^{29}Si and ^{1}H NMR of Natural and Synthetic Xonotlite

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This is the first report to show that the two ^{29}Si-NMR signals (-86.3, -87.1 ppm) of Q^2 of natural and synthetic xonotlites were clearly split, which is in accord with the crystal structure study of Kudoh et al.[1] The ^{1}H-NMR spectra were deconvoluted into three lines at 2.19, 1.86 and 5.26 ppm and assigned to structural Ca-OH, Si-OH and molecular water, respectively. The signal intensities are in good agreement with the thermogravimetric analysis.

Xonotlite [$Ca_6(Si_6O_{17})(OH)_2$] has a double-chain structure of silicate anions, branched at every third Si-O tetrahedron, which is called a dreier double chain. Xonotlite is an interesting crystal because of its unique chain-structure and its industrial utilization as a building insulation material. The ^{29}Si MAS NMR of synthetic xonotlite has been reported by Lippmaa et al.,[2] Bell et al.[3] and Cong et al.[4] They reported the two signals at –86.8 ppm (Q^2) and –97.8 ppm (Q^3) with a 2:1 intensity ratio. The ^{1}H wideline and MAS NMR signals of synthetic xonotlite were reported by Grimmer et al.[5] and Rosenberger et al.,[6] respectively. In this report, we obtained the high-resolution ^{29}Si and ^{1}H MAS NMR spectra of natural and synthetic xonotlites with good crystallinity and first observed the splitting of the Q^2 signal and succeeded in the quantitative deconvolution of the ^{1}H signals.

Two crystals, i.e., natural xonotlite[7] and synthetic xonotlite,[7] were used in this study. According to their XRD patterns, the natural xonotlite did not contain any mineral impurities and the synthetic one contained neither unreacted $Ca(OH)_2$ nor silica. The NMR measurement conditions are summarized in the note.[8]

The ^{29}Si HD-MAS spectrum of natural xonotlite is shown in Figure 1 (a). Only the Q^2 and Q^3 signals were observed while the Q^1 signal was not detected. The Q^2 was clearly split with an intensity of 1:1, contrary to previous reports.[2-4] The ^{29}Si HD-MAS spectrum of synthetic xonotlite is shown in Figure 1 (b). The Q^1 signal is observed and the Q^2 signal was split like the natural one. The chemical shifts of the natural and synthetic xonotlites showed almost the same values. The chemical shifts and the relative intensities are summarized in Table 1.

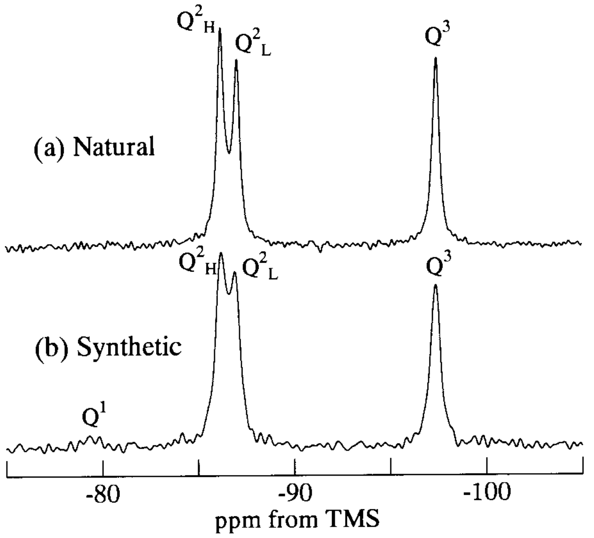

Figure 1. ^{29}Si HD-MAS NMR spectra of natural and synthetic xonotlites.

Table 1. Relative intensities (%) of Q^1, Q^2 and Q^3 of ^{29}Si HD-MAS spectra of natural and synthetic xonotlites

	Q^1	Q^2_H	Q^2_L	Q^3
Chemical shift (ppm from TMS)	-79.6	-86.3	-87.1	-97.5
Natural	0	38	30	32
Synthetic	3	37	30	30

Q^2_H, Q^2_L: higher- and lower-frequency signals of Q^2.

Q^1 is an end site of the silicate anion chain and a defect in the xonotlite crystals. This was not observed for natural xonotlite with high crystallinity.

The two signals of Q^2 were observed for both the natural and synthetic xonotlites and their intensity ratio was near 1:1, which indicates the two signals are caused not by contamination but by its proper crystal structure. The specimens of the previous studies[2-4] were synthetic and they showed a high Q^1 signal, which indicates poor crystallinity of the specimens.[10] This might be the reason why the splitting of Q^2 signal could not be detected.

