

## An in situ experimental study of the bacterial colonization and weathering of silicate surfaces.

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The aim of this experimental work is to determine some structural and/or mineralogical characteristics specific to a bacterial activity on the silicate surfaces under controlled conditions and ideal set-up for detecting them. This approach is complementary to biochemical approaches developed in the laboratory, which aim to detect and identify bacteria on mineral surfaces by PCR (Polymerase Chain Reaction). Weathering of silicate surfaces by synthetic biogenic substances and bacteria producing them are compared.

Bacterial suspension of DH5 $\alpha$  strain (*E. coli*) producing a green fluorescent protein and K84 strain (*Agrobacterium rhizogenes*) producing siderophores are prepared at different concentration ranging from 0.05 to 1 DO<sub>600nm</sub>. Silicate surfaces ((001) of micas, (010) of olivines and AT for quartz) are placed in the bottom of an optical transparent reactor and are inoculated by the bacterial suspensions in aqueous buffer or bacterium-free buffer. The colonization of the surface is followed in situ, in vivo and in real time for duration varying from 1 min to 4 days by transmission and fluorescence optical modes. Samples are then air-dried for X-ray absorption and semi quantitative fluorescence microtomographies (Simionovici et al, 2001) and for channeling Rutherford Back Scattering (c-RBS, Lemelle et al, 2002) or fixed with glutaraldehyde solutions for scanning and transmission electron microscopy (SEM and TEM respectively).

Kinetics of the colonization are described by measuring the number of bacteria per surface unit versus the deposit duration. They reveal apparent Stokes regimes for duration lower than a characteristic time  $\tau$  above which a 3D organization starts. The higher (Si/O) ratio of the mineral is, the lower  $\tau$  is because of a weaker adhesion on the surfaces. Bacterial cells are not randomly distributed on the silicate surfaces and SEM observations confirm at higher resolution these optical observations. All these results, including the TEM and the X-ray microtomographies results, converge to define specific sub-micrometer characteristics of the bacterium/mineral interfaces and of the mineral surfaces weathered by synthetic biogenic substances.

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Simionovici A., et al., (2001) *Highlights 2001*, 96.

## Hydrothermal stability of glycine and the formation of oligoglycine: Kinetics of peptide formation at 260°C and 200 bars

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We have undertaken a kinetic study of the hydrothermal stability of selected amino acids and peptides in an isothermal, isobaric and pH-controlled system. Experiments were conducted in flexible gold-bag reactors at 260°C and 200 bars maintained at pH 6.8 with phosphate buffers. A solution containing glycine was injected into the gold-cell containing organic-free distilled water pre-equilibrated at the experimental conditions. Reaction products were extracted over a period of 100 hours and analysed with HPLC by UV-detection. We observed first-order rate loss of glycine, but at rates substantially lower than previously reported<sup>[1,2]</sup>. In our experiments the glycine dimer, glycyglycine, was rapidly formed to levels 100-fold above those predicted by thermochemical calculations<sup>[3,4]</sup>. Rapid cyclization of glycyglycine to the cyclic lactam diketopiperazine was followed by a coupled pseudo-first order loss in both products with a rate constant  $k=0.18\text{h}^{-1}$ . Throughout the experiment the molal ratios of glycyglycine (GLY<sub>2</sub>) and diketopiperazine (DKP) remain constant with an observed standard free energy of cyclization for  $\text{GLY}_2 \rightleftharpoons \text{DKP} + \text{H}_2\text{O}$  of  $-1.05\text{kJ/mol}$  at 260°C in runs with starting glycine. In another series of experiments, where glycyglycine was injected into the gold-cell at 260°C, the observed standard free energy of cyclization is  $-0.93\text{kJ/mol}$ , both values agreeing well with reported free energies<sup>[5]</sup>, extrapolated to 260°C. The first order rate constant at 260°C for growth of glycyglycyglycine, the glycine trimer, is  $k=0.18\text{h}^{-1}$ . Comparison of rates for glycyglycine loss and glycyglycyglycine growth suggests that the formation of the later is due to decline of the dimer while equilibrium between glycyglycine and diketopiperazine is maintained. The present study suggest that oligomerization of amino acids proceeds in a closed system without the assistance of condensing agents or alternating temperature. Results from this work will be discussed in the context of hydrothermal prebiotic synthesis.

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