## Cu isotopic variation in the Neves-Corvo deposit, Iberian Pyrite Belt

M. GASPAR<sup>1</sup>, J.M.R.S. RELVAS<sup>1</sup>, J. CARVALHO<sup>1</sup>, P. LARSON<sup>2</sup>, G. HART<sup>2</sup>, A. PINTO<sup>1</sup>, N. PACHECO<sup>3</sup>, P.C. NOIVA<sup>3</sup>, G. BARRIGA<sup>3</sup> AND P. SANTOS<sup>1</sup>

<sup>1</sup>Departamento de Geologia/CREMINER-Univ. de Lisboa, Edifício C6, Campo Grande, 1749-016 Lisboa Portugal (mgaspar@fc.ul.pt)

<sup>2</sup>School of Earth and Environmental Sciences, Washington State Univ., Pullman, WA 99164, USA (plarson@wsu.edu)

<sup>3</sup>SOMINCOR, Soc. Mineira de Neves-Corvo, S.A., 7780 Castro Verde, Portugal (nelson.pacheco@somincor.pt)

Neves-Corvo volcanic-hosted massive sulfide deposit is one of the largest deposits of the Iberian pyrite belt (>300Mt) and unique for its high Cu and Sn grades (45Mt @ 6% Cu plus 4.5 Mt @ 12% Cu and 2.2% Sn). Neves-Corvo represents a remarkable example of a VHMS deposit with multi-sourced metal contributions, where copper enrichment due to ductile and chemical remobilization of chalcopyrite has a large expression and enormous economic significance.

This is the first report on Cu isotopes from Neves-Corvo. Copper sulfides, representing the main orebodies and mineralizing events, were separated from well-characterized samples in order to evaluate if their Cu isotopic signature could provide any insights into the ore-forming processes, post-ore modifications, and Cu fractionation mechanisms. The analyses were conducted at the Washington State University Geoanalytical laboratory using a ThermoFinnigan Neptune MC-ICP-MS.

The Cu isotopic composition of chalcopyrites from Neves Corvo, ranging from -0.57% to 0.12%  $\delta^{65}$ Cu, is comparable to that of other VHMS deposits and modern seafloor analogues. Although the dataset is still limited, preliminary results suggest that "primary" chalcopyrite is slightly but systematically lighter (-0.57% to 0.00%  $\delta^{65}$ Cu) than "secondary" chalcopyrite (0.02% to 0.12%  $\delta^{65}$ Cu; either representing ductile or fluid-assisted tectono-metamorphic copper remobilization). Bornites from the "bornite zone" have a Cu signature (-0.11‰ and -0.03‰  $\delta^{65}$ Cu) within the range of the "primary" chalcopyrites, whereas carrollite from the same ore zone is clearly distinct and heavier (0.60%  $\delta^{65}$ Cu).

New data are being generated to improve the assessment of Cu fractionation between ore types (e.g., stockwork vs. massive sulfide ore) and ore mineral assemblages (e.g., Snrich vs. Cu-rich ores; high-grade vs. low-grade).

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## Effect of surface chemistry and related texture on the diffusion coefficients and permeability of bentonites. Consequences for chemical-transport modeling

### E.C. GAUCHER AND D. GUYONNET

BRGM, 3, av. C. Guillemin BP 36009, 45060 Orléans Cedex 2, France (e.gaucher@brgm.fr)

#### **Chemistry, Texture and Transport Properties**

Geosynthetic clay liners (GCL) or clay barriers are generally built using impermeable sodium bentonite. The long term leaching of the bentonite by rainwater, groundwater, landfill leachates, alkaline cement water progressively modifies the surface chemistry of the clays. The exchange reactions convert the predominantly Na-bentonite in a Xbentonite where X can be  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $NH_4^+$ ,  $K^+$ ,  $Na^+$  .... Recent work has shown that the microtexture of the clay is strongly modified [1, 2]. In the Na-bentonite, TEM and XRD characterisations show a dispersed gel phase. In concentrated solution (NaCl, 10<sup>-1</sup>M), or in Ca/Mg-solution, an isotropic network of lens-like pores is observed, delineated by "walls" made of 40 to 60 TOT layers. Extreme situations can be found in the Cs-bentonite (aggregates of more than 100 TOT layers). The conversion of the Na-bentonite in a Ca form increases the permeability of one or two orders of magnitude. Water diffusion coefficients are found to be lower in the samples with low gel phase content. On the other hand, Na diffusion does not follow the same trend: when compared with HTO, Na diffuses faster when the gel phase content is high. This "accelerated diffusion mechanism" of cations, is enhanced due to the more easily accessible surface of clay minerals in the gel phase.

# New Developments in Chemical-transport Codes are Needed!

As a consequence of these instable microstructures, a representative long term chemical-transport modeling in GCL and clay barriers is difficult. Relations linking the proportion of Na and divalent cations at the surface of the clay with the permeability must be introduced in codes. For cations, surface and porewater diffusion coefficients have also to be considered in codes. Empirical laws that can be incorporated into codes are proposed.

[1] Guyonnet D. *et al.* (2005) *J. Geotech. Geoenv. Eng.* **131**, 740-749. [2] Melkior T. *et al.* (subm.) *J of Hydrology.*