic magmatism, the very low-grade metamorphism, and the intrusion of granitic bodies suggest a genetic link among the different phenomena.

1 GEOLOGICAL SETTING

As summarized in previous papers (i.e., Morata & Aguirre 2003, Morata & Morales 2002), the Lower Cretaceous stratified sequences (predominantly volcanic) in the Coastal Range of Chile form an almost continuous, north-trending belt c. 1200 km in length (from 25°30' to 35°30' S) and up to 100-150 km wide. Thick, volcanic plagioclase-rich porphyritic high-K calc-alkaline to shoshonitic basaltic andesites and andesites (known locally as "ocoites") sequences are present (Aguirre 1985, Vergara et al. 1995).

In the La Serena region (29°30' to 30°00' S), the Lower Cretaceous volcanism is represented by the *Arqueros Formation* (Hauterivian-Barremian, Aguirre & Egert 1965) and the *Quebrada Marquesa Formation* (Upper Barremian-Albian, Aguirre & Egert 1965). Unconformably overlying these formations is the late Cretaceous *Viñita Formation* (Aguirre & Egert 1965, 1970). All these formations are slightly folded, block-faulted, and locally intruded by calc-alkaline and oversaturated

granitoids (e.g. the Santa Gracia granitoids, with K-Ar ages in biotites ranging from 89 ± 0.6 to 98.0 Ma, Aguirre et al. 1974). Within the *Arqueros Formation* five members, three volcanic units (Ka1, Ka3, Ka5) separated by two sedimentary units (Ka2, Ka4) containing shallow-water marine fauna, have been identified (Aguirre & Egert 1965). $^{40}\text{Ar}/^{39}\text{Ar}$ Ca-plagioclase radiometric ages give concordant weighted ages of 117.0 ± 0.6 Ma and 114.3 ± 0.7 Ma (Morata et al. 2001), interpreted as the best estimate for the age of this volcanism. In the *Quebrada Marquesa Formation*, volcanic rocks are mainly present in the lower units (Aguirre & Egert 1965).

The petrology and geochemistry of the Lower Cretaceous lavas from the La Serena region have recently been defined by Morata & Aguirre (2003). Petrographically, the highly porphyritic (20-30% phenocrysts) lavas are dominated by almost unzoned Ca-rich plagioclase ($An_{57-54}Ab_{40-42}Or_{3-4}$), clinopyroxene ($Wo_{40}En_{43}Fs_{17}$), magnetite, and minor idiomorphic, altered olivine. They have a characteristic relatively high geochemical homogeneity, with high Al_2O_3 ($\geq 17\%$ wt) and low

MgO (< 5% wt) contents, classified as high-K calc-alkaline basaltic andesites to andesites. Their trace element geochemistry is typical of lavas generated in active convergent margins, with high LILE contents (Ba up to 1000 ppm and Sr up to 800 ppm), and a marked Nb-Ta trough. The isotopic geochemistry of these lavas is characterized by highly homogeneous low initial Sr ratios ($(^{87}\text{Sr}/^{86}\text{Sr})_0$ c. 0.7036) and positive ϵNd values ($\epsilon\text{Nd} = +2.9$ to $+4.7$, $(^{143}\text{Nd}/^{144}\text{Nd})_0$ c. 0.5127). A non-Andean modern setting dominated by subduction associated with intra-arc extension, subsiding at high rates, is proposed as the geodynamic setting on which this Lower Cretaceous volcanism took place.

2 VERY LOW-GRADE METAMORPHISM

The mineral phases of very low-grade metamorphism appear in certain metadomains, specially the pseudomorphism of magmatic primary phases, in the matrix and in open spaces. In the first metadomain, the most significant metamorphic phases are sericite and albite as a result of the transformation of calcic plagioclase. Chlorite, magnetite and occasionally pumpellyite appear as olivine pseudomorphs. In the matrix, the neoformed mineral phases belong to the mafic phyllosilicates, while prehnite and calcite are common in the filling of amygdale. In some of them, tiny acicular crystals of pumpellyite and idiomorphic hydrogarnet (hydrogrossular) crystals have been observed, with chlorite, epidote and albite.

