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PYROBITUMEN RELATED TO SILVER-COPPER DEPOSITS IN A CRETACEOUS VOLCANIC-SEDIMENTARY SEQUENCE: TALCUNA DISTRICT, COQUIMBO, CHILE

A b s t r a c t . In recent years, hydrocarbons have been observed in some stratabound copper deposits in the Cretaceous volcanic-sedimentary sequences in north and central Chile. At the "21 de Mayo" and "Socavon 2001" mines in the Talcuna district in north-central Chile (29°30′–29°45′ S/70°45′–71°00′ W), pyrobitumen is associated with ore minerals in Lower Cretaceous rocks. In this district, recent investigations demonstrate that the ore mineralization, traditionally regarded to be of stratabound (*manto*) type, has both structural and lithological controls. Paragenetic relations reflect a hydrothermal emplacement of both the pyrobitumen and the ore and gangue minerals, while isotopic analyses suggest an organic marine provenance of the former. Reflectivity 2.0–2.4% indicates the maturity of the pyrobitumen. Its occurrence is spatially related to sulphide mineralization (chalcopyrite, bornite, chalcocite) and to barren zones, especially in the walls of fractures and faults that were channels for post-ore diorite dikes. Organic matter was probably hydrothermally mobilized from limestones of the Arqueros Formation and precipitated first in the ore zones and then in fractured post-ore dikes. Hydrothermal fluids sealed in calcite and barite related to the pyrobitumen reveal homogenization temperatures ranging from 180 to 320°C and salinities from 6.5 to 21 wt.% NaCl equivalent. These data characterize the mineralization as a moderate- to low-temperature event involving fluids of considerable salinity.

Key-words: pyrobitumen, copper stratabound deposit, Lower Cretaceous volcaniclastics, Chile

INTRODUCTION

The presence of bitumen and its metallogenic connection with Cu-Ag mineralization in Early Cretaceous stratified units were recently described in Chile. Bitumen deposits occur both in sedimentary rocks, e.g., at Uchumí in Coquimbo (Wilson, Zentilli 1997), and in volcanic sequences, e.g., at El Soldado in central Chile (Zentilli et al. 1994, 1997; Wilson, Zentilli 1997) and in the Copiapo district (Cisternas et al. 1999).

The present study is focused on the characteristics of the pyrobitumen found in two mines in the volcanic-clastic continental sequence of the Quebrada Marquesa For-

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mation (QMF): "21 de Mayo" and "Socavon 2001", located in the Talcuna district, Coquimbo. In these mines, copper mineralization, mainly comprising bornite, chalcopyrite and chalcocite, is both vein type and *manto* type. The geology of the district was described by Boric (1985) and Camus (1986). The physico-chemical conditions of the hydrothermal mineralization have been inferred by the authors from a study of fluid inclusions in gangue minerals that are associated with the ore minerals and the pyrobitumen.

GEOLOGICAL SETTING

The copper deposits of the Talcuna district (29°30′–29°45′ S/70°45′–71°00′ W) occur in the Quebrada Marquesa Formation (Aguirre, Egert 1965). The QMF is a sequence of andesitic lavas and epiclastic and pyroclastic continental rocks deposited in a tectonic basin close to the coeval magmatic arc. It marks the transition from marine volcanic conditions of the Arqueros Formation (AF) to a continental environment of the Viñita Formation (VF) that discordantly overlies the AF (Aguirre, Egert 1965).

Both the AF and QMF were intruded by an Upper Cretaceous (K-Ar 89–108 Ma) batholith and small stocks assigned to the Late Cretaceous — Early Tertiary. These stocks also cut the VF (Moscoso et al. 1982). Around the intrusive rocks, hydrothermal alterations are well developed.

In the Talcuna district, the QMF is represented by a 1500-m sequence of breccias, lapilli tuffs, andesites and tuffaceous sandstones, containing small intercalations of calcareous sandstones and shales. The whole sequence is crosscut by ENE to NE trending diorite dikes.

MINERALIZATION CONTROLS

At the "21 de Mayo" and "Socavon 2001" mines, mineralization occurs in banded and brecciated (hydraulic and collapse) veins with copper, lead and silver sulphides. The mined ore contains 1–2% Cu, 0.1–0.5% Pb and 15–30 ppm Ag. There are two main mineralization controls: NNW trending normal faults that were the feeder channels for the mineralizing fluids, and a stratigraphic-lithologic position that confines the economic zones to the intervals where these feeder channels intersect the most "receptive" units, e.g., the lapilli tuffs.

