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Nanometer-sized, divalent-Mn, hydrous silicate domains in geothermal brine precipitates

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Abstract

X-ray diffraction, infrared spectroscopy, and X-ray absorption (XANES and EXAFS) spectroscopy were combined to characterize poorly crystalline Mn-rich silicate scale deposited from brine at a geothermal field in Indonesia. The precipitate has a vitreous pink-amber appearance, a nearly pure SiO_2-MnO-H_2O chemical composition, and a bulk Mn/Si atomic ratio of 0.63. X-ray microfluorescence indicated that the sample consists of Mn-free and Mn-containing silica domains, whose Mn/Si ratio (1.2 ± 0.4) ranges between those of 2:1 and 1:1 phyllosilicates. The XRD pattern is characterized by a broad scattering band spanning from ~6 to ~2.5 Å with weak modulations at 5.3, 3.5, and 2.72 Å, and a faint band at 1.605 Å. A surrogate was synthesized in an O_2-free atmosphere by mixing and aging at 150 °C an $MnCl_2$ and a sodium meta-silicate solution for 3 hours. Its XRD pattern was similar to the scale sample, but the two reflections at 2.72 and 1.605 Å were enhanced and the former was asymmetrical as in randomly stacked layered compounds. Diffraction data are consistent with a mixture of amorphous silica and a poorly ordered manganoan sheet silicate with a domain size of 40–50 Å for the scale and 50–60 Å for the surrogate material. The divalent oxidation state of manganese was confirmed by XANES spectroscopy, and the presumed existence of trioctahedral $[Mn^{2+}]_3$(O,OH) clusters having a clay-like local structure was corroborated by the existence of a weak vibration band at 600–650 cm^{-1} in infrared spectra. The connectivity of Mn octahedra was examined using EXAFS spectroscopy by comparing the local structure of Mn in the scale sample and in a large series of Mn compounds having different kinds of Mn octahedra and Si tetrahedra linkages. The manganoan scale has a polyhedral local structure resembling that of sheet silicates, in which metal octahedra are joined along edges and share corners with ditrigonal SiO_4 rings. Similar short-range ordering has been described in Fe- and Al- silicate scales, but the Mn-silicate scale has a lower domain size owing to the greater misfit between the lateral dimensions of the Mn and Si sheets. The strain induced by the shrinkage of the Mn sheet to fit the Si sheet(s) is alleviated by the nanometer size of the two-dimensional hydrous silicate domains.