The presence of prehnite+pumpellyite, together with albite, epidote and chlorite, limits metamorphism to the prehnite-pumpellyite facies at around 200-270°C and $P < 4\text{kb}$.

3. MINERALISATIONS

According to Aguirre & Egert (1965), Oyarzun et al. (1998), and Morata & Morales (2002), it is possible to distinguish three kinds of mineralisation (*e.g.* Oyarzun et al. 1998) in the La Serena area:

* Stratiform Mn mineralisation in the highest levels of the *Arqueros Formation* and in the base of the *Quebrada Marquesa Formation* (Aguirre & Mehech 1964).

* Stratabound Cu-(Ag) mineralisation (“Mantos tipo Chile”), associated with lappilli tuffs and bitumen of the *Quebrada Marquesa Formation* (Boric 1985; Maksaev & Zentilli 2002).

* Veins of Ba-Ag mineralisation that intersect the lavas sequence of the *Arqueros Formation* (Aguirre & Egert 1965).

3.1. Stratiform manganese mineralisation

The stratiform Mn mineralisation has been studied at Mina Alta and El Manzanito mines in the Kqm_1 unit of the *Quebrada Marquesa Formation*, which consists of volcanoclastic breccias, andesitic lavas (to a certain extent brecciated) and lesser sandstones and lutites. The Mn mineralisation is stratiform and occurs in sandstones (which are interlayered with andesites of the *Quebrada Marquesa Formation*). These mineralised layers are 5-10 m thick and have great lateral continuity. They can be followed for several kilometres, comprising a marker horizon in the region.

The ore mineralogy of this mineralisation consists of braunite, piemontite and minor quantities of pyrolusite, with hematite being very scarce (Fig. 1). Barite, albite and calcite, and occasionally white mica are present as gangue phases. The main textural characteristics and the mineral chemistry determined by SEM and EPMA of ore mineralogy are:

* Braunite, the major phase in the deposit, has a massive character or is present as an idiomorphic aggregate of crystals. It has a composition with variable contents of Mn (25.59 – 39.08% at.), Fe (0.07 – 11.83% at.), Si (5.06 – 7.50% at.), Al (0.05 – 1.60% at.), Ca (1.07 – 3.92% at.), which is intermediate between the end members braunite I ($\text{Mn}^{2+}\text{Mn}^{3+}_6\text{SiO}_{12}$) and nelterite ($\text{CaMn}_6^{3+}\text{SiO}_{12}$).

* Piemontite is relatively abundant and forms as masses or as micro-veins. It has a very variable composition of Al (3.19 – 10.28% at.), Fe (0.01 – 5.47% at.) and Mn (2.78 – 10.35% at.), with Al and Mn showing an inverse correlation.

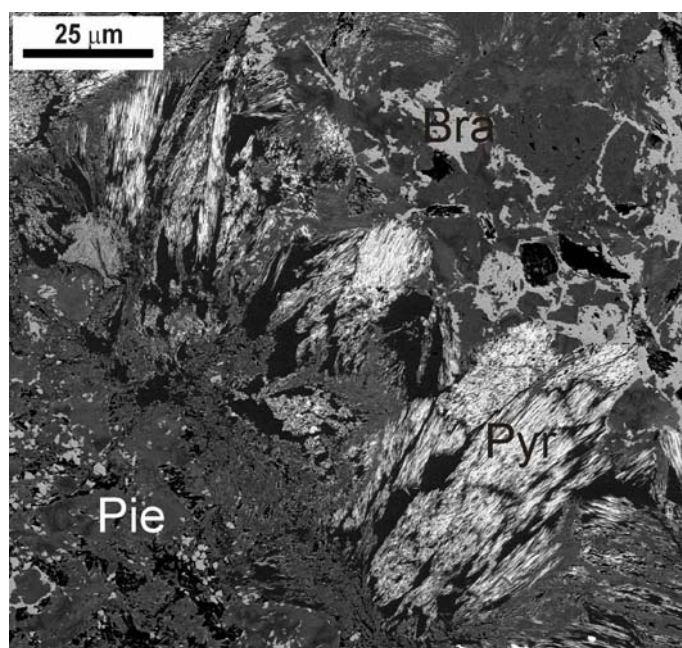


Figure 1. BSE image of an intergrowth between braunite (Bra) and piemontite (Pie) that is replaced by pyrolusite (Pyr).

