

## **Microbial biomineralization in weathered volcanic ash deposit and formation of biogenic minerals by experimental incubation**

**MOTOHARU KAWANO<sup>1,\*</sup> AND KATSUTOSHI TOMITA<sup>2</sup>**

<sup>1</sup>Department of Biochemical Sciences and Technology, Faculty of Agriculture, Kagoshima University, 1-21-24 Korimoto, Kagoshima 890-0065, Japan

<sup>2</sup>Department of Earth and Environmental Sciences, Faculty of Science, Kagoshima University, 1-21-35 Korimoto, Kagoshima 890-0065, Japan

### **ABSTRACT**

Microbial biomineralization in a weathered volcanic ash deposit from the 1914 to 1915 A.D. eruption of Sakurajima volcano was investigated by transmission electron microscopy (TEM) and energy dispersive X-ray analysis (EDX). The solution chemistry of pore water was also analyzed to elucidate saturation conditions. In addition, experimental incubations of bacteria collected from the volcanic ash were performed to confirm bacterial mineralization. TEM revealed that the weathered volcanic ash contains significant amounts of spherical to rod-shaped bacteria ranging from  $1.3 \times 10^8$  to  $2.6 \times 10^8$  cell/g, most of which have cell wall surfaces that are completely covered or decorated by either massive aggregates of allophane-like granular materials or irregular aggregates of smectite-like fibers and/or flakes. EDX confirmed that the granular minerals have chemical compositions similar to proto-imogolite allophane, whereas the smectite-like fibers and/or flakes show a wide range of chemical compositions corresponding to the compositional field between allophane and nontronite. The volcanic ash contains about 22 wt% of pore water, which is slightly acidic, relatively low redox potential, and enriched in Si, Na, Cl<sup>-</sup>, and SO<sub>4</sub><sup>2-</sup> ions. The saturation indices (SI) calculated by the PHREEQC geochemical code indicate that the pore water is almost saturated with respect to amorphous Al(OH)<sub>3</sub>, ferrihydrite, amorphous silica, and cristobalite, and significantly oversaturated with respect to silicate minerals in the order: halloysite < kaolinite < montmorillonite < allophane < nontronite. The allophane-like granular minerals seem to be preferentially precipitated by bacterial interaction with Al and Si ions in the pore water as a metastable phase. The poorly ordered smectite-like fibers and/or flakes may be transformed from the allophane-like materials as an intermediate phase between allophane and nontronite by the driving force originated from the greatest SI value of nontronite. The experimental incubation confirmed that amorphous silica containing a small amount of Fe is formed on the bacterial cell surfaces in liquid media with both Fe and Si ions. Likewise, beidellite-like smectite associated with the bacterial surfaces is produced in liquid media containing both Al and Si ions. However, no minerals are produced in the same media containing no metal ions or no bacteria. These results imply that bacteria play an important role in the accumulation of metal ions and in the formation of silicate minerals during weathering of volcanic ash.