

FLUIDS FROM NEVES CORVO MASSIVE SULPHIDE ORES

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Short Neves Corvo presentation

Neves Corvo is the most important mine (past and present) of Iberian Pyrite Belt (IPB) which in turn is the biggest metallogenic province of VMS deposits in the World. Neves Corvo was discovered in 1977, started operations in 1988 with SOMINCOR and since then has been the first Copper and Tin producer in Europe. The two main differences from other deposits in IPB are the high-grade Cu ores (with large volumes with more than 20 % Cu, mainly in chalcopyrite but also in tennantite-tetraedrite) and the abundance and grades of the Tin ores (locally with metric blocks of almost pure cassiterite).

Sample petrography

Samples from location 1 (stope C 780 3B 01 at Corvo orebody): the quartz is intensely intergrowth with the sulphide. The original S_0 plane is preserved. Quartz dimension range from 1 to 10 mm. Cathodoluminescence (CL) observations, kindly performed by Jens Gotze (Freiberg, Technische Universität), show three quartz types. One has ephemeral blue CL, another has yellow CL; this type shows fragments of growth zones. The third quartz recognized in CL has brown CL. However, it is difficult to establish criteria to know the order of crystallization of these quartz, even by CL.

Another interesting petrographic characteristic is the existence of both pyrite and chalcopyrite in growth zones of small euhedral quartz (~0,5 mm). We could also observe an incipient recrystallization recognized by a clearing of small parts of the border of some quartz grains, normally in contact with chalcopyrite.

Sample from zone 2 (borehole NL 28 at Lombador orebody) is very different from the precedent mainly because chalcopyrite is almost absent. There are no visible orientation at the hand-specimen scale or even microscopically. In this samples two very different quartz can be distinguished. One (type 2A), presumably the first, could be interpreted as micro conduits around 2 mm in diameter. This quartz reminds that described by Vanko et al. (1991) "*small millimetre scale vugs and irregular tubules that are 1 mm across...some of this tubules...are filled completely with quartz*". Also Gaspar (1996) shows photos from Neves Corvo massive ores interpreted as parts of chimneys or micro channels of (sulphide) feed. Another type of quartz (2B), that occurs some meters below, seems to fill spaces in the pyrite matrix. It is interconnected with thin fractures. This quartz is hyaline and not milky like the previous mentioned quartz type.

Sample from zone 3 (stope N 789 1B 02 at Neves orebody) is a quartz- rich barren massive sulphide (ME, sub-economic ore). The planar orientation, although visible, is less obvious than samples from Corvo. Quartz looks like a cement. The quartz CL is exclusively bright yellow, what suggests only one quartz generation (Gotze, personal communication). Textural relationship suggests that this quartz is coeval with the sulphides. Quartz dimensions are minor than in the samples from the other locations. The majority are around 50 μm ; larger grains attend 0.8 mm.

Fluid inclusion (FI) types

Two main types of fluids could be observed in the samples: (1)- Low salinity aqueous fluids (Lw) represented by biphasic fluid inclusions with Flw between 0,7 and 0,9. (2)- Aqueous-carbonic fluids (Lw-c) that often form clathrates on cooling. These FI have Flw between 0.4 and 0.9 with an average around 0.7.

In sample 1 there are Lw fluids that are normally randomly distributed in the crystals. The Lw-c fluids also occur and are often placed along intercrystalline boundaries. However, few of them also occur in growth zones. The Lw-c FI that does not form visible clathrates could be a transition type to Lw. Sample 2 has also both types of FI with the Lw-c fluids practically detected only by Raman (which denotes a very weak gas content). A third type of fluid only observed in one sample from 2B quartz is a hypersaline fluid composed by water (liquid + vapour) plus a cubic solid phase presumably halite. These inclusions have Flw = 0.9. Crystals in the neighbourhood of these fluids show typical Lw fluids. Sample 3 has few FI. They are Lw with typically Flw = 0.9. They often seem placed along intracrystalline trails.

Microthermometric and Raman results

The measured temperatures were: temperature of last ice melting (TmI), temperature of clathrate melting (TmC) temperature of final homogenisation (TH). First melting was always difficult to observe because of the small dimensions of the FI (frequently less than 10 μm) and because it is a sluggish process. All TH were in the liquid phase.

