K035-003 Room: C403 Time: May 31 9:30-9:45

The dissolution mechanism of Mg2SiO4 forsterite: Constraints from 29Si and 1H MAS NMR

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The dissolution of silicate minerals in aqueous solutions is a key issue in the geological and environmental sciences. Forsterite plays an important role during the weathering of ultramafic and mafic rocks, which determine important parts of the geochemical cycles of Si and Mg. However the dissolution mechanisms of forsterite and other silicate minerals are still matters of controversy despite extensive dissolution rate measurements and spectroscopic studies using techniques such as X-ray photoelectrospectroscopy (XPS). We now report the results of new nuclear magnetic resonance (NMR) measurements which shed light on this issue.

A Mg_2SiO_4 forsterite sample was synthesized from a mixture of MgO and SiO_2 at ambient pressure and 1500C. The hydrated sample was prepared by immersing a gently crushed forsterite sample in deionized water at 90C for two days, rinsing the reacted powder with fresh deionized water three times and then drying at 100C for 20 minutes. Single-pulse 1H and 29Si magic angle spinning (MAS) NMR spectra, 1H Hahn-echo MAS NMR spectra with various delay times, and 1H-29Si cross polarization (CP)-MAS NMR spectra were collected for both the initial unhydrated material and the hydrated samples. The 1H NMR and 1H-29Si CP-MAS NMR techniques are particularly sensitive to protons at the mineral surface.

The 29Si MAS NMR spectrum of the unhydrated sample contains a single peak at -61.8 ppm with a full-width-at-half-maximum (FWHM) of 0.2 ppm, that can be attributed to the isolated SiO_4 tetrahedra (Q0) in the forsterite structure. The 29Si MAS NMR of the hydrated sample is identical to that of the unhydrated, suggesting that there is no disorder in the bulk of the mineral. The 1H-29Si CP-MAS NMR spectrum of the hydrated sample contains two peaks of similar intensities near -86 and -93 ppm, which can be assigned to Q2 and Q3 species (SiO_4 tetrahedra sharing 2 and 3 corners with other tetrahedra), respectively. Because this technique is sensitive to Si in close proximity to H, these species are most likely to be on the hydrated surface of forsterite. The 1H NMR spectrum of the hydrated forsterite sample contains two partially overlapping peaks: a relatively narrow peak centered around 0.4 ppm, and a broader, asymmetric peak with a maximum near 4.6 ppm. These peaks have a common, short 1H spin-lattice relaxation time (T1 less than 1 s), similar to surface water species of silica gels. The 4.6-ppm peak decays more rapidly than the 0.4-ppm peak, with increasing delay time for the 1H Hahn-echo sequence, most likely as a result of stronger H-H dipolar coupling. The 0.4-ppm peak can be assigned to MgOH, and the 4.6-ppm peak may be from SiOH and/or tightly bound surface molecular H_2O, with various degrees of hydrogen bonding.

These results place new constraints on the dissolution mechanism of forsterite. In particular, the lack of a Q0 peak, and the presence of Q2 and Q3 peaks, in the 1H-29Si CP-MAS NMR spectra of the hydrated sample suggest that the dissolution of forsterite is accompanied by the formation of a polymerized hydration layer consisting mainly of Q2 and Q3 units. The detection of a large amount of MgOH by 1H NMR implies that the hydration layer retains a significant amount of Mg. The presence of this reconstructed layer may play a dominant role in determining the dissolution kinetics of forsterite.