Noble gas measurements in pore water from sedimentary rocks

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Noble gases are a uniquely powerful tool to trace groundwater provenance across sedimentary formations, due to their chemical inertness and well-known isotope signatures (atmosphere/air-saturated water, radiogenic crust and primordial mantle), and increasing concentrations with time by radioactive decay.

We further developed and modified a sampling method originating from Heidelberg [1] for extracting the noble gas dissolved in the porewater on freshly drilled rock cores. After several weeks at room temperature in a gas-tight container, the noble gas residing in pore water diffused out of the sample into the ring space of the container, whose internal pressure normally had risen from 10^{-3} to about 10 mbar. This room-temperature procedure ensured that noble gases only derive from porewater and not from minerals. The container was then connected to a purification system and the porewater gas expanded inside the entire line. Major active gases were removed by cryogenic separation in a series of steel traps containing charcoal at 77 °K and subsequently by getters. Methane was successfully removed using a special design consisting of four different getters: A CuO getter to oxydise hydrocarbon gas to CO_2 and H_2O, a TiO_2 getter to remove all major gases (H_2O, CO_2, N_2) by adsorption, and a ceramic and a Zr-Al getter to remove H_2. After gas purification, He, Ne and Ar concentrations were measured by a quadrupole mass spectrometer.

Our case study focused on low-permeability Paleozoic argillaceous limestone of the Cobourg Formation from the Michigan Basin (Ontario, Canada). The initial sampling consisted of 32 drill core samples across a 860m-long profile down to the Precambrian basement. The encountered pore fluids have very high salinity and high dissolved gas concentrations (methane, CO_2, etc.). We obtained a gradient of He concentrations that increase with depth, with values up to 1.6E-2 cm^3 STP/g_{water}, the highest values reported so far. The combination of age and noble gas concentrations as a function of depth potentially allow to obtain values of effective diffusion coefficients by modelling, in order to assess the relevant mass transport mechanism.

[1] Osenbrück *et al.* (1998) *Geochim. Cosmochim. Acta* **62,** 3041-3045.

Effect of fS_2 on Pd solubility in silicate melts – Implications for PGE enrichment processes in sulfide melts

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Sulfides found in magmatic PGE deposits (e.g., Merensky Reef, Bushveld Complex; JM Reef, Stillwater Complex) are typically enriched in the platinum-group elements (PGE) relative to their parental magma. The mechanism that produces the enrichment in PGE is still a subject of ongoing discussion, namely the role of S, as well as other chalcophile elements, as possible ligands for PGE in silicate melts. Previous experimental studies have, for instance, shown that Pt and Pd are complexed strongly by ligands such as Te^{n+} [1]. Given that both Te and S are chalcogenes, it is likely that PGE are dissolved in silicate melts being associated with S^{2-} as a ligand.

To test if S^{2-} enhances PGE solubility in silicate melt, we are investigating experimentally the solubility of Pd in natural basaltic silicate melts as a function of sulfur fugacity (fS_2), in a relative fS_2 range above Fe-FeS but below sulfide saturation [2]. Palladium is studied in preference to the other PGE because Pd is most chalcophile and has the highest solubility of all PGE in silicate melts. The silicate matrix is a picrite composition and is equilibrated with a Pd loop at 1300°C in a 1-atm vertical gas mixing furnace. Relative fO_2 conditions range from FMQ to FMQ-2. All experiments are reversed by running simultaneously charges initially free of Pd and charges doped with PdO. Run products are quenched to clear glasses in air, which is subsequently analysed for major elements and dissolved S by electron microprobe, and for Pd by LA-ICPMS. In order to avoid overestimation of Pd contents due to nanonugget contamination, only flat parts of the time-resolved laser spectra are quantified to calculate Pd solubilities in the silicate melt.

Preliminary results show that the Pd solubility is distinctly elevated by the additions of S^{2-} to the silicate melt, at an fO_2 of FMQ-2 and fS_2 close to, but below sulfide saturation [2]. Solubility of Pd in the silicate melt appears to be promoted by preferential association of Pd with the S^{2-} ligand. If this proves true also for the other PGE, the results will have profound implications for PGE enrichment processes in magmatic sulfide melts exsolving from S-saturated silicate melts.

[1] Helmy *et al.* (2007) *Contrib Mineral Petrol* **153,** 577–591.
[2] Bockrath *et al.* (2004) *Chem Geol* **208,** 265-271.