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CHARACTERIZATION OF SILICON AND ALUMINUM SPECIES IN IRON ORES USING SOLID STATE NMR[1]

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Abstract

Silicon and aluminum in iron ores, usually simplified as SiO_2 and Al_2O_3, actually belong to more complicated gangue minerals such as silicates and aluminosilicates. These minerals consist of not only well-crystallized minerals, but also disordered ones such as clay minerals. In granulation of iron ore particles, hydration and dispersion behavior of clays might play an important role. Therefore, analysis of silicates and aluminosilicates is one of the important themes in iron ore characterization. In this study, solid state NMR techniques were applied for this purpose. This technique, a nuclide specific method, allows us to investigate the local chemical environments around targeted nuclei. ^{27}Al and ^{29}Si NMR spectra of five brands of iron ores are successfully acquired although NMR has been believed to be unsuitable to the analysis of materials containing a lot of paramagnetic ions. As the result of comparison, these iron ores are categorized in two groups, group 1 and 2, according to the type of minerals characterized by ^{27}Al and ^{29}Si NMR spectra. In summary, alumina (α-Al_2O_3), 4-coodinated Al, and 5-coodinated Al are commonly observed in ^{27}Al MAS NMR spectra of both groups. Another main Al species in group 1 is assigned to kaolinite ($Al_2Si_2O_5(OH)_4$), while that in group 2 is assigned to fluorine-bearing aluminosilicates. From the ^{29}Si MAS NMR spectra, it is found that main Si in group 1 mainly occurs as phyllosilicates with Q^3 linkage, which is almost consistent with the result of ^{27}Al MAS NMR experiments. In group 2, the ratio of Si belonging to tectosilicates with Q^4 tetrahedral linkage is higher than in group 1. Characterization by using other analytical methods should be also required to assign main Si components to specific minerals. Despite of the difficulties, the solid state NMR method is found to be useful to characterize Si and Al species in bulk ore samples, and to understand the feature of ores based on the gangue minerals phases.

Key words: Aluminum; Silicon; Solid state NMR.

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1 INTRODUCTION

Obtaining high grade iron ores has recently become difficult with an increasing market demands. In this situation combined with the environmental regulation for CO_2 emission, effective utilization of low grade iron ores has been required.
The low grade iron ores is characterized by relatively high concentration of silicon (Si) and aluminum (Al) which are typical compositions of gangue minerals. In a conventional estimation, Si and Al are solely expressed by the chemical composition as their simple oxides, SiO_2 and Al_2O_3. However, such an expression actually differs from mineral phases where Si and Al are incorporated into.
Kumar *et al.* (2007) investigated the iron ores containing 5-7 mass% SiO_2 and 8-12 mass% Al_2O_3, and reported that Si and Al occurs in the form of aluminum, siliceous, and aluminosilicate minerals such as gibbsite, diaspore, bohemite, clays(kaolinite, illite), and quartz.[1] In their study, the characterization has been performed using SEM-EDX, XRD, and ore petrography.
Microscopic method such as EPMA and SEM-EDX are certainly useful to confirm the mineral phases. However, it is difficult to obtain the bulk average information of gangue mineral phases. Powder XRD method combined with Reitvelt analyses can quantify the minerals phases in a given sample, and would be useful to obtain the bulk information. However, diffraction peaks of gangue minerals are often buried in those of main iron oxides/hydroxides when SiO_2 and Al_2O_3 concentration are just a few mass %.
In this study, we have applied solid state nuclear magnetic resonance (NMR) method to characterization of the Si and Al species in iron ores. Solid state NMR, a nuclide specific method, is expected to make up for the region which other analytical methods cannot cover, and consequently build up the characterization methodology.

