

Glasses in the system NaAlSiO_4 - KAlSiO_4 - SiO_2 : preliminary study of structural characteristics using ^{29}Si MAS NMR spectroscopy

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ABSTRACT. — Nuclear Magnetic Resonance analyses on nuclei of ^{29}Si on glasses of the series $\text{NaAlSi}_2\text{O}_6$ - KAlSi_2O_6 (Jd-Leuc) and $\text{NaAlSi}_3\text{O}_8$ - KAlSi_3O_8 (Ab-Or) have been carried out. The chemical shift δ ranges between -93 and -94.2 ppm for the join Jd-Leuc, while it varies between -97.8 and -98.7 ppm for the join Ab-Or. The chemical shift decreases, increasing the Si/Al and the K/Na ratios of the liquid. The presence of different Q^4 (mAl) units, their different statistical distribution, or change in the bond angle could be responsible for the observed δ variations. Moreover the spectra of the glasses of the series Jd-Leuc suggest that Al in jadeitic glasses enters tetrahedral coordination instead of octahedral, as for the Jadeite crystal.

Key words: Silicate melts, system NaAlSiO_4 - KAlSiO_4 - SiO_2 , n.m.r. spectroscopy, polymerization degree.

RIASSUNTO. — Sono state eseguite analisi con spettrometro a risonanza magnetica nucleare su nuclei ^{29}Si di vetri delle linee $\text{NaAlSi}_2\text{O}_6$ - KAlSi_2O_6 (Jd-Leuc) e $\text{NaAlSi}_3\text{O}_8$ - KAlSi_3O_8 (Ab-Or). Il chemical shift δ varia da -93 a -94.2 ppm per la linea Jd-Leuc, mentre varia da -97.8 a -98.7 ppm per quella Ab-Or. Il chemical shift δ diventa più negativo aumentando il rapporto Si/Al e quello K/Na del liquido. Questa variazione può essere imputata a diversi fattori come la presenza di diverse unità Q^4 (mAl), una loro diversa distribuzione percentuale, oppure a variazioni dell'angolo di legame. La mancanza di picchi doppi negli spettri dei vetri della serie Jd-Leuc conferma, inoltre, le analogie strut-

turali, già riscontrate da vari autori, fra queste due composizioni contrariamente a quanto ci si aspetterebbe dalla struttura delle rispettive fasi cristalline.

Parole chiave: Liquidi silicatici, sistema NaAlSiO_4 - KAlSiO_4 - SiO_2 , spettroscopia di n.m.r., grado di polimerizzazione.

Introduction

In recent years, many studies have used different techniques to investigate the structural features of silicate melts: Kundsén Cell Mass Spectrometry (KCMS) (FRASER & RAMMENSEE, 1987; FRASER et al., 1983), calorimetric measurements (RICHER & BOTTINGA, 1982; FRASER & BOTTINGA, 1985), Raman Spectroscopy (BRAWER & WHITE, 1977; MYSEN et al., 1985 and reference therein) Mossbauer Spectroscopy (BOON, 1971) and X-Ray diffraction (RDF) (TAYLOR & BROWN, 1979a, b).

This study has examined a series of aluminosilicate glasses in the system NaAlSiO_4 - KAlSiO_4 - SiO_2 using Magic-Angle Spinning Nuclear Magnetic Resonance (MAS NMR) Spectroscopy. This system, which includes many of the most important granitic

minerals, has been investigated along two joins: (i) $\text{NaAlSi}_2\text{O}_6$ - KAlSi_2O_6 (jadeite-leucite), and (ii) $\text{NaAlSi}_3\text{O}_8$ - KAlSi_3O_8 (albite-orthoclase). As confusion can arise between crystals and melts of the same composition, from here on we will use the abbreviations Jd, Leuc, Ab, Or for the $\text{NaAlSi}_2\text{O}_6$, KAlSi_2O_6 , $\text{NaAlSi}_3\text{O}_8$ and KAlSi_3O_8 components of the system; we identify solid phases with the names jadeite, leucite, albite and orthoclase. In this way, $\text{Jd}_{50}\text{Leuc}_{50}$ signifies a glass with 50% $\text{NaAlSi}_2\text{O}_6$ and 50% KAlSi_2O_6 .

The aims of this work are: (i) to investigate the structural changes caused by cations with different ionic radii in silicate melts with different Si/Al ratios, (ii) to provide further information about the utility of MAS NMR to the study of glasses.