The upper limit of the mineralization is an iron-manganese bed that acted as a barrier to the circulating fluids. The manto- and the vein-type mineralized zones are cut by an NE-NNE system of dextral-normal faults and displaced as a result at 10–100 m.

PYROBITUMEN OCCURRENCES

Pyrobitumen was found both in mineralized and barren zones. In the mineralized zones, it is associated with the sulphide minerals and intergrown with calcite, barite

and zeolites. In the barren zones, bitumen is mainly located in the dikes and at vein intersections.

Pyrobitumen related to ore zones. Thin and polished sections were used in morphological observations and helped interpret the paragenetic sequence. The pyrobitumen is black, amorphous (isotropic), brittle, exhibits vitreous lustre and displays conchoidal fracture. It occurs in angular fragments, small veins and irregular masses among the sulphides (Fig. 1).

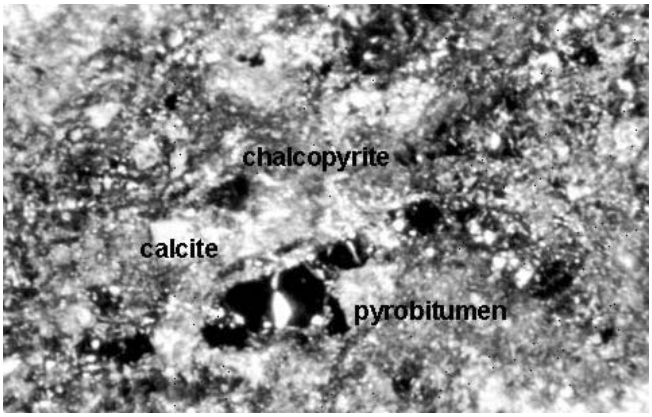

Fig. 1. Intergrowths of chalcopyrite (grey), calcite (white) and pyrobitumen (black) in a brecciated vein. Magn. 40x

In the brecciated veins, the pyrobitumen is fractured and forms irregular masses. In the banded veins, it is attached to their walls or intergrown with the ore minerals. In both cases, it coexists in simple intergrowths with bornite and chalcopyrite, and with chalcocite that replaces other sulphide minerals, but is also of hydrothermal origin.

The pyrobitumen is also intergrown with barite, calcite and zeolites that occur in veins, fractures and vugs in the mineralized zones. These gangue minerals fill contraction cracks that developed in the bitumen during its solidification (Fig. 2).

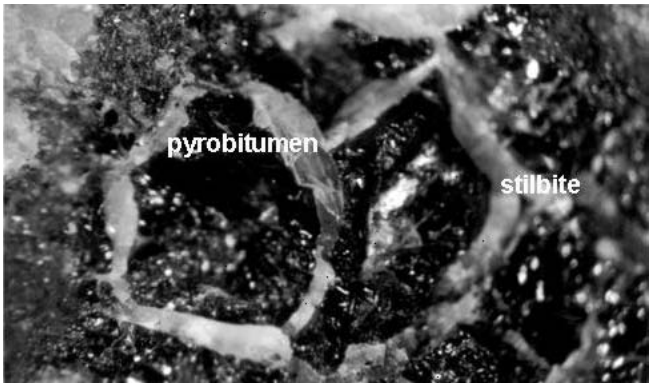

Fig. 2. Stilbite (white) in the solidification contraction cracks of pyrobitumen (black). Magn. 40x

Pyrobitumen related to barren zones. Fine particles of this pyrobitumen mostly occur as masses in open fractures. They can be found mainly at the intersections of the NNE trending dikes with stratified rocks, both in their walls and in small feather veins.

PYROBITUMEN ANALYSIS

Reflectance. Reflectance is one of the most useful parameters describing maturation of organic matter. It is directly applicable to the study of the thermal history of petroleum and provides a continuous numerical scale that measures the process of maturation and metamorphism (reflectance increases with structural ordering of organic matter). In the present study, reflectance was measured in two briquettes prepared from pyrobitumen fragments according to the random procedure. The measured R_0 is equivalent to the percentage of light reflected under the microscope without polarizer. In both briquettes, the reflectance of 30 particles was measured.

The reflectance values obtained (Table 1) range between 2.0 and 2.4% and suggest that the organic matter was subjected to a moderate thermal alteration.