2 MATERIALS AND METHODS

Five ore samples were prepared for solid state NMR analysis. These samples were grounded under 20 μm. Their chemical compositions are shown in Table 1. Si and Al concentration range from 0.9 to 5.1 *mass*%, and 1.3 to 2.7 *mass*%, respectively.
High resolution solid state NMR spectra can be acquired for the powder samples that were rotated around the axis of 54.7^{o} (magic angle) to the external magnetic field. The axis of an NMR spectrum is expressed by chemical shift in *ppm* scale, showing a small difference of resonance frequency of a sample from referenced one.
In preliminary experiments, ^{29}Si and ^{27}Al MAS NMR spectra of the ore samples were acquired at various strengths of magnetic fields (7.01*T*, 11.4*T*, 16.4*T*) to optimize the experimental conditions. Consequently all solid static NMR spectra were recorded using an Agilent Inova-500 (11.4 *T*) spectrometer at the resonance frequencies of 130.244 MHz for ^{27}Al and 99.305 MHz for ^{29}Si.
The ^{27}Al MAS NMR spectra were collected using 1.2mm zirconia rotors at the spinning frequency of 60 kHz. A $\pi/10$ pulse ($0.38\mu s$) was irradiated with the recycle delay of 5 s to ensure quantitative analysis. The ^{29}Si MAS NMR spectra were collected using 3.2mm zirconia rotors at the spinning frequency of 20 kHz. Solid echo two-pulse sequence was applied with the π/2 pulse length of 1.4 μs and the recycle delay of 15 s. For chemical shift assignment, ^{27}Al and ^{29}Si MAS NMR spectra of several minerals were also collected.

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Table 1. Chemical composition (*mass* %) of iron ore samples

	CW	FeO	Total Fe	Si	Al	Ca	Mg	P
Ore A	6.61	0.09	50.24	5.10	2.17	0.35	0.30	0.030
Ore B	6.46	0.11	54.97	3.12	2.68	0.035	0.082	0.12
Ore C	7.33	0.11	55.02	3.24	1.87	0.059	0.065	0.046
Ore D	2.22	0.11	63.13	0.99	1.33	0.048	0.052	0.048
Ore E	2.59	0.07	59.00	2.99	2.06	0.064	0.087	0.081

3 RESULTS AND DISCUSSION

3.1 ^{27}Al MAS NMR Experiments

Figure 1 shows deconvoluted ^{27}Al MAS NMR spectra of the five ore samples. Each NMR spectrum shows main peaks at the chemical shift at around 0 ppm, indicating that Al in these ore smaples occurs as 6-coordinated Al ($Al^{[VI]}$).
Based on the chemical shift of main components, these iron ores are categorized in two groups, group 1 and 2, according to the type of minerals characterized by ^{27}Al and spectra. Group 1 consists of ore A, B, and C, whereas group 2 consists of ore D and E. Group 1 shows two resonance peaks at approximately 3.0-5.0 ppm, while group 2 shows a resonance one at approximately 0.1-0.9 ppm. This is small but apparent difference in chemical shift. The peak observed at 5.0 ppm is assigned to kaolinite $Al_2Si_2O_5(OH)_4$, which is one of the 1:1 phyllosilicates. The peak at 3.0 ppm could be assigned to be 2:1 phyllosilicates such as montomorillonite $Na_{0.33}Al_2Si_4O_{10}(OH)_2$, illite $K_{1-x}Al_2(Si_{3+x}Al_{1-x})O_{10}(OH)_2$, and muscovite $KAl_2(Si_3Al)O_{10}(OH)_2$). Phyllosilicate type of clay minerals are therefore one of the main Al-bearing gangue minerals in group 1.
On the other hand, the observed at 0.1 ppm in group 2 is not fit into Al oxides (α-Al_2O_3, γ-Al_2O_3, $Al(OH)_3$, boemite AlOOH, spinel $MgAl_2O_4$) and most of aluminosilicates (kaolinite, montmorillonite, halloysite $Al_2Si_2O_5(OH)_4{\cdot}2H_2O$, illite, muscovite. As seen from Figure 1, $Al^{[VI]}$ in Al oxides shows resonance peak at 8.0-15 ppm, and that in aluminosilicates shows resonance peak at 2.5 -5.0 ppm.
On the basis of solid state ^{27}Al NMR studies of Al-bearing compounds,[(2)] $Al^{[VI]}$ coordinated by fluorine (F) is suggested to show the peak more shielded than 1 ppm at the magnetic field strength of 11.4*T*. The ^{27}Al MAS NMR spectra of tourmaline $(Na^+,Ca^{2+})(Li^+,Mg^{2+},Al^{3+})_6(BO)_3Si_6O_{18}(F,OH)_4$), cryolite Na_3AlF_6, and topaz $Al_2SiO_4F_6$ where F coordinates to Al were also acquired (Figure 1). The ^{27}Al MAS NMR spectra of these minerals certainly show resonance peaks at the chemical shift ranging from 0.1 to -5 ppm. From the results, the component observed at 0.1-0.9 ppm in group 2 is tentatively assigned to F bearing-aluminates and -aluminosilicates. The suggestion has to be examined by other analytical methods.
The common features of group 1 and 2 are expressed by the peaks observed at approximately 14 ppm, 25 ppm, and 59 ppm. The peak at 14 ppm is clearly assigned to α-Al_2O_3. The resonance peak at 59 ppm is assigned to 4-coordinated Al, ($Al^{[IV]}$). In Group 1, a part of the $Al^{[IV]}$ could arise from 2:1 phyllosilicates such as montmorillonite, illite, and muscovite. The component observed at 25 ppm is assigned to 5-coordinated Al($Al^{[V]}$) that is often observed in aluminosilicates treated at hydrothermal condition. Therefore, this component might be generated by weathering and diagenesis.
In summary, aluminum in group 1 (ore A, B, and C) occurs as α-Al_2O_3, 1:1 phyllosilicates (kaolinite), 2:1 phyllosilicates (muscovite etc.), and $Al^{[V]}$ species. On

