

COMMUNICATION

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Direct evidence of Lowenstein's rule violation in swelling high-charge micasReceived 00th January 2012,
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The structure of high-charged micas, Na-n-mica (n=2 and 4), a family of synthetic silicates with wide range of applications, was investigated by use of ¹⁷O solid-state NMR at natural abundance in order to preserve quantitative spectral information. The use of very high-field and highly sensitive probehead, together with ¹⁷O NMR literature data allowed for detection of isolated signal at 26 ppm to be assigned partially to AlOAl, as evidence of the violation of the Lowenstein's rule for Na-4-mica.

Swelling high-charged micas are a new family of the synthesized silicates with important applications in contaminant removal¹ and acid catalyst.² Their properties depend on both total layer charge and the active center distribution on the framework.³ However, some major challenges about aluminum (as active center) distribution still needs to be addressed. For example, Na-4-mica exhibit a Si/Al ratio equal to one and according to Lowenstein's rule, only one Si environment, namely Si(3Al), should be observed. However, Alba *et al.*^{3a} observed, using ²⁹Si MAS NMR, up to five different silicon environments which can be interpreted either by a violation of Lowenstein's rule or by a Si/Al ratio lower than 1. Other authors, who reported a need for clarity, made similar observations and interpretations.⁴ Solid-state MAS NMR is a powerful technique to probe the local structure of those systems for which X-ray diffraction methods fail in distinguishing between Al and Si atoms as well as in giving the protons' position. For example, ²⁷Al MAS NMR provides unambiguous access to the aluminum coordination as tetra-, penta- and hexa-coordinated Al environments are found in clear distinct chemical shift range.⁵ In mica systems, though, ²⁷Al MAS

NMR fails to bring distinction in the Al chemical environment within a coordination type due to the large distribution of NMR parameters that dominates the spectral feature.^{3a}

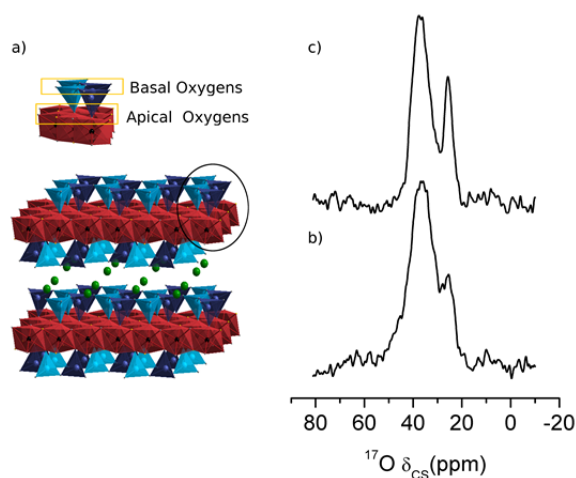


Figure 1. a) Mica structure for which dark and light blue tetrahedra represent the Si and Al tetrahedral environments, respectively; red octahedra represent octahedral Mg and green circles correspond to the interlayer Na. In the upper figure, basal and apical oxygens are displayed. b) Na-2-Mica and c) Na-4-Mica ¹⁷O NMR spectra recorded at 800MHz at natural abundance.

For the last decade, many MAS NMR studies have involved oxygen-17, an NMR-active nucleus with informative parameters that can be related directly to the local structure. Indeed, ¹⁷O chemical shift values (δ_{CS}) and quadrupolar coupling constants (C_Q) depend upon the identity, the number and the distance to nearest-neighbor atoms and are spread over

a large range (> 1000 ppm for δ_{CS}).⁶ However, due to its low natural abundance (0.034%), solid-state NMR studies have often required prior isotopic enrichment which is laborious, expensive, and homogeneity of enrichment is often not ensured. More recently, Blanc *et al.*⁷ have used electron spin transfer using Dynamic Nuclear Polarization (DNP) to enhance the ^{17}O NMR signal of a series of model compounds at ^{17}O natural abundance. Unfortunately, DNP enhancing method is difficult to adapt to low porosity materials, such as micas, without affecting the structure, since the source of electron is obtained through the impregnation of a radical agent.⁸

