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STUDIES OF ^{29}Si SPIN-LATTICE RELAXATION TIMES AND PARAMAGNETIC IMPURITIES IN CLAY MINERALS BY MAGIC-ANGLE SPINNING ^{29}Si-NMR AND EPR

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High-resolution solid state ^{29}Si-NMR spectra and EPR spectra have been examined on twelve natural philosilicates. It has been found that presence of paramagnetic impurities is markedly effective in shortening the ^{29}Si spin-lattice relaxation times (10 to 1000 ms), and in broadening the linewidths and is favorable for the use of solid state high-resolution ^{29}Si NMR as a tool for structural studies of inorganic materials.

Up to present, structural studies of minerals with long range ordering have been carried out mostly by X-ray diffraction. This method, however, is not useful to minerals with poor crystalline state or in amorphous state, such as clay minerals. Solid state high-resolution NMR of ^{29}Si was first applied to silicates and aluminosilicates by Lippmaa et al.,$^{1)}$ and was proved an useful analytical technique for characterization of Si in a solid state.$^{2-4)}$ Recently, ^{29}Si-NMR was applied to identify imogolite in clay fractions$^{5)}$ or to detect slight difference in surroundings of silicon atoms in kaolins.$^{6)}$ In all of those investigations, chemical shift is mainly used as a criterion of the identification. The purpose of this paper is to evaluate ^{29}Si-NMR as a new method for structural study of the natural clay minerals from the standpoint of relaxation times. As a result, it was found that proper amounts of paramagnetic impurities are effective in shortening ^{29}Si spin-lattice relaxation times and facilitate the observation of ^{29}Si-NMR.

Twelve philosilicates listed in Table 1 were measured by magic-angle spinning (MAS) ^{29}Si-NMR and EPR spectroscopies. All ^{29}Si-NMR spectra were recorded at 59.604 MHz on a Brucker CXP-300 at 23°C. The standard ^{13}C MAS probe and the Derlin rotor were used for ^{29}Si measurements. The rotor spinning rate was about 3KHz. Repetition time was 2 s throughout all experiments except for T_1 measurements. Usually, FID's were accumulated 100 to 2000 times. Each ^{29}Si-NMR spectrum of nine samples(#1 to #9) shows apparent single absorption with a different linewidth and with a chemical shift as shown in Table 1. ^{29}Si spin-lattice relaxation times(T_1's) were measured by the standard inversion-recovery pulse sequence (180°-τ-90°) under MAS(Fig.1). All EPR measurements

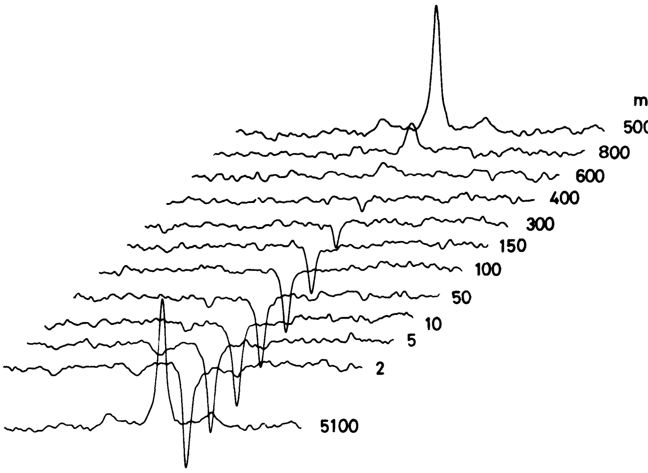

Fig. 1. Measurement of spin-lattice relaxation times of ^{29}Si nuclear spin in pyrophillite. The individual τ values used in the inversion-recovery sequence were shown in the figure.

Table 1. Spectral parameters of ^{29}Si-NMR and EPR of minerals.

number	sample name	sample chemical formula	type	δ a) ppm	$\Delta\nu_{1/2}$ Hz	T_1 ms	concn. of Fe^{3+} b)
	Halloysites	$Al_4Si_4O_{10}(OH)_8\ 4H_2O$	1:1				
# 1	Shimmei kaolin			-93.3	180	83	1.7
# 2	Hadong kaolin			-93.1	200 c)		3.1
	Kaolinites	$Al_4Si_4O_{10}(OH)_8$	1:1				
# 3	Kampaku kaolin			-92.7	107		1.5
# 4	Georgia kaolin			-92.5	262	240	6.8
# 5	Gaerome clay			-92.8	232 c)		4.3
# 6	Kibushi clay			-92.9	306		9.7
# 7	Pyrophillite	$Al_2Si_4O_{10}(OH)_2$	2:1	-95.7	107	910	1.1
# 8	Talc	$Mg_3Si_4O_{10}(OH)_2$	2:1	-97.4	260		1.5
# 9	Montmorillonite	$Al_2Si_4O_{10}(OH)_2\ nH_2O$	2:1	-94.1	362	47	13.0
#10	Chlorite	$(Mg,Fe,Al)_6[Si,Al]_4O_{10}(OH)_8$	2:1		broad		3.1
#11	Phlogopite	$KMg_3[Si_3Al]O_{10}(OH)_2$	2:1		broad		8.0
#12	Illite	$KAl_2[Si_3Al]O_{10}(OH)_2$	2:1		broad		3.1

a) Chemical shift from TMS. Hexamethylsiloxane (+6.6 downfield from TMS) was used as a secondary standard. b) Arbitrary unit normalized by weight of sample and instrumental parameters. c) NMR spectrum shows a shoulder at about -91 ppm. Linewidth was estimated after separation of two peaks.