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the other hand, aluminum in group 2 (ore D & F) occurs as α-Al_2O_3, $Al^{[V]}$ species, and a species where Al might be coordinated by fluorine.

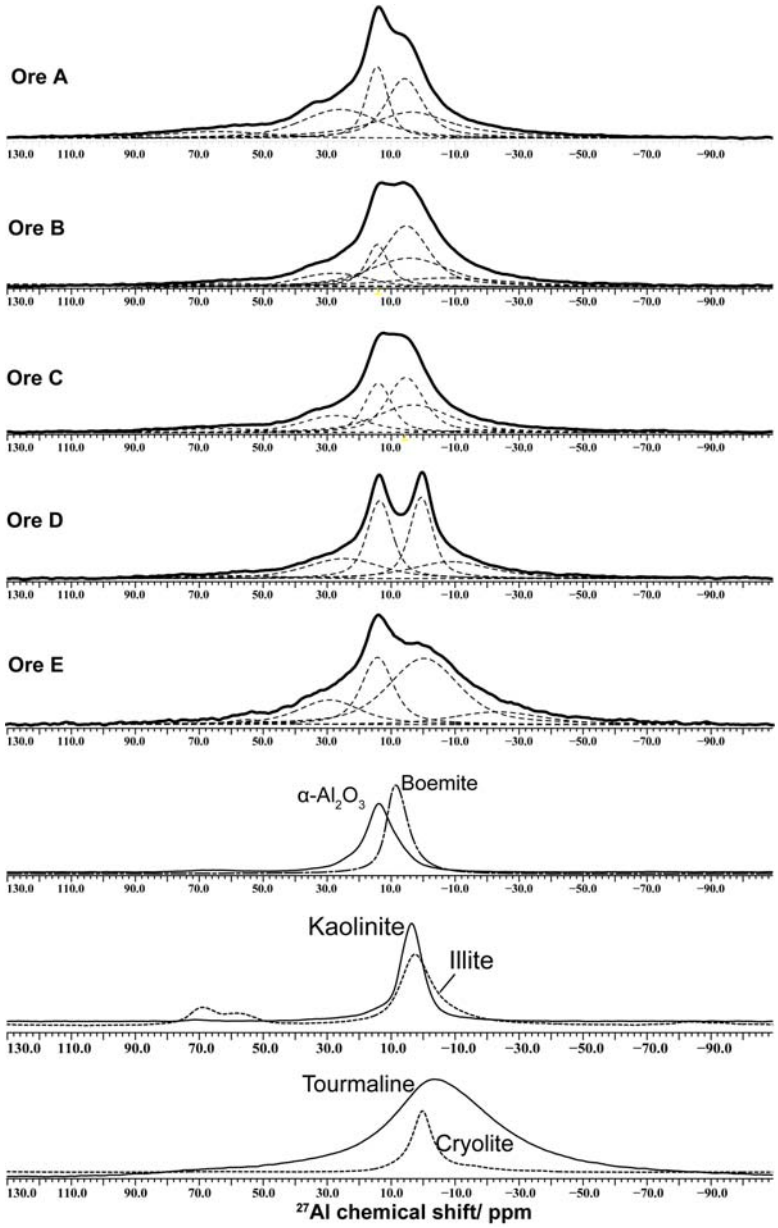

Figure 1. ^{27}Al MAS NMR spectra with deconvoution results for