



## Quantifying the role of microorganisms in silicate mineral dissolution at the conditions of CO<sub>2</sub> storage in basalts

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Numerous laboratory and field studies indicate that bacteria can significantly affect aluminosilicate and Al, Fe oxides dissolution rates at the earth-surface conditions. Much less is known on the effect of bacteria on “basic” Ca, Mg-bearing silicate dissolution rates, especially in the context of underground setting of CO<sub>2</sub> storage sites in basaltic aquifers. This work reviews our results on olivine (Fo<sub>91</sub>) and amorphous basaltic glass ( $\beta$ -glass) dissolution kinetics in batch and mixed-flow reactors in the presence of aerobic gram-negative bacteria (*Pseudomonas reactans*, HK 31.3) extracted from deep underground oxygen-bearing water of basaltic aquifer and in the presence of typical fungi, *Rhodotorula graminis di Menna Y-336T*. The release rate of mineral constituents was measured as a function of time in the presence of live, actively growing, dead cells and microbial exometabolites in constant-pH (6 to 9), bicarbonate-buffered (0.001 to 0.05 M), nutrient-rich and nutrient-free media in mixed-flow reactors at 0-30 bars of CO<sub>2</sub>. Intracellular uptake and reversible surface adsorption of Mg, Si and  $\beta$ -glass constituents by live and inactivated cells were assessed in growth and adsorption experiments.

It follows from results of this study that the presence of carbonate/bicarbonate ions and alkaline solutions (pH  $\geq$  9), typical for basaltic aquifers, should significantly inhibit the impact of microbial activity and cell exometabolites on olivine dissolution rate. In acidic, CO<sub>2</sub>-saturated solutions at pH  $<$  5 the impact of heterotrophic bacteria is also minor. Only in neutral, carbonate-free solutions do live but starving cells and dissolved organic ligands measurably enhance the forward dissolution rates. The effect of *P. reactans* and *Rhodotorula graminis* on major element release during basaltic glass dissolution in all studied conditions was negligibly small within the experimental reproducibility. This implies an existence of rather narrow window in which the underground biota may actually affect basic silicate reactivity at the conditions of CO<sub>2</sub> storage. At the typical scenario of CO<sub>2</sub> sequestration in basaltic aquifers, initially acidic, CO<sub>2</sub>-saturated solutions will be progressively replaced by neutral, HCO<sub>3</sub><sup>-</sup>-bearing solutions. Note that *in-situ* carbonate mineralization will decrease the concentration of dissolved inorganic carbon while maintaining the pH around 7. During this stage of CO<sub>2</sub> sequestration, one may expect a pronounced and positive effect of underground biota on mineral reactivity. Finally, in the post injection period, as the CO<sub>2</sub>-rich front moves into the aquifer, pH increases to  $>$  7 following carbonates/silicates dissolution as shown by reactive transport simulations. At these pH values, the aqueous C-speciation changes from H<sub>2</sub>CO<sub>3</sub>\* to HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup> which should result in an inhibition of both olivine and carbonate mineral dissolution. Noteworthy that aqueous bacteria and organic ligands are in no way capable of preventing this drop in olivine and calcite dissolution rate as followed from results of recent studies of mineral dissolution kinetics.