Noble gases in fluid inclusions in speleothems

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Speleothems contain various paleoenvironmental proxy records on long time scales with high temporal resolution. Air and water inclusions formed during speleothem growth both represent potentially valuable archives of past climate conditions. First semi-quantitative analyses of air inclusions indicate that the major components (N2, O2, Ar) are present in near-atmospheric abundances. In contrast, trace gases (CO_2, N_2O, CH_4) are enriched in the inclusions and hence the cave air. Therefore, similar to air trapped in ice cores, air inclusions in speleothems have the potential to reconstruct past climate conditions in regions where no ice is available. The concentrations of dissolved noble gases in water inclusions directly reflect the atmospheric pressure as well as the temperature and salinity of the water at the time of formation of the inclusions. To infer past climate conditions, the parameters T, p, S and “excess air” have to be determined from four measured noble gas concentrations (Ne, Ar, Kr, Xe), analogous to the noble-gas thermometer employed in lakes and groundwater. The separation of noble gases from air and water inclusions is crucial to determine paleotemperatures from noble gases is water inclusions. Microscopical investigations show that air and water inclusions differ in size and position within the speleothem. Hence, a sufficient separation should be achievable by extracting noble gases in two subsequent steps (crushing and heating). First results show that crushing mainly opens inter-granular air inclusions whereas heating cracks intra-granular water and air inclusions. However, the noble gas signature after heating is dominated by noble gases from water inclusions.

The salinity of the drip water before incorporation into the speleothem - determined by microthermometry - ranges from 7 – 15 ‰ and therefore can be assumed to be equal to that of freshwater. Since tritiogenic and radiogenic 3He in the water inclusions are probably negligible, 3He is purely atmospheric, in contrast to 4He. This would allow 3He to be used as an additional constraint to reconstruct the paleoenvironmental conditions.

With the potential of a quantitative separation of noble gases from air and water inclusions before analysis and additional measurements of 3He, the determination of paleotemperatures from noble gases in fluid inclusions seems to be possible.

In summary, dissolved noble gases from water inclusions, as well as the trace gas abundance from air inclusions are emerging proxies that will complete the available methods to reconstruct past climate conditions from speleothemes.

Selenite reduction by nano-crystalline green rust, magnetite, siderite and mackinawite: EXAFS identification of Se species

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Selenium oxoanions are abiotically reduced on Fe(II/III) hydroxide (green rust) and Fe(0) metal surfaces to Se oxidation states of 0, -I or –II with relatively slow reaction kinetics [1, 2]. The unequivocal phase characterization by EXAFS spectroscopy, which is a key for the determination/prediction of Se solubility, was hindered by incomplete reduction, insufficient spectral data ranges and the similarity in short-range structures of the potential mineral phases. In a recent study [3], however, we were able to clearly identify the reduction product of selenite co-sorbed with Fe^{2+} to montmorillonite as nano-particulate, trigonal Se(0) by collecting low-noise EXAFS spectra at 15 K (Rossendorf Beamline at ESRF, Grenoble, France) and by employing advanced data analysis methods [4, 5].

Here, we present data on the reduction of selenite by green rust, magnetite, siderite and mackinawite. In the presence of green rust, selenite was completely reduced to trigonal Se(0) within one day, which was further converted to ferroselite (orthorombic $FeSe_2$) within one month. The associated Fe(II) oxidation and magnetite formation quantified by Moessbauer spectroscopy allowed us to establish the following reaction scheme: $32\ [Fe^{II}_{12}Fe^{III}_{5}(OH)_{34}\ Cl^{-}_{5}\ nH_2O](s) + 38\ Se^{IV}O_3^{2-} \Leftrightarrow 19\ [Fe^{II}Se^{-I}_{2}](s) + 175\ [Fe^{II}Fe^{III}_{2}O_4](s) + 160\ Cl^{-} + 502\ H_2O + 84\ H^{+}$

Similar to green rust, mackinawite and magnetite reduced all selenite within one day, whereas reduction by siderite was incomplete. Depending on type of mineral and Se-to-mineral ratio, trigonal Se(0), ferroselite or achavalite (hexagonal FeSe) formed. The observed differences in reaction end products and reduction kinetics may significantly affect Se bioavailability and Se migration.

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