The solubility of Au and Cu in andesite melts

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We conducted experiments in MHC cold seal vessels at 1000 °C and 200 MPa to study the solubility of Cu and Au in andesite melts as a function of the Cl and S content of the silicate melt and oxygen fugacity of the system. A gold activity of 0.99 and a Cu activity of 0.01 were imposed by using AuCu alloy capsules.

At an fO_2 of NNO-0.2, the solubility of Au shows a positive linear correlation with the S concentration in the melt, and increases from 41 ± 8 ng/g (1 σ) in a S-free melt to 1547 ± 52 ng/g in a melt with $344\pm20 \ \mu$ g/g S, a condition near pyrrhotite saturation. Chlorine has a relatively minor positive effect on Au solubility; a S-free andesite melt with 1.00 ± 0.01 wt% Cl contained only 112 ± 20 ng/g Au.

The effect of fO_2 on the solubility of Au is significant, leading to 0.18 ± 0.04 log unit increase in Au solubility for 1 log unit increase in fO_2 in a S-free, Cl-bearing melt, which is approximately consistent with +1 valence of Au in the silicate melt. In S-bearing melts, the effect of fO_2 on gold solubility is further complicated by the following (or a similar) reaction: Au+FeS(melt)+H₂O(melt)=AuSH(melt)+FeO(melt)+0.5H₂(g) Accordingly, a maximum in Au solubility is observed just at the low fO_2 end of the S²⁻/S⁶⁺ transition, however, it is much smaller than that shown by Botcharnikov *et al.* (2011) [1].

The apparent solubility of Cu at an fO_2 of NNO-0.2 and aCu of 0.01, ranges between 45 ± 1 and $78\pm1 \ \mu g/g$ and shows a weak positive correlation with the S and Cl concentration in the melt. Moderate excess solubily over that predicted assuming a dominant CuO_{0.5}(melt) species is observed in S-bearing experiments in the fO_2 range of the S²⁻ to S⁶⁺ transition and above. Variation in the K₂O/Na₂O and FeO/Na₂O ratios in the melt did not significantly affect Au and Cu solubilites.

Model volatile/melt parition coefficients of Cu and Au suggest that volatiles exsolving from andesite magmas are efficient at extracting Au, but inefficient at extracting Cu.

[1] Botcharnikov, Linnen, Wilke, Holtz, Jugo & Berndt (2011), *Nature Geoscience* **4**, 112-115.

Cryogenic cave carbonates – A new tool for estimation of former permafrost depths

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Geochemical processes in the Earth's critical zone largely depend on the presence or absence of a permafrost (perennially frozen ground, i.e. soil and rock remaining at or below 0 °C for at least two consecutive years, [1]). While the areal extent and depth of present-day permafrost zone are relatively well known [1], the extent, duration, and depth of permafrost during Pleistocene glacials are much less understood. Here we present a new tool for the estimation of former permafrost minimum depth based on the occurrence of a specific type of secondary carbonate in caves.

Cryogenic cave carbonate (CCC) is a unique type of secondary carbonate formed in caves during freezing of common calcium bicarbonate water by the expulsion of dissolved load by the growing ice. CCCs can be identified based on their typical morphology and occurrence, by U-series dating fitting into glacials, and especially by specific C- and O-isotope geochemistry, which proves their formation during water freezing [2, 3, 4]. CCCs were formed at the transitions from glacials to interglacials or from stadials to interstadials and occur as accumulations of loose crystals and crystal aggregates on the cavity bottom, where they were deposited after melting of the ice filling of the cavity. CCCs show a unique isotope composition with δ^{18} O values down to -25 % (PDB), and δ^{13} C values up to +6 %.

We collected data for all known CCC occurrences in a belt parallel to the southern edge of the Weichselian continental glaciation (southern Poland, Slovakia, Czech Republic, central Germany), dated them by U-series method, and evaluated their depths under the surface. When using data from isolated cavities only, which cannot be cooled by air circulation, a minimum Weichselian permafrost depths in this belt can be estimated at 30–70 m under the surface (the study was supported by the project GA CR P210/10/1760).

[1] French (2007) *The periglacial environment*, 3rd ed., 458 p.
[2] Žák *et al.* (2004) *Chem. Geol.* 206, 119-136. [3] Richter & Riechelmann (2008) *Internat. J. Speleology* 37, 119-129. [4] Žák *et al.* (2008) *Quat. Internat.* 187, 84-96.

Mineralogical Magazine

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