TABLE 1

Reflectance of pyrobitumen

No. of data	Mean	Minimum	Maximum	Standard deviation
30	2.196	2.041	2.417	0.081

Isotope data. The isotopic determinations were conducted at Actlabs Ltd., Canada. The average $\delta^{13}C$ value for the bitumen is –28.8‰. As marine organisms that utilize carbon dioxide rather than HCO_3^- to build their cellular material produce a significant deficiency in $\delta^{13}C$ due to photosynthesis (Hunt 1979), $\delta^{13}C$ values between –25 and –30‰ strongly suggest a photosynthetic origin of the organic matter studied. Therefore, this value is consistent with an organic marine origin for the carbon and the supposition that the bitumen was formed by the maturation and destruction of hydrocarbons which had migrated into the rock fractures.

In addition, a $\delta^{34}S$ value of –18.4‰ determined in bornite is compatible with bacterial sulphate reduction that provided the sulphidic sulphur.

Trace elements. The analyses were made using ICP/MS (Total Digestion method) at Actlabs Ltd., Canada. The most significant trace element in the pyrobitumen (Table 2) is sulphur (~0.5%). The copper content (149 ppm) is consistent with the close association between the pyrobitumen and the copper sulphides, while the high silver content (6.0 ppm) can be explained by the fact that native silver is found filling open spaces. The analyses also reveal high barium contents (1990 ppm), reflecting a close relation between the pyrobitumen and barite veins.

The pyrobitumen contains 34 ppm of vanadium. Although this is not a very high value, it can be related to copper lead vanadate (mottramite) associated with oxide

TABLE 2

Trace elements present in pyrobitumen (ppm)

V	34.0	Ce	2.26	Tm	0.034
Co	2.0	Pr	0.25	Yb	0.22
Th	0.05	Nd	1.08	Ba	1 990
U	0.19	Sm	0.27	Pb	16.0
Y	2.7	Eu	0.053	As	11.0
Zr	3.0	Gd	0.27	Sr	67.0
Nb	0.2	Tb	0.05	Ag	6.0
Sb	0.6	Dy	0.33	Zn	26.0
Lu	0.037	Ho	0.07	Cu	149.0
La	1.23	Er	0.23	Ni	5.0
Ta	0.03	Hf	0.1	S	0.156%

copper minerals found nearby (1.5 km to the NE). Domeyko noted the presence of this vanadate in 1845 in his "Elements of Mineralogy" (Domeyko 1903). The pyrobitumen also contains appreciable amounts of lead, zinc and arsenic.

FLUID INCLUSIONS

Fluid inclusions were examined in calcite and barite, the gangue minerals present in the veins. The calcite samples were collected from the Mercedes Vein in the "21 de Mayo" mine and the Anita Vein in the "Socavon 2001" mine, while the barite samples from the Vein No. 5 in the "21 de Mayo" mine and the Vein No. 2 in the "Socavon 2001" mine (Figs 3, 4).

Fluid inclusions in calcite. Only the biphase primary inclusions (L+V) were studied. They exhibit regular, oblong to rounded shapes.

The homogenization temperatures measured in calcite inclusions from the "21 de Mayo" mine give a mean value of 233°C with a minimum of 146°C, a maximum of 360°C (Table 3) and a mode of 200°C. The salinity values range between 5.26 and 9.21 wt.% NaCl equivalent with a mean value of 7.17 and a mode of 7.5.

In calcite from the "Socavon 2001" mine (Table 4), the homogenization temperatures measured give a mean value of 178°C with a minimum of 115°C, a maximum of 311°C and a mode of 200°C. Salinities range between 5.71 and 23.05 wt.% NaCl equivalent with a mean value of 18.24 and a mode of 21.0.

Fluid inclusions in barite. Only primary biphase inclusions (L+V) were measured in the samples from two mines in question. In the Vein No. 5 ("21 de Mayo" mine) and Vein No. 2 ("Socavon 2001" mine), the inclusions are isolated with irregular shapes.

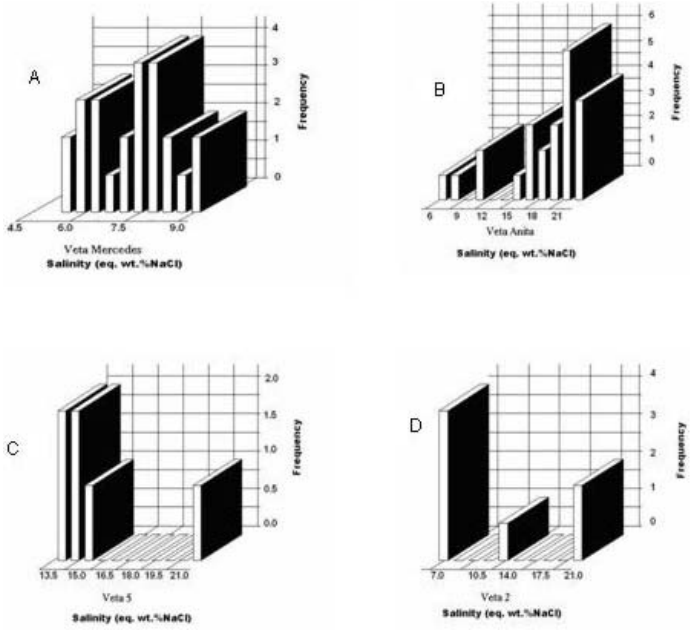

Fig. 4. Distribution of salinities of fluid inclusions in gangue minerals in the "21 de Mayo" and "Socavon 2001" mines