Structural information from ^{29}Si MAS NMR

Many papers have examined the relation between chemical shift, δ , and structural arrangement in both silicate minerals and melts. The value of δ depends on bond length, bond angle and bond strength (KIRKPATRICK et al., 1985; SMITH et al., 1984; SMITH & BLACKWELL, 1983). In addition, there is a link between chemical shift and degree of polymerization (OESTRIKE et al., 1987 and reference therein), as characterized by the number of oxygen which bridge between Si atoms (TOOP & SAMIS, 1962).

To identify the structural units that can be present in silicates, LIPPMAA et al. (1980) introduced the term Q^n , where n is the number of bridging oxygens linked to a Si atom. They showed that for each value of n (for Q^n , $n = 0-4$), there was a specific range of chemical shift, increasing degree of polymerization corresponding to more negative chemical shift (LIPPMAA et al., 1980, 1983; MAGI et al., 1984). Moreover, the presence of Al makes the situation more complicated, as the range of the different Q^n units gets larger if we consider the number and type of NNN (Next-Nearest-Neighbour) atoms around Si (i.e. $Q^n(\text{mAl})$, where m is the number of NNN). Thus in a structure consisting of Q^4 units, the value of chemical shift can range

between -84.6 (for ^{29}Si at $Q^4(4\text{Al})$ sites) up to -112.8 ppm (for ^{29}Si at the $Q^4(\text{OAl})$ sites) (LIPPMAA et al., 1983; MAGI et al., 1984).

Sample preparation

The starting material was prepared by weighing out the necessary amounts of pure gels of $\text{NaAlSi}_2\text{O}_6$, KAlSi_2O_6 , $\text{NaAlSi}_3\text{O}_8$ and KAlSi_3O_8 , and subsequent grinding under acetone. The mixtures were fused in a Pt/Au crucible for 45 minutes at 1450°C . It was not possible to prepare glasses with Leuc $> 50\%$, because of the high melting point (1680°C for pure Leuc). Under the microscope, the glasses were clear and without any signs of incipient crystallization. A.A. analyses are within $\pm 5\%$ of the ideal value, and no appreciable volatilization of Na or K was detected. A Bruker CPX 200 Spectrometer, operating a 39.7 MHz, was used with MAS (Magic Angle Spinning) of about 3.5 KHz. Trimethylsilyl silicate ester (with chemical shift of 11.5 ppm) was used as standard. The mixtures were doped with 0.4 wt% of Fe_2O_3 in order to reduce the relaxation time (FRASER & CLAYDEN, 1987).

Working with glasses (and melts) one cannot expect the usual narrow peaks obtained with crystals, because of the obvious disorder present in non-crystalline materials (FRASER & CLAYDEN, 1987; OESTRIKE et al., 1987). For this reason, the determination of the peak position can give problems as slightly different values can be obtained with different procedures; however, these variations are systematic between them. For this work the peak positions were calculated using a Gaussian fit to the experimental data.

MAS NMR of glasses on the join Jd-Leuc

Spectra are shown in Fig. 1; Fig. 2 shows the chemical shifts and Table 1 list values of δ and halfwidth (peak-width at halfheight). The value of δ for pure Jd agrees quite well with that published by MURDOCH et al. (1985). The spectra are well-defined and show no secondary peaks, supporting the assumption of a simple Gaussian peak-shape model.

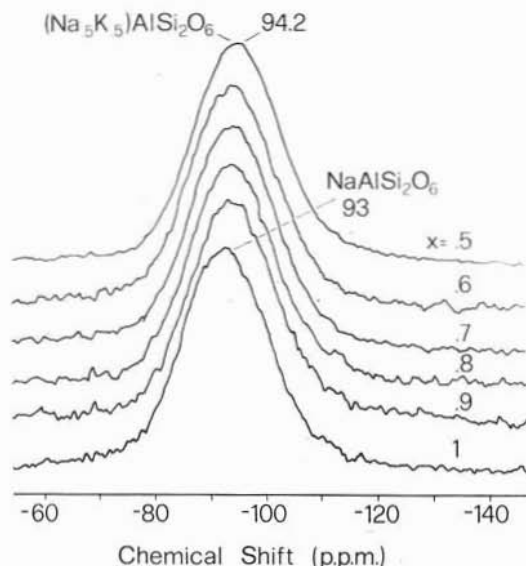


Fig. 1. — ^{29}Si MAS NMR spectra of glasses on the join $\text{NaAlSi}_3\text{O}_8$ - KAlSi_3O_8 . X is the composition expressed in mole fraction $\text{NaAlSi}_3\text{O}_8$.