* The pyrolusite appears as tiny tabular crystals in veinlets and as fibrous-radial aggregates, probably derived by transformation from Mn-rich piemontite (Fig. 1). However, the composition is very pure with only minor quantities of Si (0.13 – 2.84% at.), Fe (0.00 – 1.79% at.) and Al (0.00 – 1.11% at.).

The following sequence of precipitation has been observed: hematite → braunite+piemontite → pyrolusite. The principal factor that determines the mineral sequence and the mineral chemistry of Mn phases was f_{O_2} . Thus, an evolution to higher f_{O_2} to the final stage of sequence can be assumed.

This mineralisation is a manganese silicate type, with braunite, and, to a lesser extent, piemontite and oxides. The mineralogy of this deposit is consistent with their formation from Mn-rich hydrothermal fluids in a volcano-sedimentary environment. Such hydrothermal fluids are connected with magmatic activity in the same zone.

3.2. Cu-Ag stratabound mineralisation

Cu-Ag mineralisation appears as disseminations in volcanic rock, veins, bands, or as vacuole fillings spatially associated with hydrothermal alteration of the rock. Preliminary studies with optic microscopy, SEM-EDX and EPMA have shown that the mineralisation mainly consists of bornite and chalcopyrite, with significant quantities of fahlore, sphalerite and galena (Fig. 2). Ag-Cu sulphides, cobaltite and hematite have been found as accessory minerals, with the most abundant gangue minerals being calcite, barite, albite and sericite. The only Ag-bearing phase is the Ag-Cu sulphide (stromeyerite, $AgCuS$, included in bornite). The other metallic phases contain Ag in minor proportion are: bornite (0.01 – 0.33% at.), fahlore (0.03 – 0.15% at.) and chalcopyrite (0.00 – 0.05% at.). Other typically Ag-bearing phases, such as galena or fahlore, have only minor quantities of silver: galena close to nil and fahlore lower than 0.15% at., with a slight trend towards greater proportion of Ag towards the tennantitic end-member. To summarise, a strong correlation between Cu and Ag is observed, with Ag being more abundant where bornite is present.

3.3. Ba-Ag mineralisations in veins

Ba-Ag deposits studied appear in the Llanos de Arqueros. They consist of veins of barite that contain different Ag-bearing phases. Optical microscopy, SEM-EDX, and EPMA identified the presence of at least four different Ag-bearing phases: Ag-Cu sulphide, Ag sulphide, native Ag±Hg, and Ag chloride (bromide) (Fig. 3). In addition, there are other metallic Cu-bearing phases: bornite, Cu sulphide, and fahlore. The gangue minerals in the veins consist of barite, albite, calcite, chlorite,

copper carbonate and anhydrite as a later phase. The SEM-EDX and EPMA studies of ore mineral have provided the following chemical information:

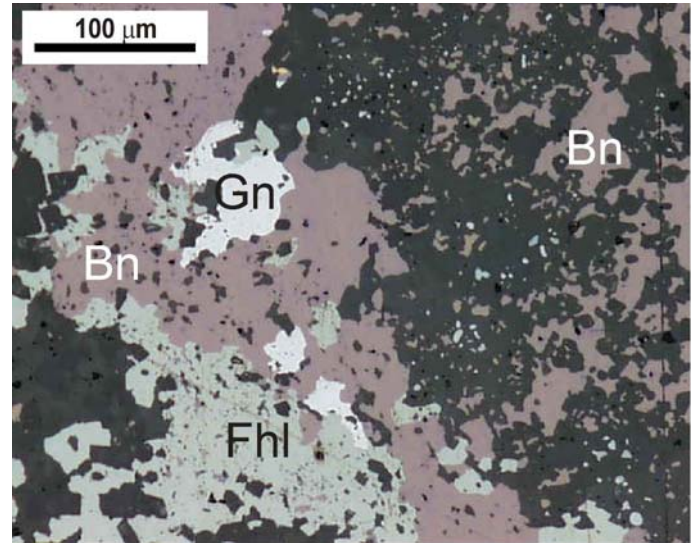


Figure 2. Reflected microphotograph of a vein with bornite (Bn), fahlore (Fhl) and galena (Gn).