A. Mercedes Vein — calcite; B. Anita Vein — calcite; C. Vein No. 5 — barite; D. Vein No. 2 — barite

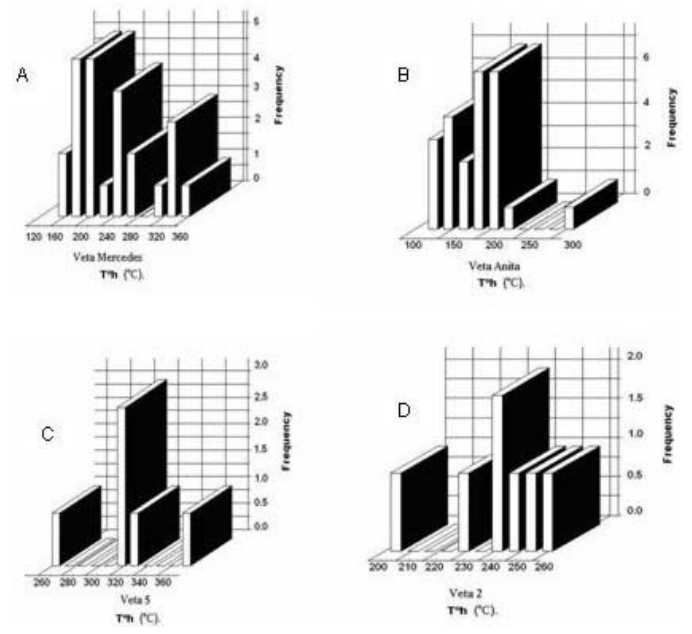

Fig 3. Distribution of homogenization temperatures of fluid inclusions in gangue minerals in the "21 de Mayo" and "Socavon 2001" mines

A. Mercedes Vein — calcite; B. Anita Vein — calcite; C. Vein No. 5 — barite; D. Vein No. 2 — barite

TABLE 3

Data on fluid inclusions in calcite – Mercedes Vein, "21 de Mayo" mine

Data	Tc [°C]	Te [°C]	Tf [°C]	Th [°C]	Salinity [wt.% NaCl eq.]	Size [μm]
Mean	–49.43	0.73	–4.52	233.80	7.17	5.43
Standard dev.	1.89	3.42	0.80	63.58	1.13	3.20
Minimum	–53.60	–33.70	–6.00	146.30	5.26	2.50
Maximum	–44.60	–13.00	–3.20	360.00	9.21	12.50
Median	–49.65	–20.95	–4.70	212.15	7.45	5.00
Number of measurements						
	24	22	24	24	24	24

TABLE 4

Data on fluid inclusions in calcite – Anita Vein, "Socavon 2001" mine

Data	Tc [°C]	Te [°C]	Tf [°C]	Th [°C]	Salinity [wt.% NaCl eq.]	Size [μm]
Mean	–66.40	–43.32	–16.46	178.27	18.24	10.78
Standard dev.	11.01	9.85	5.42	39.86	4.90	3.82
Minimum	–84.50	–53.40	–23.80	115.00	5.71	5.00
Maximum	–38.00	–20.00	–3.50	311.00	23.05	20.00
Median	–70.00	–47.20	–18.15	183.65	20.30	10.00
Number of measurements						
	28	27	28	28	23	28

TABLE 5

Data on fluid inclusions in barite – Vein No. 5, "21 de Mayo" mine

Data	Tc [°C]	Te [°C]	Tf [°C]	Th [°C]	Salinity [wt.% NaCl eq.]	Size [μm]
Mean	–64.83	–35.33	–12.10	321.33	15.84	3.75
Standard dev.	6.15	3.28	3.47	37.39	2.97	1.03
Minimum	–77.00	–42.00	–19.00	258.00	13.62	2.50
Maximum	–60.00	–33.50	–9.70	375.00	21.68	5.00
Median	–62.65	–34.10	–10.95	322.50	14.92	3.50
Number of measurements						
	6	6	6	6	6	6