Despite the broad peaks and the small variation of the chemical shift, a definite negative correlation between the chemical shift and Leuc content is observed.

MAS NMR of glasses on the join Ab-Or

Fig. 3 shows the spectra of the various glasses of the Ab-Or series; Fig. 4 shows the values of chemical shift as a function of composition, and Table 2 reports δ and the linewidth. The chemical shift of An and Or correspond very closely with those reported by FRASER & CLAYDEN (1987) and MURDOCH et al. (1985), whereas it is slightly lower than the values of OESTRIKE et al. (1987) (Fig. 5). Our values parallel also quite well those found by SMITH et al. (1984) for the series albite-microcline. The shape of the peaks is also similar to that of the other series. The value of chemical shift of Ab is higher than that of Jd (4.3 ppm), and a clear variation toward more negative values of δ is shown with increasing Or content in the glasses.

Discussion

From the figures reported above the

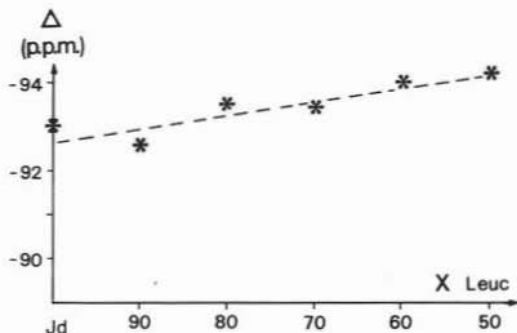


Fig. 2. — ^{29}Si chemical shift of glasses of the series $\text{NaAlSi}_3\text{O}_8$ - KAlSi_3O_8 as a function of composition.

following salient points can be drawn.

a) The value of δ become more negative with increasing Si/Al in glasses of both systems (Fig. 5). At the same Na/K ratio, the chemical shift is about 4 ppm higher (more negative values) for the Ab-Or glasses than for the Jd-Leuc glasses. Following LIPPMAN et al. (1980) the values of δ suggest the existence of Q^4 (2Al) units in the Jd-Leuc glasses ($-92.5 \rightarrow -95.4$ ppm) and Q^4 (1Al) units in the Ab-Or glasses ($-96.7 \rightarrow$

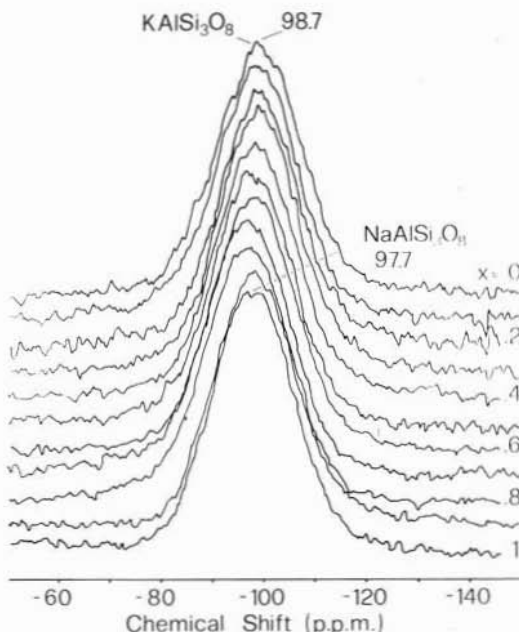


Fig. 3. — ^{29}Si MAS NMR spectra of glasses on the join $\text{NaAlSi}_3\text{O}_8$ - KAlSi_3O_8 . X is the composition expressed in mole fraction $\text{NaAlSi}_3\text{O}_8$.

TABLE 1

Values of the ^{29}Si chemical shift and linewidth at half height for the series $\text{NaAlSi}_2\text{O}_6$ - KAlSi_2O_6

Glass composition (mole fraction $\text{NaAlSi}_2\text{O}_6$)	^{29}Si (p.p.m.)	Linewidth at half height (p.p.m.)
$\text{NaAlSi}_2\text{O}_6$ ($X_{\text{Leuc}}=0$)	93.0	18.5
0.1	92.6	18.5
0.2	93.5	18.8
0.3	93.4	18.5
0.4	94.1	18.7
0.5	94.2	18.6

—100.9). The presence of these two different mAl units could be responsible for the δ variation. However YANG et al. (1986) in heated, disordered albite found Q^4 (4Al) sites, and it is lawful expecting that the same thing happened in non-crystalline materials.

