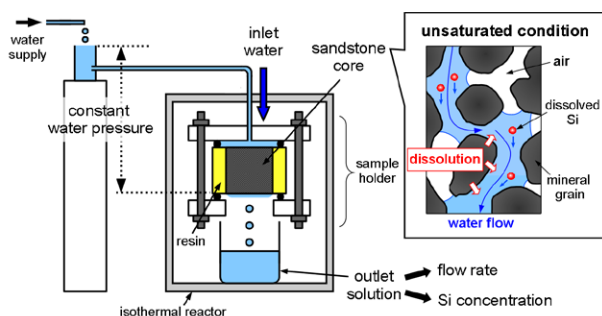


## Relationship between water saturation and mineral-water contact area of a sandstone

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Mineral-water contact area (reactive surface area) of a rock is an essential parameter for quantitative treatment of water-rock interaction. Although mineral-water contact areas have been often estimated by the gas adsorption method and image analysis, pore spaces in rocks near the Earth's surface are not always filled only with water but also with air. In such unsaturated condition, only a portion of mineral surfaces may contact water. However, knowledge of the dependence of mineral-water contact area on water saturation (the proportion of pore water volume to total pore volume) has been very limited. In the present study, we performed the dissolution experiments using a sandstone under various water saturations. Fontainebleau sandstone from France, having a porosity of 7% and being composed of ~100% quartz, was used. In the experiments (Fig. 1), a constant water pressure was applied to the rock core whose water saturation was adjusted in advance, and volumetric flow rate  $Q$  [ $\text{m}^3 \text{s}^{-1}$ ] and concentration of dissolved Si [ $\text{mol m}^{-3}$ ] were measured. Mineral-water contact ratio  $\alpha$ , the proportion of mineral-water contact area at the given water saturation to that at the saturated condition, can be calculated by the following relationship:  $Q \times [\text{Si}] = k_{\text{diss}} \times A \times \alpha$ , where  $k_{\text{diss}}$  [ $\text{mol m}^{-2} \text{s}^{-1}$ ] is the dissolution rate of quartz and  $A$  [ $\text{m}^2$ ] mineral-water contact area at the saturated condition. It was found that the mineral-water contact ratio is almost unchanged even if water saturation decreases. We attribute this result to the existence of water films wetting mineral surfaces.



**Figure 1:** Experimental setup for measuring mineral-water contact area at various water saturations.

## Linking nitrogen isotope systematics and microbiology in a subsurface geothermal water stream, Hishikari Gold mine, Japan

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We report biogeochemistry of a subsurface geothermal water stream in the Hishikari gold mine, Japan. The stream, which is derived from a subsurface anaerobic aquifer containing plentiful  $\text{CO}_2$ ,  $\text{CH}_4$ ,  $\text{H}_2$ , and  $\text{NH}_4^+$ , emerges in a mine tunnel 320 m below the surface, providing nutrients for a lush microbial community that extends to a distance of approximately 10 m in the absence of sunlight-irradiation. 16S rRNA gene analyses showed a change of microbial community structure along the stream. In the upstream site (72°C), dominant phylotypes were methane-oxidizing bacteria, and hydrogen- and sulfur-oxidizing bacteria. In contrast, dominant phylotypes were closely related to ammonia-oxidizing archaea (AOA) and nitrite oxidizing bacteria (NOB) in the midstream and downstream sites (65 and 57°C). Abundance of archaeal *amoA* gene ( $10^9$  copies/g mat) is much higher than that of bacterial *amoA* gene ( $10^{5-6}$  copies/g mat). Water chemistry systematically changes along the stream. From the upstream to downstream sites,  $\text{CH}_4$ ,  $\text{H}_2$  and  $\text{NH}_4^+$  contents decrease, while  $\text{NO}_2^-$  and  $\text{NO}_3^-$  contents increase, respectively. These results indicate a tight coupling of microbial community structure and chemical dynamics of C, H, and N in the subsurface hydrothermal ecosystem.

We extensively studied the nitrogen dynamics driven by thermophilic AOA and NOB. Contents and  $\delta^{15}\text{N}$  values of inorganic N species in the geothermal water are as follows:  $\text{NH}_4^+$ : 166 to 255  $\mu\text{M}$ , 0 to 7‰;  $\text{NO}_2^-$ : 0 to 27  $\mu\text{M}$ , -25 to -27‰;  $\text{NO}_3^-$ : 0 to 67  $\mu\text{M}$ , -1.8 to -2.3‰. Importantly, content and  $\delta^{15}\text{N}$  value of total fixed-N little change along the stream. By using two-step reactions model in a closed system, we have estimated apparent isotopic fractionations and relative ratio of reaction rate coefficients of ammonia oxidation and nitrite oxidation in the subsurface hydrothermal ecosystem.