* Ag-Cu sulphide: EPMA show that it possesses great chemical variability ($Ag_{0,77-2,69}Cu_{0,90-1,44}S_1$), indicating that it does not correspond accurately to any known mineral formula. A possible explanation is that such micro-analyses correspond to sub-microscopic intergrowth of jalpaite (Ag_3CuS_2), stromeyerite ($AgCuS$) and native Ag.

* Native Ag: Corresponds to alloys of Ag (87.4 – 93.4% at.) with Hg (5.6 – 10.0 % at.).

* Ag sulphide: This is acanthite (no cubic habit observed, suggesting an argentite precursor) with small quantities of As (0.20 – 0.68% at.).

It should be noted that the other ore minerals also have small quantities of Ag: bornite (0.05 – 1.05% at.), Cu sulphides (0.21 – 0.76% at.) and fahlore (0.81% at.).

From the study of these Ag-bearing phases the following conclusions can be derived:

* The mineralisations are systematically associated with barite, which appears in veins with textures of precipitation in open spaces. For this reason, it is deduced that the Ag mineralisation was controlled by later hydrothermal processes, which remobilized the Ag from preexisting phases. These processes are specially favourable at the barite/calcite interface, which typically develops a Cu-bearing carbonate band with enrichment in Ag-bearing phases.

* According to Boyle (1997), the presence of Ag salts is the product of a concentration of Ag in arid environment under conditions of high evaporation. This suggests, in the regional context, that at least part of the mineralisation, mainly with respect to Ag chlorides, has taken place in conditions of subarid evaporation, possibly in zones of very shallow platform where evaporation was high. If this is true,

the enrichment processes must be contemporaneous with the formation of banded anhydrite, which fills karstic cavities.

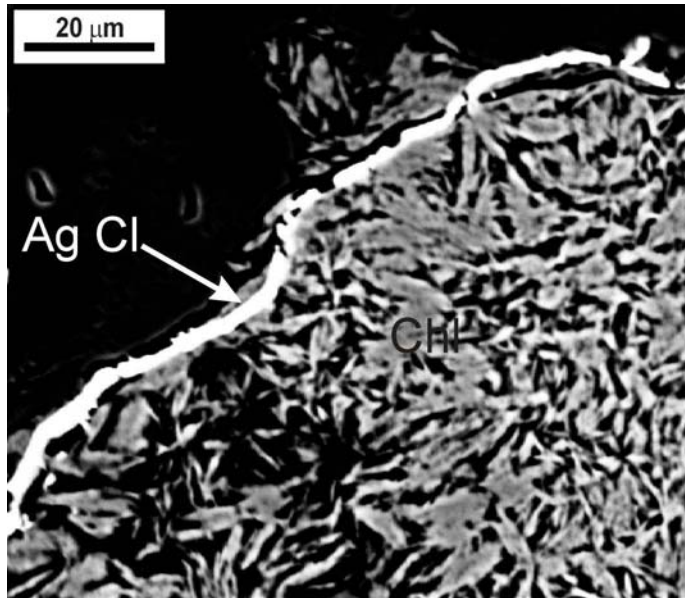


Figure 3. BSE image of a chlorite (Chl) aggregate surrounded by Ag chloride layer (AgCl) in a calcite and barite vein.

