

Microbial selenium and iron reduction under high pressure

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The Earth's subsurface is characterized by hostile conditions for life in terms of temperature, pressure and nutrient availability. Among the factors governing microbial dissimilatory metal reduction and thus carbon oxidation in the subsurface, pressure may have a broad impact on reaction rates and yields. The understanding of metal reduction in natural environments, especially in the subsurface, can be first comprehended thanks to studies of metal reduction in pure cultures.

We investigated the effects of pressure on the reduction of Se (IV) and Fe (III) to Se (0) and Fe (II), respectively by the bacterial model *Shewanella oneidensis* MR-1. This strain is a mesophilic and piezosensitive counterpart of psychrophilic and piezophilic *Shewanella* representatives that have often been isolated from deep-sea environments. Kinetics of Se (IV) and Fe (III) reduction were monitored *in situ* under high hydrostatic pressure by X-ray Absorption Spectroscopy (XAS) in an autoclave. Most measurements were performed at the BM30B beamline of the European Synchrotron Radiation Facility (ESRF, Grenoble, France). Experiments were conducted from 0.1 MPa to 150 MPa at MR-1 optimal temperature of 30°C. The effects of pressure on cell survival were evaluated by comparing the Colony-Forming Units (CFU) before and after pressure incubations.

Metal reduction occurs in cultures of MR-1 at pressures in excess of 100 MPa. This shows that the metabolic activity of a microbe, despite being piezosensitive, extends far beyond its pressure limits for growth at 50 MPa. Consequently, considering only the ability to grow in the conditions of the deep subsurface as a proof of metabolic activity may lead to an underestimation of the impact of the biosphere in deep environments. Although the experimental conditions may not match exactly environmental subsurface conditions, we show here that the metabolic activity of a surface microbe potentially brought to the deep subsurface can affect significantly biogeochemical cycles such as those of selenium, but more importantly those of iron and carbon.

Effect of B/Al ratio on the dissolution of nepheline glass, Na₃(Al, B)₁₋₄Si₄O₁₆

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The dissolution kinetics of five glasses along the NaAlSiO₄-NaBSiO₄ join were used to evaluate how the structural variations associated with boron-aluminum substitution affect the rate of dissolution. The composition of each glass varied inversely in mol% of Al₂O₃ (5 to 25 mol%) and B₂O₃ (20 to 0 mol%) with Na₂O (25 mol%) and SiO₂ (50 mol%) making up the remaining amount, in every case Na/(Al+B) = 1.0. Single-Pass flow-through experiments (SPFT) were conducted under dilute conditions as a function of solution pH (from 7.0 to 12.0) and temperature (from 23° to 90°C).

Analysis of unreacted glass samples by ²⁷Al and ²⁹Si MAS-NMR suggests Al (~98% ⁴¹Al) and Si atoms (~100% ⁴¹Si) occupy a tetrahedral coordination whereas, B atoms occupy both tetrahedral (⁴¹B) and trigonal (¹³B) coordination. The distribution of ¹³B fractionated between ¹³B (ring) and ¹³B (non-ring) moieties, with the ¹³B (ring)/¹³B (non-ring) ratio increases with the B/Al ratio. The MAS-NMR results also indicated an increase in the fraction of ⁴¹B with an increase in the B/Al ratio. The ²⁷Al peak maxima shift to lesser values with an increase in the B/Al ratio which suggests mixing between the ⁴¹Al and ¹³B sites, assuming avoidance between tetrahedral trivalent cations (⁴¹Al-O-⁴¹B avoidance).

Results from SPFT experiments suggest a forward dissolution rates, based on Na and Si release, for homogeneous glasses are independent of the B/Al ratio, whereas dissolution rates based on Al and B release are not. Normalized dissolution rates based on B release increase with the molar fraction of ¹³B (ring).

Finally in accord with previous studies, these data suggest rupture of either the Al-O or Si-O bonds as the rate-limiting step controlling the dissolution of these glasses.