Glasses in the system NaAlSiO₄-KAlSiO₄-SiO₂: preliminary study of structural characteristics using ²⁹Si MAS NMR spectroscopy

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ABSTRACT. — Nuclear Magnetic Resonance analyses on nuclei of ²⁹Si on glasses of the series NaAlSi₃O₈ - KAlSi₃O₈ (Jd-Leuc) and NaAlSi₅O₁₄ - KAlSi₅O₁₄ (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 Q⁴ (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 NaAlSiO₄ - KAlSiO₄-SiO₂, n.m.r. spectroscopy, polymerization degree.

Introduction

In recent years, many studies have used different techniques to investigate the structural features of silicate melts: Kundsen Cell Mass Spectrometry (KCMS) (FRASER & Rammensee, 1987; FRASER et al., 1983), calorimetric measurements (Richet & 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 alumino-silicate glasses in the system NaAlSiO₄-KAlSiO₄-SiO₂ 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) NaAlSi$_2$O$_6$-KAlSi$_2$O$_6$ (jadeite-
leucite), and (ii) NaAlSi$_3$O$_8$-KAlSi$_3$O$_8$
(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
NaAlSi$_2$O$_6'$
KAlSi$_2$O$_6'$ NaAlSi$_3$O$_8$ and
KAlSi$_3$O$_8$ components of the system; we
identify solid phases with the names jadeite,
leucite, albite and orthoclase. In this
way, Jd$_{50}$Leuc$_{50}$ signifies a glass with
50% NaAlSi$_2$O$_6$ and 50% KAlSi$_2$O$_6$.

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, $\delta$, and structural
arrangement in both silicate minerals and
melts. The value of $\delta$ 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)
troduced 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;
Maggi 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-Neibourgh) atoms around Si
(i.e. $Q^m$ (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 $Q^4$ (4Al) sites)
up to $-112.8$ ppm (for $^{29}$Si at the $Q^4$ (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 NaAlSi$_2$O$_6$, KAlSi$_2$O$_6$, NaAlSi$_3$O$_8$
and KAlSi$_3$O$_8$, 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 OA
wt% of Fe$_2$O$_3$ 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
$\delta$ and halfwidth (peak-width at halfheight).
The value of $\delta$ 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
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GLASSES IN THE SYSTEM NaAlSiO₄-KAlSiO₄-SiO₂: PRELIMINARY STUDY OF STRUCTURAL ETC.

Fig. 1. ²⁹Si MAS NMR spectra of glasses on the join NaAlSi₂O₆-KAlSi₂O₆. X is the composition expressed in mole fraction NaAlSi₂O₆.

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 Oestriks et al. (1987) (Fig. 5). Our values parallel also quite well those found by Smith et al. (1984) for the series albitemicrocline. 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 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 Lippmann et al. (1980) the values of δ suggest the existence of Q⁴ (2Al) units in the Jd-Leuc glasses (−92.5 → −95.4 ppm) and Q⁴ (1Al) units in the Ab-Or glasses (−96.7 → −94.2 ppm).
TABLE 1
Values of the $^{29}$Si chemical shift and linewidth at half height for the series NaAlSi$_2$O$_6$ - KAISi$_2$O$_6$

<table>
<thead>
<tr>
<th>Glass composition</th>
<th>$^{29}$Si</th>
<th>Linewidth at half height</th>
</tr>
</thead>
<tbody>
<tr>
<td>(mole fraction NaAlSi$_2$O$_6$)</td>
<td>(p.p.m.)</td>
<td>(p.p.m.)</td>
</tr>
<tr>
<td>NaAlSi$_2$O$<em>6$ ($X</em>{\text{Leuc}}=0$)</td>
<td>93.0</td>
<td>18.5</td>
</tr>
<tr>
<td>0.1</td>
<td>92.6</td>
<td>18.5</td>
</tr>
<tr>
<td>0.2</td>
<td>93.5</td>
<td>18.8</td>
</tr>
<tr>
<td>0.3</td>
<td>93.4</td>
<td>18.5</td>
</tr>
<tr>
<td>0.4</td>
<td>94.1</td>
<td>18.7</td>
</tr>
<tr>
<td>0.5</td>
<td>94.2</td>
<td>18.6</td>
</tr>
</tbody>
</table>

—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 NaAlSi$_3$O$_8$ - KAISi$_3$O$_8$

<table>
<thead>
<tr>
<th>Glass composition</th>
<th>$^{29}$Si</th>
<th>Linewidth at half height</th>
</tr>
</thead>
<tbody>
<tr>
<td>(mole fraction NaAlSi$_3$O$_8$)</td>
<td>(p.p.m.)</td>
<td>(p.p.m.)</td>
</tr>
<tr>
<td>NaAlSi$_3$O$<em>8$ ($X</em>{\text{Or}}=0$)</td>
<td>97.7</td>
<td>18.9</td>
</tr>
<tr>
<td>0.1</td>
<td>97.8</td>
<td>19.6</td>
</tr>
<tr>
<td>0.2</td>
<td>97.5</td>
<td>20.0</td>
</tr>
<tr>
<td>0.3</td>
<td>98.3</td>
<td>19.7</td>
</tr>
<tr>
<td>0.4</td>
<td>98.4</td>
<td>19.2</td>
</tr>
<tr>
<td>0.5</td>
<td>98.5</td>
<td>18.0</td>
</tr>
<tr>
<td>0.6</td>
<td>98.5</td>
<td>18.9</td>
</tr>
<tr>
<td>0.7</td>
<td>98.4</td>
<td>17.6</td>
</tr>
<tr>
<td>0.8</td>
<td>98.9</td>
<td>17.7</td>
</tr>
<tr>
<td>0.9</td>
<td>98.5</td>
<td>18.4</td>
</tr>
<tr>
<td>KAISi$_3$O$<em>8$ ($X</em>{\text{Or}}=1.0$)</td>
<td>98.7</td>
<td>19.0</td>
</tr>
</tbody>
</table>

Deconvolution techniques of the NMR spectra in order to work out the contribution of the different sites has been unsuccessfull (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 Si/(Si + 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 than 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 trydime-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 NaAlSi_2O_6 composition resemble the stuffed-trydime structure of nepheline rather than that of jadeite.

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