

Using noble gases for real-time tracing of oxygen turnover in aquatic systems

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Our recent experimental developments on membrane inlet mass spectrometric systems allow the quasi-continuous measurements of dissolved gas concentrations in natural waters under field conditions. Dissolved He, Ar, Kr, N₂, O₂, and CO₂ concentrations can be quantified within minutes with high precision [$\pm 1\%$, 1].

The method was employed in a peri-alpine river to analyze the temporal and spatial dynamics of oxygen turnover during bank infiltration.

During *low* river discharge, the measurements indicated that aeration of groundwater is dominated by direct hyporheic exchange, and that the transport of solutes and heat are decoupled. The combined Ar-O₂ analysis allowed the in-situ oxygen consumption rate and its dependence on the water temperature to be determined. During *high* river discharge after a flood event, we found that significant amounts of excess air were produced in the vicinity of the studied groundwater wells. The formation of excess air and the corresponding oxygen input into the groundwater varied according to the confining conditions within the aquifer and therefore also co-varied with different ecological process zones.

Our results show that the combined analysis of noble and biogeochemically active gases yields valuable information on the dynamics and the importance of different gas exchange mechanisms in aquatic systems with respect to biogeochemical oxygen turnover and thus groundwater quality

[1] Mächler *et al.* ES&T, 46, 7927-8522, 2012.

Co-evolution of the ocean-atmosphere-sediment system through Phanerozoic time

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Attempts to unravel the history of seawater chemistry go back as far as E. Halley [1] and J. Joly [2] and more recently W. W. Rubey [3] and H. D. Holland [4] among others. We have shown previously [5] that seawater chemical changes on the multi-million year time scale through Phanerozoic time reflect the essential state of the ocean-atmosphere-sediment system with respect to major lithophile and organic component fluxes constrained by a number of observations from the sedimentary rock record.

Despite relatively rapidly changing periods like the end Permian and PETM episodes, the system appears homeostatic and self-regulating and produces two dominant chemostatic modes despite apparent time lags among various variables that suggest different biogeochemical pathways leading to the modes: (Mode I) elevated atmospheric CO₂ and depressed seawater Mg/Ca and SO₄/Ca ratios, pH and carbonate saturation states (the calcite-dolomite seas) versus (Mode II) depressed atmospheric CO₂ and elevated seawater Mg/Ca and SO₄/Ca ratios, pH and carbonate saturation states (the aragonite seas). Transitions between the two modes are modified and overprinted by irreversible evolutionary and ecosystem changes. One example involves the shift of the locus of biogenic carbonate sediment deposition through radiation of pelagic calcifiers and the expansion of dolomite deposition enabling development of Mode I seawater chemistry in the Mesozoic. In addition, Paleozoic deep seas might have been sites of inorganic carbonate accumulation "lost" via subduction. Without this accumulation it is difficult to account for high atmospheric CO₂ concentrations and Mode I seawater chemistry during much of Paleozoic time.

[1] Halley (1715) *Phil. Trans.* **29**, 296-300. [2] Joly (1899) *Sci. Trans. Royal Dublin Soc.* **7**, 23-66. [3] Rubey (1951) *Geol. Soc. Am. Bull.* **62**, 1111-1148. [4] Holland (1972) *Geochim Cosmochim. Acta* **36**, 637-651. [5] Arvidson *et al.* (2006) *Am. J. of Sci.* **306**, 135-190. Guidry *et al.* (2007) In: *Evolution of Primary Producers in the Sea*, 377-403. Mackenzie *et al.* (2008) *Mineral. Mag.* **72**, 329-332. Arvidson *et al.* (2011) *Aquat. Geochim.* **17**, 735-747.