The aim of the present communication is to show that natural abundance ^{17}O MAS NMR at very high magnetic field (18.8T) brings unambiguous and direct evidence of Lowenstein's rule compliance or violation in Na-n-mica systems. We have selected two synthetic Na-n-mica ($n=2$ and 4). They are swelling and highly-charged sodium fluorophlogopites, 2:1 phyllosilicates with Mg in the octahedral sheet and a high charge density due to isomorphous substitution of Al^{3+} for Si^{4+} in tetrahedral sheet.⁹ These 2:1 phyllosilicates are made from the combination of two basic building blocks: a sheet of edge-sharing $[\text{MO}_4]$ units, $M = \text{Si}$ or Al , (the tetrahedral sheet) and another one of edge-sharing $[\text{MgO}_4\text{F}_2]$ (the octahedral sheet) (Figure 1a). The Si or Al tetrahedra share three of the four oxygens with other tetrahedra and form a rough hexagonal honeycomb in the basal plane. The fourth oxygen of the $[\text{MO}_4]$ units, named apical oxygen, is shared with the octahedral sheet. Consequently, up to five oxygen environments can be encountered. The basal oxygens can be found in the following environments, SiOSi, SiOAl or AlOAl, whereas the apical oxygens are either SiOMg or AlOMg environments.

Table 1. Framework environment distribution in Na-n-mica with Lowenstein's rule compliance (model I) and with Lowenstein's rule violation (model II).

Model	n	% Oxygen sites				
		Basal Oxygens			Apical Oxygens	
		SiOSi	SiOAl ^{tet}	Al ^{tet} OAl ^{tet}	SiOMg	AlOMg
I	2	48.30	26.00	-	18.75	6.25
	4	-	75.00	-	12.50	12.50
II	4	13.94	47.75	11.25	12.50	12.50

The ^{17}O MAS NMR spectra[†] of Na-n-mica ($n=2$ and 4) (Fig. 1b and c) show signal in two well-defined chemical shift regions. The main region is spread from 30 to 50 ppm and the second one between 20 and 30 ppm. Many authors have carried out ^{17}O MAS NMR experiments on series of ^{17}O enriched aluminosilicates and the main NMR parameters (δ_{CS} and C_Q) are summarized in Figure 2. Two well-defined chemical shift regions are observed. Region A is spread from 30 to 55 ppm and corresponds to SiOSi and SiOAl^{tet}. The only way to distinguish between these two environments is by referring to the C_Q value, which is larger for Si-O-Si sites ($4 < C_Q < 6$ MHz) than for Si-O-Al^{tet} sites ($2.5 < C_Q < 3$ MHz). Region B is spread from 15 to 30 ppm and corresponds to Al^{tet}OAl^{tet} sites, only found in aluminosilicates.

To the best of our knowledge, there is no literature evidence for SiOMg and AlOMg ^{17}O NMR studies and thus, no well-defined chemical shift ranges can be found. In order to interpret our ^{17}O NMR experimental data, we hence identified the different possible environments taking into account two models (Table 1). Model I is based on the compliance to the Lowenstein's rule and therefore, the coordination of basal oxygens by two aluminium, Al^{tet}OAl^{tet}, is forbidden. The statistical distribution of the other four environments depends on the layer charge (Table 1) and, in the case of Na-4-mica, only SiOAl^{tet} in tetrahedral sheet is possible. Model II is based on the violation of the Lowenstein's rule. In such a case, for basal oxygens, three environments are possible for Si/Al=1, Na-4-mica, instead of only one environment observed with Model I. The Lowenstein's rule can be violated to varying degree and in this case we have assumed a 15% of Al-O-Al from the ^{29}Si MAS NMR data.³

