## Impact of sulfide separation on Ag and Mo budgets in arc magmas

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To understand the impact of sulfide separation on the metal budgets of Ag and Mo in arc magmas, experiments have been performed on the partitioning of these metals among pyrrhotite, a rhyolitic melt, and an immiscible Fe-S-O liquid. Previous experimental work on the partitioning of pyrrhotite and chalcopyrite with respect to Cu and Au in magmatic settings relevant to intrusion-related hydrothermal ore deposits, show a strong potential for the depletion of these metals by the segregation of the sulfide phases from silicate melts [1, 2, 3]. This sequestration of metals in sulfides may play a role in determining the relative abundances of these metals in associated deposits, or possibly even preclude ore formation. Evacuated sealed silica tube experiments were performed at 1042°C, log fO2 between FMQ and NNO, and  $\log fS_2 = -1$ bar. Partition coefficients for Ag and Mo between pyrrhotite and silicate melt (Ag 58±8 [1σSDOM]; Mo 35±3), and between Fe-S-O liquid and silicate melt (Ag 120±20; Mo 90±10) have been determined. Uncertainties represent one standard deviation of the mean. Based on these values, limits may be placed on the proportion of the initial metal budget that may be removed by the segregation of these sulfides. During Rayleigh fractionation (F=0.1) where sulfides compose 0.1wt% of the assemblage, pyrrhotite would sequester Ag (13%) and Mo (8%) less effectively that the Fe-S-O melt (24% and 19% respectively). Although these reductions might lead to variations in the tenor of associated ore they appear to be unlikely to significantly inhibit ore formation on their own. However if the magma metal budget is augmented through interactions with other magmas or by the assimilation of reduced sulfide-bearing sediments, the effects would be enhanced. Under the same conditions with 0.3wt % sulfides, po could remove 33% of the Ag and 21% of the Mo, whereas Fe-S-O melts could remove 51% of the Ag and 46% of the Mo. This suggests that exogenous additions of sulfur to arc magmas can affect their ore metal budgets.

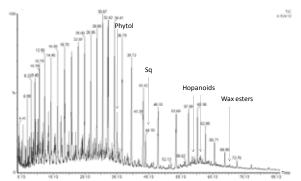
[1] Jugo *et al.* (1999) *Lithos* **46**, 573-589. [2] Lynton *et al.* (1993) *Economic Geology* **88,s** 901-915. [3] Simon *et al.* (2007) *Geochimica et Cosmica Acta* **71**, 1764-1782.

## Biomarkers preserved in fluid inclusions in quartz from the Berbes fluorite deposit (N Spain)

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The Cantabrian Zone in North Spain includes several stratabound to vein-like fluorite deposits, forming a significant MVT district. The fluorite deposits replace Paleozoic limestone which are associated to an aureole of hydrothermal alteration including dolomitization and silicification. They are interpreted as formed from the reaction of deep basinal brines with limestone, with some mixing with coeval seawater. The outer hydrothermal aureole includes abundant euhedral quartz crystals hosting abundant and large fluid inclusions that are frequently infilled with hydrocarbons. The analysis of the hydrocarbons reveals the presence of biomarkers: acyclic isoprenoids, polycyclic isoprenoids and fatty acid esters. Specifically, we found squalene, phytol and phytene, evidencing low maturation of organics.



**Figure 1:** GC/MS chromatogram (total ion count) of hydrocarbon inclusions in quartz from Berbes. Sq: squalene.

These results suggest that the hydrocarbons included in quartz source well preserved biomarkers which be of great interest for early Earth biosphere and planetary studies.

The genesis of these hydrocarbons is probably related with (a) dolomitization of the host rocks, or (b) hydrothermal degradation of underlying shale. Speculative, these processes would lead to the formation of nearby gas and oil fields.