

Excess air correction in groundwater dating with He isotopes

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He isotopes produced by the decay of tritium (tritogenic ³He) and the U/Th-series nuclides (radiogenic ⁴He) are important groundwater dating tools. A major difficulty lies in the separation of the age-sensitive non-atmospheric He components from the atmospheric components. In groundwater, this problem is aggravated by the ubiquitous presence of an excess of atmospheric gases above the atmospheric solubility equilibrium ("excess air"). The excess air He is usually inferred from the measured Ne concentration, assuming that excess air has the same elemental composition as atmospheric air. This procedure sometimes yields negative results for tritogenic ³He and radiogenic ⁴He, clearly indicating over-correction for excess air.

However, the assumption of purely atmospheric excess air composition is not generally applicable. Instead, the elemental composition of excess air can be fractionated relative to air due to either partial diffusive re-equilibration (PR) with the atmosphere [1] or closed-system equilibration (CE) between entrapped air and water [2]. The decisive parameter in the excess air correction is the He/Ne ratio of the excess air component, denoted as L_{ex} . For unfractionated excess air, L_{ex} has the atmospheric value 0.288. PR-type fractionation can lower this ratio drastically, in principle down to zero. For fractionation of the CE-type, L_{ex} is confined to values between that of air and the He/Ne ratio at solubility equilibrium (0.22 to 0.25, depending on temperature). Since both fractionation models predict a reduced value of L_{ex} , both lead to a reduction of the excess air correction for He and thus can potentially remove the problem of negative non-atmospheric components.

We re-evaluate several published ³H-³He data sets and discuss a few examples where ³H-³He studies included analysis of all noble gases. In most cases, the limited adjustment suggested by the CE-approach is sufficient to remove inconsistent results. The correction of the derived ages is minor. The PR-model tends to yield unrealistically high values for tritogenic ³He and radiogenic ⁴He. If not all noble gases are available, the combined interpretation of Ar, Ne and ²⁰Ne/²²Ne can be sufficient to determine whether the PR- or the CE-model should be applied and to estimate the fractionation parameters of the models from which L_{ex} can be estimated.

References

- [1] Stute M., et al. (1995), *Science* **269**, 379-383.
[2] Aeschbach-Hertig W., et al. (2000), *Nature* **405**, 1040-1044.

Geochemical constraints for the remediation of acidic mining lakes

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Introduction

In abandoned pit holes from lignite mining in wide areas of Eastern Germany lakes have formed that are strongly acidic (pH-values < 3) due to the oxidation of pyrite and subsequent precipitation of secondary iron minerals. In the sediments, coupling of sulfate and iron reduction to form recent pyrite could potentially contribute to neutralisation of the acidity. The extent of these processes is constrained by the geochemical conditions in these lakes, which any remediation measure based on the stimulation of carbon turnover rates has to take into account.

Discussion of results

Acidic mining lakes are characterized by the formation of schwertmannite (SHM, $Fe_8O_8(OH)_x(SO_4)_y$), which preferentially forms at pH values between 2.5 and 4 and at high sulfate concentrations. The supply of organic carbon is low and most of the autochthonously formed carbon is associated to the iron mineral surface.

The occurrence of SHM has a significant influence on the geochemistry of these lakes and defines the boundary conditions under which microbial growth can take place. The high sedimentation rates of schwertmannite ($\approx 4 \text{ g m}^{-2} \text{ a}^{-1}$) and the acidic conditions at the sediment-water-interface (SWI) leads to the formation of two geochemically different layers in the sediments. The upper acidic 5 cm are characterized by a closed iron cycle based on microbial iron reduction and reoxidation of Fe(II) to SHM at the SWI, thereby generating new acidity. Below, additional acidity is generated upon transformation of SHM to goethite. An increase of the pH occurs only at 8 - 10 cm depth with the onset of sulfate reduction. Below 10 cm an anaerobic sulfur cycle exists which is also almost completely closed with only little pyrite burying.

Conclusion

It appears that alkalinity formation in sediments of acidic mining lakes is inhibited by the high Fe deposition rate, which leads to a decoupling of iron and sulfate reduction. Even the addition of carbon to the sediment will therefore not necessarily alter the electron fluxes as long as the iron supply persists.

References

- Laskov, C., Amelung W.; Peiffer S.: Organic matter preservation in the sediment of an acidic mining lake, *Environ. Sci. Technol.*, accepted.
Peine A., Küsel K., Tritschler, A., Peiffer S. (2000): Electron flow in an iron-rich acidic sediment – evidence for an acidity-driven iron cycle, *Limnol. Oceanogr.*, **45**, 1077-1087.