were recorded at X-band on a JEOL FE1X EPR spectrometer at 23°C. Typical spectra are shown in Figure 2. Powder X-ray diffraction spectra and atomic absorption spectra were observed to confirm the impurities in minerals and the degree of crystallinity.

Silicon atom is tetrahedrally coordinated by four oxygen atoms to form a tetrahedral silica sheet, while aluminum atom is octahedrally six-coordinated to form an octahedral aluminum hydroxide sheet (gibbsite sheet) in the minerals under investigation. In the cases of halloysite and kaolinite, one unit of layer structure consists of one gibbsite sheet and one silica sheet (1:1 type), while the corresponding one consists of one gibbsite sheet and two silica sheets (2:1 type) for pyrophillite, montmorillonite, chlorite, phlogopite and illite. Talc has a 2:1 type structure, but Al ions are replaced by Mg ions. Observed chemical shifts for 1:1 type silicates were about -93 ppm and those of 2:1 type silicates were in the range of -94 to -97 ppm. This indicates that the type of layer structure in those minerals is distinguished from each other by the chemical shift.

EPR spectra show the existence of several paramagnetic species in the minerals. A sharp signal near g=4 was observed for all samples. This absorption is characteristic of high-spin Fe^{3+} ion in a rhombic crystal field7) and indicates that Al^{3+} ions in gibbsite sheet are partially substituted by Fe^{3+} ions. The concentration of Fe^{3+} ion in Al site as impurity may be roughly estimated from the amplitude of this signal, which is shown in Table 1. Other signals in the EPR spectra of minerals are assigned to Mn^{2+} ions as substituent impurity(a,b,c,e,f in Fig.2), ferromagnetic (or superparamagnetic) materials (f),8,9) Fe^{3+} ions in adjacent cation sites(a,b,c,d,e), and other radical species(b,c,d).10)

The linewidths at the half intensity of ^{29}Si-NMR absorption, $\Delta\nu_{1/2}$, are plotted against the relative concentration of Fe^{3+} ion in Al site in Figure 3. There is a marked tendency for the linewidth to increase with increasing Fe^{3+} concentration. This result demonstrates that the dipolar interaction between ^{29}Si and electron spin of Fe^{3+} ion in Al site is largely responsible for the line broadening of ^{29}Si-NMR signal. According to the results by resolution enhanced ^{29}Si-CP/MAS-NMR by

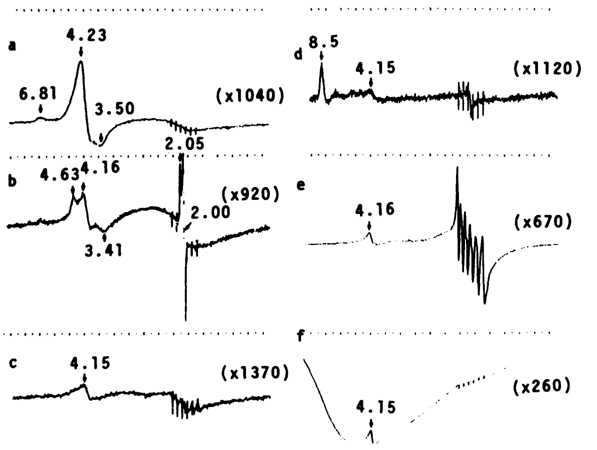

Fig. 2. EPR spectra of minerals at 23°C. a) Montmorillonite, b) Georgia kaolin, c) Shinmei kaolin, d) Pyrophillite, e) Chlorite, f) Phlogopite. Sharp and broad six lines near g=2 are due to Mn^{2+} ions as reference and as impurities in minerals, respectively. Numbers in the figure indicate effective g values. (Conditions of measurements: microwave power, 5 mW; field modulation, 5 G; gain, in parentheses; weight of each sample, 10 mg).