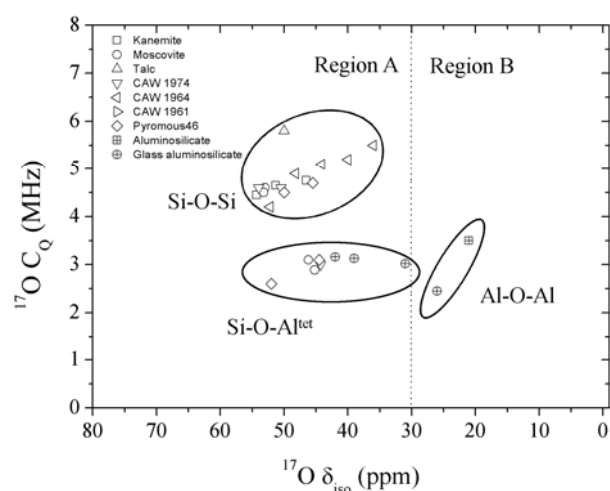


Figure 2. ^{17}O experimental C_Q and δ_{iso} of oxygen sites in layer silicates. Squares and circles are used to illustrate Kaolinite and Muscovite respectively¹⁰ whereas up triangle is for Talc¹¹. Down, left and right triangles are for samples called CAW 1974 (kaolinite + smectite, Al/Si = 2), CAW 1964 and CAW 1961 (both are a mixture of Pyrophyllite and kaolinite, with an Al/Si ratio equal to 1).¹² Diamonds are for Pyromous 46¹³ (a mixture kaolinite + montmorillonite). Crossed circles and squares are two types of aluminosilicate glasses.¹⁴

Considering the chemical shift distribution from Figure 2, it is clear that the most intense signal in the ^{17}O MAS NMR spectra of both micas is due to the overlapping of at least two contributions, SiOSi and SiOAl^{tet}. However, the assignment of the lower chemical shift signal depends on the Lowenstein's rule compliance. If Lowenstein's rule is obeyed, the NMR signal at low chemical shift does not result from Al^{tet}OAl^{tet} environments and must be due to contributions from SiOMg and/or AlOMg. If both apical oxygen environments contribute to this signal, equal relative intensities of this signal must be expected for both micas (Table 1). Since this signal is almost double in the case of Na-4-mica, only one of them, SiOMg or AlOMg, must be the responsible of this resonance. The integration of both regions is possible for ^{17}O MAS NMR

spectrum of Na-4-mica due to the small overlapping of the signals. We found that the resonance centred at 26 ppm accounts for about 25% of the total signal, which exceeds the contribution from one of the two apical oxygens and Al^{tet}OAl^{tet} environment must also be contributing to this signal (Table 1). Therefore, the ¹⁷O MAS NMR spectrum of Na-4-mica (Figure 1c) indicates that the Lowenstein's rule is not followed, validating model II.

Further considerations based on electronegativity may also shed a light into the chemical shift region of both apical oxygen environments. Based on simple quantum chemical calculations that take into account the paramagnetic contribution of the chemical shift,¹⁵ the ²⁹Si chemical shift becomes more shielded as the cation electronegativity (EN) increases.¹⁶ Figure 2 demonstrates that the substitution of two Si (EN(Si)= 1.90) by two Al (EN(Al)=1.61)¹⁶ shift the signal to lower chemical shifts by about 20 ppm, in good agreement with what is observed for other nuclei.^{17,18} Schrämm and Oldfield¹⁹ found that the ¹⁷O NMR signal shifts to lower chemical shifts as the ionic radii increases, therefore, the substitution of Si⁴⁺ (r=0.40 Å) by Al³⁺ (r=0.53 Å) should cause a lower frequency shifts of the NMR signal. By extrapolation, the ¹⁷O of the SiOMg environment must give a resonance at higher chemical shift (> 30 ppm) than AlOMg. The signal centered at 26 ppm in Na-4-mica thus results from the overlapping of AlOMg and Al^{tet}OAl^{tet} environments.

Conclusions

This communication provides the first direct evidence of Lowenstein's rule violation in swelling high-charged micas, based on natural abundant ¹⁷O MAS NMR and avoiding the problem of inhomogeneous enrichment. The confirmation of the present assignment together with a precise fitting of the ¹⁷O NMR spectrum is underway by additional use of recent DFT method that can be used to calculate NMR parameters.

Notes and references

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