

## Changes in volatile speciation during magma generation, crystallization and degassing

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Crustal magmatism and the magmatic-hydrothermal interface occur at the Earth's greatest density and chemical boundary layer. In mid-ocean ridge basalt (MORB) systems, crossing the boundary layer results in a significant change in the redox state (oxygen fugacity) of the system during emplacement, crystallization and degassing. The change in  $fO_2$  affects the speciation of volatiles in evolved fluids. The initial volatile speciation in MORB magma is determined by melting reactions in the source region and subsequent evolution of the magma during its ascent<sup>1</sup>.

MORB melts are strikingly reduced<sup>2</sup> (have very low  $Fe^{3+}/Fe^{2+}$  ratios) but contain only oxidized C and H as dissolved  $CO_2$  and  $H_2O$ <sup>3</sup>. Magnetite crystallization generates  $H_2$  by reduction of  $H_2O$  in melt or glass, evolving  $H_2$  rich fluids<sup>2,4</sup> that mix with  $CO_2$  exsolving from magma during transient dike-eruptive events (as well as crystallization) so the fluids are initially in a gross disequilibrium redox state. The same events may occur in crystallizing MORB magma chambers. The evolved fluid will trend toward an equilibrium redox state between COH species. Minor variable valance species will equilibrate to that state.

Calc-alkaline rocks are more oxidized than crystalline MORBs<sup>5</sup>, but few estimates are available for relatively primitive melts. It is possible that crystallization of those magmas also initially results in the generation of  $H_2$ -rich, reducing fluids which become more oxidized by reacting with wall rocks.

### References

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## Gas exchange in quasi-saturated porous media: Investigations on the formation of excess air using noble gases

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Excess air, the ubiquitous supersaturation of atmospheric gases in groundwater is an important aspect of the gas exchange between (soil-) air and the saturated zone. In subsurface hydrology, the presence of excess air crucially affects the quantitative interpretation of noble gases in groundwater, e. g., for the determination of paleorecharge conditions and groundwater dating. In addition, since the excess air component initially includes all atmospheric gases, the presence of excess air can result in significantly enhanced concentrations of biochemically relevant gases such as oxygen and nitrogen in the saturated zone.

Until now, a detailed knowledge about the mechanisms that lead to the generation of excess air is lacking. To gain a better understanding of the process of excess air formation, the gas exchange between the upper, quasi-saturated groundwater zone and soil air was studied in column experiments using atmospheric noble gases as tracers. The dissolution of air bubbles entrapped in the soil substrate during the water filling process was identified to be responsible for the supersaturation of dissolved atmospheric noble gases. The sum of the hydrostatic pressure that acts on the gases in the entrapped air bubbles and the capillary pressure resulting from the curvature of the bubble surface is the dominating parameter that controls the total amount of dissolved air. The composition of the dissolved gas component ranges between a pure atmospheric pattern and a fractionated composition according to the closed-system equilibration (CE-) model (Aeschbach-Hertig et al., 2000). The observed noble gas composition is influenced by the flow regime, the entrapped bubble size distribution, the initial concentrations of the dissolved gases and the composition of the entrapped gas phase. Simulations with a newly developed kinetic model for dissolved gas transport in porous media which considers the dissolution of entrapped gas bubbles yields results consistent with the experimental data.

### References

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