The overall assemblage of the fluids in samples from massive cupriferous ore of Corvo orebody shows TmI between -4.8 ° and -1.7 °C. According to FI occurrence of type I (groups, intracrystalline and along growth zones), type II (intercrystalline) and type III (transgranular) the average microthermometric results (TmI, TH) were, respectively: **I**: -2.5 °C, 241 °C; **II**: -2.3 °C, 309 °C and **III**: -3.7 °C, 247 °C. TmC were measured in eight FI (from groups and intercrystalline settings) and range between 5.8 °C and 12.5 with the mode around 12.0 °C. The quartz from micro channels of sample 2A shows both types of FI although the Lw-c only revealed gases in Raman analysis. TmI were in the range [-2.3, -3.2] °C and TH between [189, 310] °C (average

242 °C, n=18). Quartz from hyaline nodules in sample 2B shows two main FI types of occurrence: I: groups or isolated) and II (transgranular). First type has TmI between [-1.4, -2.2] °C (av. -2.0 °C) and TH between 160 ° and 222 °C (av. 182 °C). Transgranular FI has TmI between [-1.8, -2.1] °C (av. -1.9 °C) and TH between [140, 176] °C (av. 154 °C). Lw-s fluids shows firstly vapour disappearance between 95° and 110 °C (av. 104 °C, n =6) and secondly solid dissolution (also final homogenisation) in the small interval [165, 168] °C (av. 167 °C, n =6). Sample of ME ore from Neves orebody, only with Lw fluids, has TmI in the interval [-1.4, -2.6] °C, (av. -2.2 °C, n=14) and TH in the range [156, 186] °C (av. 172, n =4).

Very recently (February 2003) quantitative Raman analyses from three of the analysed inclusions revealed volatile phase compositions much richer in methane than in all other lithologies in the mine. CH₄ ranges from 63 to 80 % of the volatile phase. Similar figures were already predicted by Moura (2003) based on the relative CH₄ and CO₂ Raman peak observations. N₂ and H₂S were observed in few inclusions and in trace amounts. It is important to note that the main occurrence of the H₂O-CH₄-CO₂-NaCl fluids is concentrated in the intercrystalline fluids, which also has the highest TH's.

Temperature, salinity and gas variations

Temperature probably represents more than one episode of ore formation. The first episode could be represented by a mode around 160 °C and responsible for pyrite + quartz deposition. The second temperature interval ranges between 230° - 260 °C and probably was responsible for the quartz + chalcopyrite assemblage. A hotter fluid (280°-370 °C) was introduced later as the correlative fluid inclusions are intercrystalline between quartz crystals. This event may have been responsible for the introduction of most of the chalcopyrite as it only occurs in the cupriferous massive ore. A last episode represented by transgranular inclusions with TH around 160 °C could be responsible for the close of the hydrothermal cycle. This general trend represents the classical normal hydrothermal temperature trend for VMS deposits described by many authors elsewhere and at Neves Corvo by the former mine mineralogist Pinto in his MSc thesis (Pinto, 1999).

Salinity variations are not significant. All the inclusions have salinity between seawater salinity (3.2 % wt.eq.NaCl) and less than twice this value. The previously mentioned Lw+s fluids has ~ 30.4 % wt.eq.NaCl.

Fluid compositions

Considering that NaCl is the unique salt in solution, the Lw fluids have average compositions between 99.0 % H₂O + 1.0 % NaCl and 98.1 % H₂O + 1.9 % NaCl. The hypersaline fluids have compositions around 88.1 % H₂O + 11.9 % NaCl. The following range on global composition was estimated for the aqueous-carbonic fluids:

	H ₂ O	CO ₂	CH ₄	Na ⁺	Cl ⁻
Lower-Higher gas content	0.943-0.874	0.012-0.050	0.013-0.065	0.015-0.005	0.015-0.005

Conclusions

As far as we know this is the first fluid inclusion study of IPB massive sulphide ores. The study of FI in minerals from massive sulphide ores is not easy because of the rarity of adequate minerals. Nevertheless, in this case it was possible to collect rare and important samples that show quartz intimately intergrow with the sulphide phases. Textures suggest that both minerals grew together.

The more widespread fluid is an aqueous low salinity fluid. Another frequent fluid is a H₂O-CH₄-CO₂-NaCl low-density fluid with higher TH values. The origin of this fluid could have been reactions between water and organic matter-bearing metasediments that underlie Neves Corvo ores. A volatile magmatic contribution is unlikely in this case due to strong methane participation. The fluids were probably entrapped in the homogeneous field because all the homogenisations are in the liquid phase. We have estimated a minimum ocean depth around -2000 m based on T-P constrains of the higher TH found. However as some of the FI with highest TH has CO₂ + CH₄ the seawater column was probably between 3 and 4 km.

The quartz from the studied samples is most probably hydrothermal volcanogenic in origin. It must have been preserved from deformation by means of contrast ductility between huge sulphide masses and millimetric concentrations of quartz inside them. The fluids are identical in terms of composition and temperatures to the primary fluids observed by Almodovar et al. (1998), Toscano et al. (1997a,b) and Sanchez-España et al. (2000, 2002), Nehlig et al. (1998) and Inverno et al. (2000). However in general the salinities are more restrict. Occasional phase separation at depth and at supercritical conditions was the probable cause for the existence of the brine fluids.

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