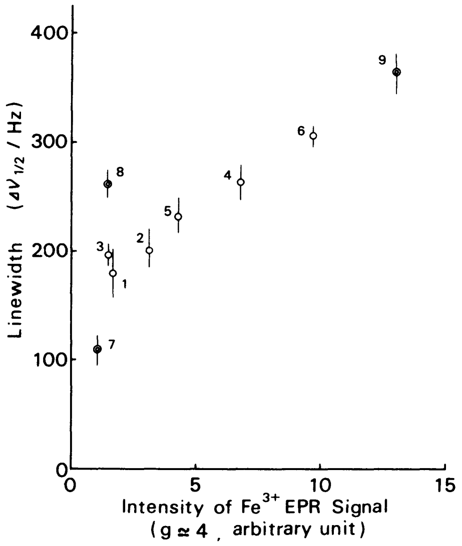

Fig. 3. Linewidths at the half intensity of ^{29}Si-NMR signals against relative concentration of Fe^{3+} ion in Al site. The 1:1 and 2:1 types of silicates are marked by single and double circles, respectively. Samples are indicated by the numbers.

Barron et al., two slightly different silicon environments are present in kaolinite, where chemical shift difference is about 27 Hz(0.45ppm) and the linewidth is about 80 Hz.$^{6)}$ Comparing our results with theirs, it is clear that in addition to the line broadening by paramagnetic impurities, the homogeneous line broadening by dipolar interaction of ^{29}Si with neighboring Al and H nuclei and the inhomogeneous line broadening due to the species with subtle conformational varieties were also observed together.$^{11-13)}$ In Figure 3, the linewidths of talc and pyrophillite deviate from the general tendency. In those two cases, main paramagnetic species are different from those in other seven samples. That is, Mn^{2+} ion replaces Mg^{2+} site in talc and a different type of Fe^{3+} ion(g=8.5) from usual Fe^{3+} ion in a rhombic field(g=4) was observed in pyrophillite by EPR(Fig. 2d). Taking into account the line broadening due to magnetic inhomogeneity(≃40 Hz), it can be said that spin-spin relaxation times (T_2's) of ^{29}Si in minerals is mainly influenced by paramagnetic impurities.

In the nuclear relaxation caused by fixed paramagnetic impurities, the dipolar interaction between electron spin and nuclear spin and the spin diffusion process become important.$^{14)}$ For the spin diffusion process, we have

$$1/T_1 = 4\pi NbD ,$$

where b is a certain length, which might be called the scattering amplitude of a single impurity, D is a diffusion constant and N is the number of impurity per a unit volume. The values of b and D may be regarded as constant in all samples investigated, because the structural relationship between Si and Al atoms is the same for all samples. Thus, spin-lattice relaxation time, T_1, is inversely proportional to the number of impurity, N, i.e. the concentration of effective paramagnetic species. In the case of kaolinite, content of Fe ion is in the range of 0.01% to 0.5% as Fe_2O_3.$^{15)}$ If we assume that all Fe ions replace Al site in gibbsite sheet, T_1's are calculated to be about 1500 ms and 30 ms for 0.01% and 0.5% Fe_2O_3 in kaolinite, respectively, under the reasonable conditions that a distance between Si atoms is 3.02 A and a longitudinal relaxation time of electron spin of Fe ion is 10^{-7} s. The observed T_1 value in Georgia kaolin is 240 ms. Accordingly, spin diffusion process can explain spin-lattice relaxation times of ^{29}Si in minerals. As shown in Table 1, the observed

T_1 values are not necessarily correlated to the concentration of Fe^{3+} ion in Al site, although there is a tendency that T_1 becomes shorter in minerals with higher concentration of Fe^{3+} ion. Contribution of paramagnetic species, other than Fe^{3+} in Al site, also has to be taken into consideration. Further discussion waits for both the quantitative and the structural analysis of paramagnetic species in detail. In the case of Georgia kaolin, N is calculated to be $1 \times 10^{19}/cm^3$ under the assumption mentioned above and this means that one Al ion per about 1400 Al ions in gibbsite sheet is substituted by one Fe ion. Usually, total concentration of Fe ion in a mineral can be determined by conventional methods, but the amount of Fe ion in a special site is difficult to determine by any of them. When the spin-lattice relaxation times of ^{29}Si are discussed in further detail, it may become possible to solve this problem.

It is generally believed that ^{29}Si in minerals is isolated and the spin-lattice relaxation time is very long. However, when some elements in the lattice of minerals are replaced by paramagnetic impurities (this situation occurs very often in natural minerals), ^{29}Si spin-lattice relaxation through electron spin plays an effective part, facilitating the observation of ^{29}Si-NMR. Actually, paramagnetic impurity was scarcely observed in quartz and albite in tectosilicate and great numbers of accumulation and long repetition time were necessary to gain ^{29}Si-NMR signals.[16)]

In the case of samples(#10 to #12), ^{29}Si-NMR showed broad lines and some spinning sidebands. Oldfield et al. reported that spinning sidebands may be due not to chemical shift anisotropy, but rather to the presence of large magnetic susceptibility broadening.[17)] As shown in Figure 2e, chlorite does not show any strong superparamagnetic signal. It is thought that chemical shift anisotropy is very large in this material.

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