TABLE 2

Values of the ^{29}Si chemical shift and linewidth at half height for the series $\text{NaAlSi}_3\text{O}_8$ - KAlSi_3O_8

Glass composition (mole fraction $\text{NaAlSi}_3\text{O}_8$)	^{29}Si (p.p.m.)	Linewidth at half height (p.p.m.)
$\text{NaAlSi}_3\text{O}_8$ ($X_{\text{Or}}=0$)	97.7	18.9
0.1	97.8	19.6
0.2	97.5	20.0
0.3	98.3	19.7
0.4	98.4	19.2
0.5	98.5	18.0
0.6	98.5	18.9
0.7	98.4	17.6
0.8	98.9	17.7
0.9	98.5	18.4
KAlSi_3O_8 ($X_{\text{Or}}=1.0$)	98.7	19.0

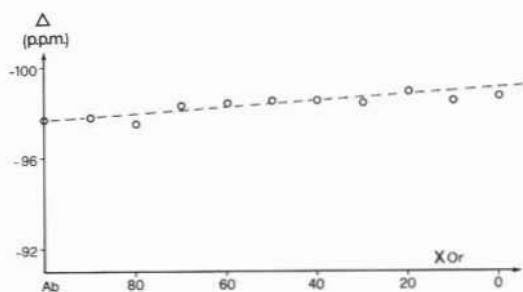


Fig. 4. — ^{29}Si chemical shift of glasses of the series $\text{NaAlSi}_2\text{O}_6$ - KAlSi_2O_6 as a function of composition.

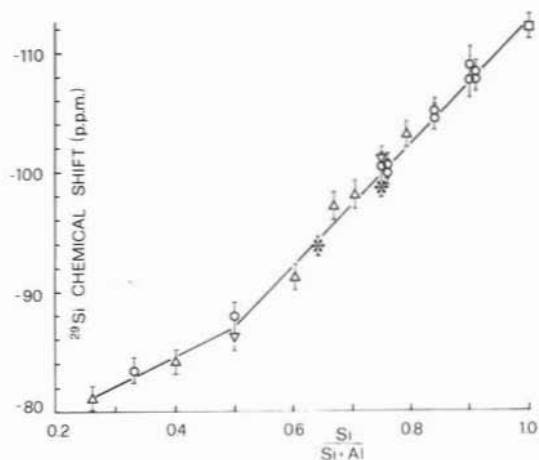


Fig. 5. — Variation of the ^{29}Si chemical shift as function of $\text{Si}/(\text{Si} + \text{Al})$ ratio. Data are from: \square = KIRKPATRICK et al. (1985); ∇ = MURDOCH et al. (1985); Δ = ENGELHARDT et al. (1985); \circ = OESTRIKE et al. (1987); * = this study.

Deconvolution techniques of the NMR spectra in order to work out the contribution of the different sites has been unsuccessful (OESTRIKE et al., 1987). Therefore a different distribution of the same mAl units (ranging from $m = 0$ to 4) could also take into account for the measured values of δ at different $\text{Si}/(\text{Si} + \text{Al})$ ratio. Moreover it has been observed that the introduction of Al causes a variation in the ring size, (TAYLOR & BROWN, 1979a, b; HENDERSON et al., 1985) i.e. in the bond angle, and, therefore, in the chemical shift (KIRKPATRICK et al., 1985).

b) Notwithstanding the broad peaks, a clear variation toward more negative values δ with increase in K component is observed for Jd-Leuc and Ab-Or glasses. Being the Si/Al

ratio constant this variation could be due to a modification of the ring size, i.e. the bond angle and bond length, introducing K with a bigger ionic radius than Na.

c) The presence of only one peak in the spectra of the two series suggests that only one Q^n unit is present, and the small variation in the chemical shift further support this idea. It is known that Ab, Or and Leuc glasses have similar structural arrangements that the corresponding crystals (FRASER et al., 1983; TAYLOR & BROWN 1979a, b) whereas Jd glass seems to be different. Al entering in tetrahedral rather than octahedral coordination in Jd melts, has been already suggested by various researchers (TAYLOR & BROWN, 1979b; FRASER et al., 1983; HAMILTON et al., 1986). TAYLOR & BROWN (1979b) found that RDF of Jd glass is closer to trydimite-like arrangement than to jadeite-like arrangement. FRASER et al. (1983) pointed out that the mixing properties of glasses along Jd-Leuc series are very similar, despite the known structural differences between the respective crystals. The results of this study are compatible with this model, confirming the structural analogy between Jd and Leuc glasses, such that glasses of $\text{NaAlSi}_2\text{O}_6$ composition resemble the stuffed-trydimite structure of nepheline rather than that of jadeite.

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