TABLE 6

Data on fluid inclusions in barite – Vein No. 2, "Socavon 2001" mine

Data	Tc [°C]	Te [°C]	Tf [°C]	Th [°C]	Salinity [wt.% NaCl eq.]	Size [μm]
Mean	–57.68	–21.00	–9.71	239.78	12.22	4.75
Standard dev.	14.29	13.17	7.87	20.10	7.64	1.19
Minimum	–79.10	–38.20	–21.80	201.50	6.16	3.50
Maximum	–41.30	–10.00	–3.80	263.00	23.05	6.50
Median	–58.00	–11.20	–4.20	242.00	6.74	4.00
Number of measurements						
	7	7	7	7	7	7

The homogenization temperatures measured in the Vein No. 5 (Table 5) range from 258 to 375°C with a mean value of 321°C. Salinities are about 15.8 wt.% NaCl equivalent.

In Vein No. 2 (Table 6), the homogenization temperatures range from 201 to 263°C with a mean value of 240°C. Salinities are about 12.22 wt.% NaCl equivalent.

DISCUSSION AND CONCLUSIONS

The paragenetic relations between the pyrobitumen and associated minerals in the fractures and veins indicate that the pyrobitumen formed early in the sequence. Textural relations between the pyrobitumen and zeolites, and the absence of graphite, constrain the temperature range to which the pyrobitumen was subjected. The data from fluid inclusions in barite and calcite, minerals co-genetic with the pyrobitumen, reveal a temperature range of 180–320°C and a salinity range of 6.5–21.0 wt.% NaCl equivalent. All these data lead to the conclusion that the mineralization took place at moderate to low temperatures and involved fluids of considerable salinity

The organic matter exhibits relatively high reflectivity values (2.0–2.4%) that confirm its pyrobitumen status. Textural relations with the host rocks point out to its hydrothermal remobilization. The δ^{13} C values measured match the values of petroleum from marine sources. The organic matter was most probably derived from the limestone beds of the Arqueros Formation.

Paragenetic relations with the ore and gangue minerals indicate that the pyrobitumen was emplaced into the host rock by hydrothermal solutions that also carried the sulphides and deposited them in the banded and brecciated veins. The pyrobitumen occurrences in barren zones, especially in the fractures and faults that acted as channels for post-mineralization diorite dikes, as well as in fractured dikes themselves suggest remobilization and further migration of the organic matter.

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PIROBITUMINY W ZŁOŻACH SREBROWO-MIEDZIOWYCH W KREDOWEJ SERII WULKANOKLASTYCZNEJ REJONU TALCUNA, COQUIMBO, CHILE

Streszczenie

W ostatnich latach stwierdzono obecność pirobituminów w wielu stratoidalnych złożach miedzi w północnej i środkowej części Chile. W rejonie Talcuna (29°30′–29°45′ S/ /70°45′–71°00′ W) złoża takie występują w skałach dolnej kredy i zawierają 1–2% Cu,

0,1–0,5% Pb i 15–30 ppm Ag. Paragenezy minerałów kruszcowych i płonnych i morfologia skupień pirobituminów są charakterystyczne dla utworów hydrotermalnych. Mineralizacja ta, tradycyjnie opisywana jako typu stratoidalnego (*manto*), wykazuje związek zarówno z tektoniką jak i litologią. Uskoki stanowiły drogi przepływu roztworów i krystalizacji minerałów żyłowych, a na ich przecięciu z określonymi horyzontami serii wulkanoklastycznej (np. tufy lapillowe) tworzyły się pseudopokładowe ciała rudne (*manto*). Pirobituminy współwystępują z minerałami kruszcowymi (chalkopiryt, bornit, chalkozyn), są też obecne w płonnych strefach spękań, wypełnionych pomineralizacyjnymi dajkami diorytowymi. Refleksyjność pirobituminów zmienia się w granicach 2,0–2,4%, a analizy izotopowe wskazują na pierwotnie morskie pochodzenie substancji organicznej (wartości $\delta^{13}C$ pomiędzy –25 i –30‰). Substancja organiczna była zatem mobilizowana z wapieni formacji Arqueros, prawdopodobnie przez migrujące roztwory hydrotermalne, i wytrącała się w dwóch etapach, najpierw w strefach okruszcowanych, a później w spękaniach dajek. Temperaturę tych roztworów określono na 180–320°C na podstawie temperatur homogenizacji inkluzji ciekło-gazowych w kalcycie i barycie, które współwystępują z pirobituminami, a zasolenie na 6,5–21% wag. NaCl eq.