

Mineral and chemical evolution of fragmental massive sulfide ores

V.V. MASLENNIKOV^{1*}, R.R. LARGE²,
S.P. MASLENNIKOVA¹ AND L.V. DANYUSHEVSKIY²

¹Institute of Mineralogy UB RAS, Miass, Russia
(correspondence: mas@mineralogy.ru)

²CODES, Tasmania University, Hobart, Australia
(Ross. Large@utas.edu.au)

The styles of mineral and chemical evolution of fragmental massive sulfide ores at the Urals and Rudny Altai VMS deposits depends on the primary composition of sulfide clasts and impurity of adjacent sediments.

In the early diagenetic stage, pyrrhotite fragments are replaced by sooty pyrite with increasing grades of Au, Ag, V and U. Pseudomorphic chalcopyrite-2 and sphalerite-2 have inherited Ni, Mn, As, Pb, Tl, Au, Ag, and Te from replaced colloform pyrite fragments. In the submarine supergene zone, chalcopyrite-2 may be partly replaced by bornite or tennantite enriched in Ag and Bi. In pyrite-rich fragmental ores, sphalerite-1,2 is commonly dissolved, but in sphalerite-rich clastic sediments, sphalerite-2 is a dominant product of the sulfide evolution. In submarine supergene zones, all sulfides can be replaced by oxyhydroxides and then transformed to hematite and magnetite in later metamorphic stages. In the last stage of diagenesis, fine grained pyrite is overgrown by pyrite euhedra while chalcopyrite-2 and sphalerite-2 are recrystallized to twin crystal aggregates depleted in most of the trace elements. These mineral consequences are typical of clastic sulfides associated with jasper at the margins of the massive sulfide. In calcareous and serpentinite-rich clastic sulfide sediments, pyrite nodules are commonly the products of diagenesis. In carbonaceous clastic sulfide sediments, diagenesis results in nodular as well as framboidal pyrite. Fine grained diagenetic pyrite inherits high contents of trace elements from ore clasts. In the metamorphic stage, the diagenetic pyrites are replaced by pyrrhotite and euhedral pyrite. The range of submarine supergene and metamorphic alteration assemblages of fragmental massive sulfide ores is due to dissolution of clastic and diagenetic sulfides or their recrystallization and refining.

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[1] Danyushevsky, Robinson, Gilbert, Norman, Large, McGoldrick, Shelley (2011) *Geochim Explor Environm Anal* 11: 51–60.

Accurate measurement of diffusion profiles in altered wellbore cement using XMCT

HARRIS E. MASON^{1*}, WYATT L. DUFRANE¹,
STUART D.C. WALSH¹ AND SUSAN A. CARROLL¹

¹Physical and Life Sciences Directorate, Lawrence Livermore National Laboratory, 7000 East Ave, Livermore, CA 94551

(*corresponding author: mason42@llnl.gov)

Recent, intense effort has been focused on characterizing and modeling the degradation of wellbore cements exposed to CO₂-rich brines due to their role in geologic carbon storage. Scanning electron microscopy (SEM) and micro X-ray computed micro-tomography (XCMT) show the development of three discrete alteration layers in the reacted wellbore cement: a portlandite depleted zone, a Ca-carbonate zone, and an amorphous zone. Alteration models have assumed discrete, sharp contacts between these layers where the chemistry and mineralogy change drastically. Despite the power of XCMT to provide detailed 3D images of these alteration zones, little has been done to refine the geometrical models of wellbore cement alteration using these data.

Interpretation of XCMT images of wellbore cement can be problematic given the large distribution in grain and pore sizes as well as similarities of the mineral compositions and densities. Application of simple grayscale thresholds to XCMT data to identify alteration zones is problematic because of the zones span a narrow range in composition and density. Instead of thresholding, we rely on an advanced user-guided segmentation method which extracts the reaction zones by looking for not only differences in greyscale, but also in texture. This method allows us to more accurately define reaction boundaries and their extent in three dimensions.

With the reaction zone extents as guides, we take the analysis a step further and build 3D maps of mineral and elemental abundances. Using the geochemical model [1] and specific mineral linear X-ray attenuation coefficients we calculate what phases are present and their relative abundances in each zone. The end result shows that the reaction regions are defined by rather diffuse regions where multiple reactions can occur simultaneously, rather than by sharp regions.

[1] H.E. Mason *et al.*, *Environ. Sci. Technol.* 2013: 47, 1745

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