## Zircon-hosted apatite inclusions: A powerful tool for reconstruction of Cl contents in melts

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Chlorine in the exsolved volatile phase plays an important role in complexing with metals in the extraction and concentration of metals in magmatic-hydrothermal ore deposits. Therefore, tracking the concentration and evolution of Cl in the parent melt is of particular importance in understanding how such deposits form. In theory, the incorporation of Cl into apatite could be used to track the volatile content of melts; however, low closure temperatures and the rapid diffusion of halogens in apatite make it susceptible to sub-solidus re-equilibration by later thermal events and hydrothermal fluids. This susceptibility compromises its ability to retain the primary halogen signature. However, the common occurrence of apatite as an inclusion phase in zircon crystals, together with the refractory nature of zircon, open up the possibility that such inclusions may preserve primary Cl<sub>melt</sub> compositions [1].

The Rio-Blanco-Los Bronces porphyry copper district is located in central Chile and hosts several world class porphyry copper deposits as well as barren intrusions [2]. This makes it an excellent area for an investigation of the role of Cl<sub>melt</sub> in the formation of porphyry copper deposits, as well as the effect of sub-solidus re-equilibration of Cl in apatite. For this study we analysed apatite crystals that occur both in the groundmass and as inclusions in zircons in four samples from the Los Bronces porphyry copper district using EPMA for halogen and major elements and LA-ICP-MS for trace elements. These samples include a barren intrusion unrelated to mineralisation that precedes mineralisation by around 10 Ma, and pre-, syn- and post-mineralisation porphyries.

Apatite inclusions hosted in zircon crystals typically exhibit a large range in Cl concentrations (<0.5 – 2.5 wt.% Cl), with all inclusion data exhibiting polymodal distributions of Cl concentrations. By contrast, groundmass apatites from all samples are characterised by uniformly low Cl concentrations (<0.5 wt.% Cl). These results are consistent with the apatite crystals in the groundmass having experienced sub-solidus re-equilibration related to the pervasive hydrothermal alteration in the district. The wide range in Cl concentrations recorded by the apatite inclusions is interpreted to reflect changing  $Cl_{melt}$  for the duration of apatite and zircon crystallisation, perhaps linked to volatile saturation and preferential partitioning of Cl into the aqueous phase. Additionally, the apatites hosted in zircon crystals show significant inter-sample variations, evolving from low Cl concentration (<0.5 wt. % Cl) in the barren intrusion, to higher Cl concentrations (0.5 – 2.5 wt.% Cl) in the samples closely temporally associated with porphyry Cu mineralisation. These data suggest that  $Cl_{melt}$  was significantly higher (0.05 – 0.40 wt.%  $Cl_{melt}$ ) in the melts associated with porphyry copper mineralisation compared with the precursor barren magmatism (~0.04 wt.%  $Cl_{melt}$ ) [3].

We conclude that due to the rapid diffusion of halogens in apatite in the presence of melt or hydrothermal fluid, the study of apatite inclusions hosted in zircon crystals is required to reconstruct primary melt compositions and to track the evolution of Cl concentrations in porphyry-forming magmas. This study reveals high Cl<sub>melt</sub> concentrations in the magmas related to mineralisation in the Los Bronces district, a property that would have facilitated the efficient extraction and concentration of metals.

## References:

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[2] Toro, J.C. et al. (2012). SEG Special Publication 16:105-126.[3] Li, H. and Hermann, J. (2017) Am. Mineral. 102:580-594.