five ore samples. ^{27}Al MAS NMR spectra for some aluminooxides, aluminosilicates, alumina-fluorindes compounds are also shown. The dottet lines in ore samples show components obtained by spectral deconvolution.

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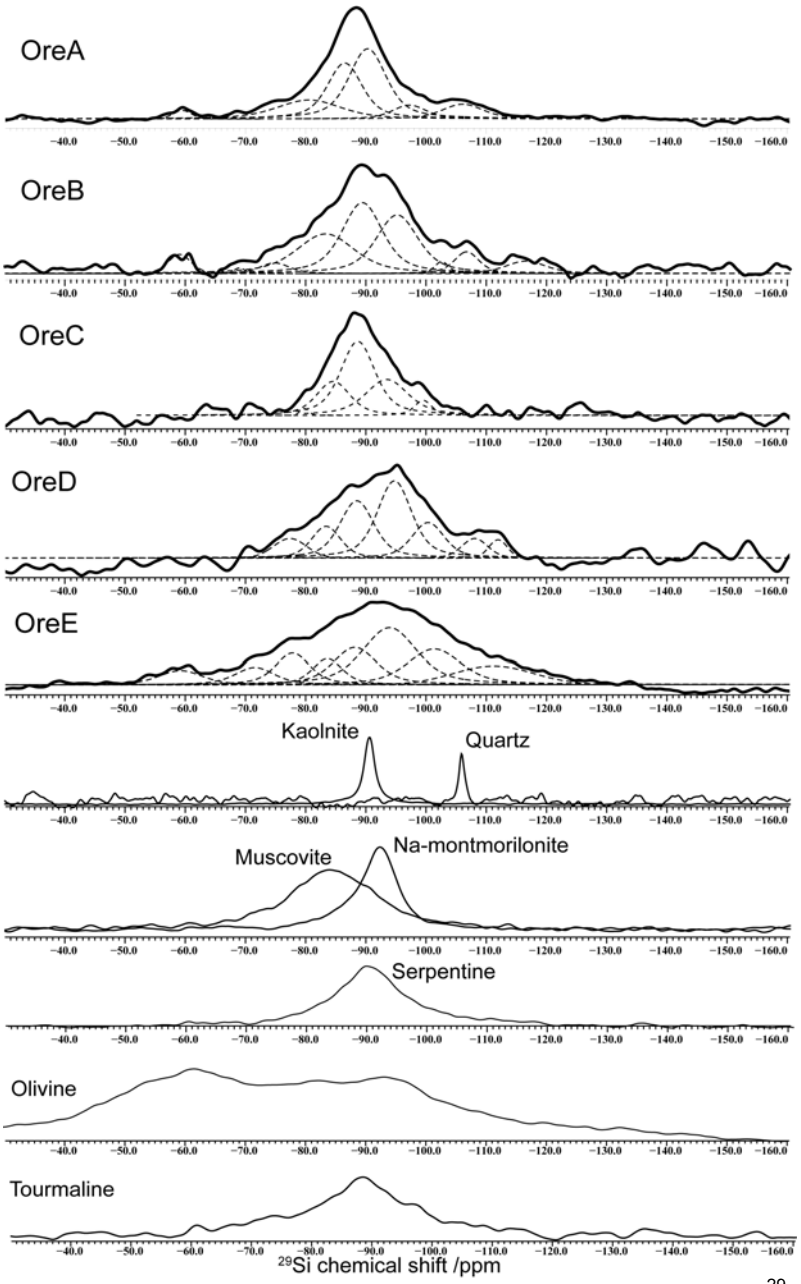