According to the analysis of the xonotlite crystal structure by Kudoh et al.,[1] the two Q^2 sites have different mean Si–O bond lengths and mean Si–O–Si bond angles as shown in Figure 2. Wollastonite [β-$CaSiO_3$], which has dreier single chains similar

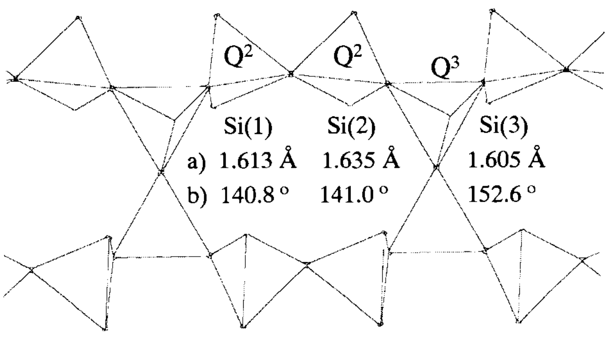

Figure 2. Schematic diagram of a double-chain structure of silicate anions in xonotlite consisting of two Si sites of Q^2, Si(1) and S(2), and one Si site of Q^3, Si(3). a) mean Si–O bond length, b) mean Si–O–Si bond angle from Kudoh et al.[1]

to the dreier double chains of xonotlite, was expected to show three different ^{29}Si NMR signals according to its crystal structure[11] which were observed by Sebald et al.[12] The Q^2_H and Q^2_L in Figures 1 must correspond to Si(1) and Si(2) in Figure 2. The ^{29}Si signal shifts toward the lower frequency with a decrease in the mean Si–O bond lengths[13] and with an increase in the mean Si–O–Si bond angles.[14] However, Si(1) has a smaller mean bond length and a smaller mean bond angle when compared to Si(2). Consequently, it is difficult to assign these two signals using the above empirical correlations.

Figure 3 shows the ^{1}H MAS NMR spectra of the natural and synthetic xonotlites. A sharp signal at 2.2 ppm with a shoulder and a broad signal at 5.0 ppm were observed. The signals were deconvoluted into three lines at 2.19, 1.86 and 5.26 ppm. The relative intensities of these signals were 73%, 18% and 9% for the natural xonotlite and 65%, 24% and 11% for the synthetic xonotlite.

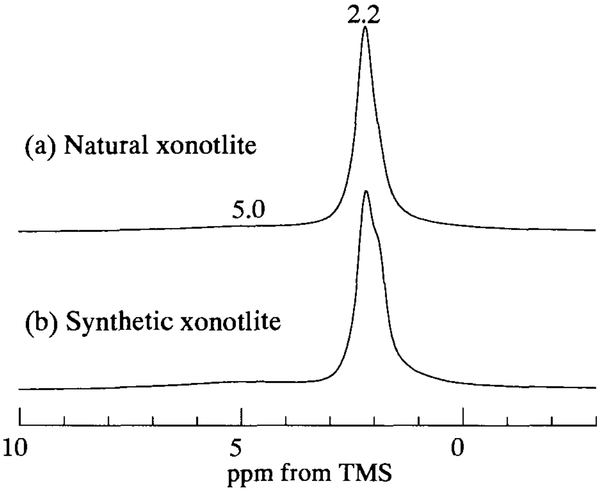

Figure 3. ^{1}H MAS NMR spectra of natural and synthetic xonotlites.

Xonotlite not only has structural OH in the crystal but also molecular water and Si-OH.[15] The TG losses from the specimens were analyzed and divided into three parts, room temperature – 200 °C – 700 °C – 850 °C. The ratios of the TG losses in each temperature range were 10%, 17% and 73% for the natural one and 10%, 24% and 66% for the synthetic one. These results are in good agreement with the ^{1}H NMR signal intensities. Moreover, the signal at 5.26 ppm disappeared by vacuum-drying at 80 °C for 1 d. The chemical shift of 1.86 ppm is very near to 1.7 ppm that is assigned to the isolated (non-H-bonded) Si-OH of silica gel by Bronnimann et al.[16] Therefore, the signals at 5.26, 1.86 and 2.19 ppm can be assigned to the molecular water, Si-OH and structural OH, respectively.

Kudoh et al.[1] estimated the location of H at the central Ca–O among the four Q^2 units of the double chain. Rassem[17] summarized the ^{1}H NMR chemical shifts of calcium silicate hydrates and assigned the OH of xonotlite (2.0 ppm)[6] as Ca-OH. Therefore, the signal at 2.19 ppm can be assigned to the structural Ca-OH.

References and Notes

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7 The natural xonotlite came from Ohmi-machi, Keijoh-gun, Nihgata Prefecture, Japan. The results of its wet chemical analysis were as follows: SiO_2 50.80, Al_2O_3 0.38, Fe_2O_3 0.05, CaO 44.70, Na_2O 0.78, K_2O 0.02, MnO 0.01, Ig. loss 3.18, total 99.92 (wt%). The synthetic xonotlite was hydrothermally synthesized at 250 °C for 60 h from CaO and silicic acid.

8 NMR spectra were recorded using a Bruker DSX300 (7.05 T). ^{29}Si high power decoupling (HD-MAS) spectra were obtained using a $\pi/4$ pulse (2.75 μs) with a recycle time of 500 s and a MAS rate of 5 kHz. The ^{1}H NMR was acquired using an ordinary single-pulse sequence with a $\pi/2$ pulse (4.6 μs), a recycle time of 25 s, 16 pulses and a MAS rate of 12 kHz. The ^{29}Si chemical shift of 3-(trimethylsilyl)-propane sulfonic acid sodium salt (DSS) was 1.534 ppm[9] and the ^{1}H shift of water was 4.877 ppm.[9]

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