Accurate analysis of noble gas concentrations in water samples of a few milligrams

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We developed a new method to precisely analyse noble gas concentrations in samples containing small quantities (~1mg) of water in pores or fluid inclusions. The method includes an accurate determination of the mass of the extracted water and the measurement of noble gas abundances using standard methods. The amount of water is calculated from the pressure of the water vapor in a calibrated volume at a known temperature to avoid condensation. The uncertainty of the so determined water masses is ~1%.

The method was applied to fluid inclusions in stalagmites - which typically contain 0.1-1 wt.‰ of water - with the goal to determine cave temperatures from noble gas concentrations. We analysed stalagmites from the Middle East, Turkey and Switzerland.

We extracted the noble gases and the water in two analytical steps, i.e. crushing followed by subsequent heating (280°C - 600°C). For a successful reconstruction of noble gas temperatures (NGTs) the amount of noble gases originating from air inclusions – that are also abundant in stalagmites - needs to be low, as air-derived noble gases mask the temperature dependent signal of the noble gases from water inclusions. Therefore, the extraction in two analytical steps is essential, because the crushing steps significantly reduce the amount of noble gases that are released from air inclusions in subsequent heating steps.

Our results demonstrate that it is in principle feasible to determine NGTs in fluid inclusions in stalagmites. Calculated NGTs for modern samples correspond well with the present temperature in the cave. However, for the majority of samples, the calculation of NGTs is hampered since particularly the light noble gases (He, Ne) are enriched due to a noble gas component that seems to be bound in the calcite lattice. We developed a conceptual model, that describes a size-dependent trapping of atmospheric noble gases during the growth of the stalagmite and the resulting consequences for the calculation of NGTs.

Interrelations between pore fluid chemistry, secondary mineral formation, and hydraulic permeability in feldspar-rich sandstones under hydrothermal conditions

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Geothermal energy production from deep sedimentary reservoirs interferes with thermodynamic fluid-mineral equilibria. Different dissolution and/or precipitation reactions might thus be induced, which may affect the hydraulic permeability of the reservoir rocks.

To constrain this interrelation for the model system quartz-feldspar-water, laboratory experiments and simulations were conducted under hydrothermal conditions. We intended to investigate the mechanisms and kinetics of potential dissolution-precipitation processes and their consequences for rock permeability.

A high-pressure high-temperature permeameter was used to conduct long-term permeability and electrical rock conductivity measurements at a maximum temperature of 160°C. Different types of natural and analog sandstones were investigated. The maximum run duration was approximately 4 months.

Complementary batch experiments were performed with quartz-feldspar powders and distilled water at saturation vapor pressure and 150°C. The resulting fluids were analyzed with ICP-OES and the reacted powders were characterized with XRD and SEM. Finally, the saturation indices of secondary minerals were calculated using PHREEQC.

For feldspar-rich sandstones and at stagnant flow conditions the electrical rock conductivity showed an asymptotical increase indicating that the respective pore fluid approaches saturation. Fluid samples taken from the batch experiments support this observation. Finally, the simulations of a plagioclase-quartz-water equilibrium at 150°C indicate that Ca-montmorillonite, kaolinite, and gibbsite are supersaturated in the resulting fluid.

The related potential for secondary mineral formation implies a risk of permeability damage in the present fluid-rock system even at comparatively low temperatures. The generally observed decrease in rock permeability will be critically discussed in this context but also regarding the precipitation kinetics and thermo-mechanical effects.