3 CONCLUSION

In the area studied, a systematic spatial association of different phenomena has been observed (the different kinds of hydrothermal mineralisation, the basic magmatism, the very low-grade metamorphism and the intrusion of granitic bodies) suggesting a genetic link between them. The nature of the studied mineral phases and their mineral chemistry is in keeping with the observed genetic relationship.

ACKNOWLEDGEMENTS

The research has been supported by the CSIC-University of Chile cooperation project 2001-CL-00015 and CSIC/2001/02-08, the project BTE-2001-3308 of the DGI of Ministerio de Ciencia y Tecnología, the RNM 0131 Research Group of Junta de Andalucía, the "Plan Propio" of Granada University and the I001-99/2 DID project of the University of Chile.

REFERENCES

- Aguirre, L. 1985. The Southern Andes. In: Nairn, A.E.M., Strehli, F.G. & Uyeda, S. (Eds.). *The ocean basins and margins, Vol. 7^a. The Pacific Ocean*. New York, Plenum Press. 265-376.
- Aguirre, L., Charrier, R., Davidson, A., Mpodozis, C., Rivano, S., Thiele, R., Tidy, E., Vergara, M. & Vicente, J.C. 1974. Andean magmatism: its paleogeographic and structural setting in the central part (30° - 35° S) of the Southern Andes. *Pacific Geology* 8: 1-38.
- Aguirre, L. & Egert, E. 1965. Cuadrángulo Quebrada Marquesa, provincia de Coquimbo. *Carta Geológica de Chile, Instituto de Investigaciones Geológicas*. Santiago, 15, 92 pp.
- Aguirre, L. & Egert, E. 1970. Cuadrángulo Lambert (La Serena), provincia de Coquimbo. *Carta Geológica de Chile, Instituto de Investigaciones Geológicas*, Santiago, 23, 14 pp.
- Aguirre, L. & Mehech, S. 1964. Stratigraphy and mineralogy of the manganese sedimentary deposits of Coquimbo province, Chile. *Economic Geology* 59: 428-442.
- Boric, R. 1985. Geología y yacimientos metálicos del distrito de Talcuna, IV región de Coquimbo. *Revista Geológica de Chile* 25: 57-75.
- Boyle, D.R. 1997. Iodargyrite as an indicator of arid climatic conditions and its association with gold-bearing glacial tills of the Chibougamau - Chapais area, Quebec. *Canadian Mineralogist* 35: 23-34.
- Maksaev, V. & Zentilli, M. 2002. Chilean strata-bound Cu-(Ag) deposits: an overview. In Porter, T.M. ed. *Hydrothermal Iron Oxide Copper-Gold & Related Deposits: A Global Perspective*: 185-205. Adelaide: GC Publishing.
- Morata, D. & Aguirre, L. 2003. Extensional Lower Cretaceous volcanism in the Coastal Range (29°20'-30°S), Chile: geochemistry and petrogenesis. *Journal of South American Earth Sciences* (in press).
- Morata, D., Aguirre, L., Féraud, G., Fuentes, F., Parada, M.A. & Vergara, M. 2001. The Lower Cretaceous volcanism in the Coastal Range of central Chile: geochronology and isotopic geochemistry. *III South American Symposium on Isotope Geology*. Extended Abstracts Volume (CD). 321-324. Sociedad Geológica de Chile, Santiago, Chile.
- Morata, D. & Morales, S. 2002. Estudio preliminar del quimismo de las mineralizaciones de Ag asociadas al magmatismo del Cretácico inferior en la cordillera de la Costa de la Serena, Chile (29°50'lat.S). *Boletín Sociedad Española de Mineralogía* 25-A: 67-68.
- Oyarzun, R., Ortega, L., Sierra, J., Lunar, R. & Oyarzun, J. 1998. Cu, Mn and Ag mineralization in the Quebrada Marquesa Quadrangle: the Talcuna and Arqueros district. *Mineralium Deposita* 33: 547-559.
- Vergara, M., Levi, B., Nyström, J. & Cancino, A. 1995. Jurassic and Early Cretaceous island arc volcanism, extension, and subsidence in the Coast Range of central Chile. *Geological Society of America Bulletin* 107: 1427-1440.