Figure 2. ^{29}Si MAS NMR spectra with deconvolution results for five ore samples. ^{29}Si MAS spectra for some silicate minerals are also shown.

3.2 ^{29}Si-MAS NMR experiments

Figure 2 shows ^{29}Si MAS NMR spectra of the five ore samples. Compared to ^{27}Al-MAS NMR spectra, ^{29}Si MAS spectra suffers from low signal intensity despite of long acquisition time since natural abundance of ^{29}Si are quite low (4.67%) and acquisition efficiency is limited by quite long spin-lattice relaxation time.
Nevertheless, deconvolution of each spectrum allows us to qualitatively understand the feature of ores. The chemical shift of ^{29}Si MAS NMR reflects the network structure of SiO_4 polyhedra, and described as Q^n notation where the superscript *n* shows a number of bridging oxygen in SiO_4. Since the ^{29}Si chemical shift moves to upper field (more negative values in chemicals shift) as the number *n* increases, we can roughly understand the degree of polymerization of silicates.

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As well as for the ^{27}Al MAS NMR spectra, ^{29}Si MAS NMR spectra in Figure 2 can be classified into two groups according to the feature. It is found that the main components in group 1 (ore A, B, and C) are found at the chemical shift region from -84 to -94 ppm, while those in group 2 are found at the more upper field from -89 to -101 ppm. The main components observed at from -84 to -90 ppm in group1 are considered to be phyllosilicates with Q^3 linkage such as kaolinite, muscovite, and serpentine (Mg, Fe)$_3$Si$_2$O$_5$(OH)$_4$. This result is qualitatively consistent with that from the ^{27}Al-MAS NMR experiments, where kaolinite, a kind of phyllosilicates, is found to be a main Al species.

As a result of chemical shift comparison, the main component observed at -94 ppm in group 2 is not be assigned to aluminosilicates such as kaolinite, muscovite, and montmorillonite. As alternative possibilities, the component might be phyllosilicates without Al, or F-bearing aluminosilicates. For instance, F-bearing tourmaline shows a resonance peak at around -95 ppm.

In group 2, the ratio of components with the chemical shift less than -94 ppm is higher compared to group 2. This result indicates that the ratios of Si incorporated into tectosilicates such as quartz are higher compared to group 1. In the ores A, B, and D, the resonance is observed at approximately -59 ppm that is considered to be nesosilicate such as olivine.

In summary, the ^{29}Si MAS NMR spectra in group 1 indicate that main components are phyllosilicates, which is qualitatively consistent with that of the ^{27}Al MAS NMR experiments. In group 1, the ratio of Si belonging to tectosilicates is higher than in group 2. However, to assign the spectral components to specific minerals, the characterization combined with other analytical methods is required.

4 CONCLUSIONS

^{27}Al and ^{29}Si solid state NMR spectra are acquired for five ore samples. Based on the spectral features, ^{27}Al and ^{29}Si MAS NMR spectra can be divided into two groups in the same manner. The conclusions are summarized as below:

- In both of the groups, α-Al_2O_3, and five- and four- coordinated Al are commonly observed in the ^{27}Al MAS spectra. Another main component in group 1 is found to be kaolinite, while that in group 2 is suggested to be fluorine-bearing aluminosilicates.
- From the ^{29}Si MAS NMR experiments, the main Si species in group 1 is found to be phyllosilicate, which are qualitatively consistent with that from ^{27}Al MAS experiments. In group 2, the ratio of Si belonging to silicate species with Q^4 tetrahedral linkage are higher compared to group 1. To characterize the Si species more definitely, support data from other analytical methods are required.

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