Constraints on the incorporation mechanism of chlorine in peralkaline and peraluminous Na_2O-CaO-Al_2O_3-SiO_2 glasses. (Revision 1)

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ABSTRACT

Incorporation mechanisms of Cl in peralkaline and peraluminous Na_2O-CaO-Al_2O_3-SiO_2 glasses as a model system for phonolitic melts were investigated using ^{35}Cl, ^{23}Na, ^{27}Al and ^{29}Si magic angle spinning (MAS) nuclear magnetic resonance (NMR) spectroscopy. The size and large distribution of electric field gradients for ^{35}Cl causes loss of signal in the MAS NMR experiment and this, in combination with the low concentration of Cl and the large chemical shift dispersion, means that even at the highest available fields we are at the limits of MAS NMR. Nevertheless clear differences in the Cl environment in peralkaline and peraluminous glasses can readily be seen. In both glass types Cl exists in relatively symmetric Na-Ca-Cl environments. The ^{35}Cl chemical shift indicates that the Cl environement is dominated by the presence of Na cations, consistent with the Na/Ca ratio of 5/1 in the glasses. ^{35}Cl MAS NMR spectra of the peraluminous glasses show a larger chemical shift distribution and a more positive isotropic chemical shift, ~ -75 ppm, than the peralkaline glasses,

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~ -100 ppm. They also have a larger quadrupole coupling constant with a larger distribution, indicating greater disorder in the peraluminous glasses. It is likely that there are more Ca cations present in the Cl environments in the peraluminous glasses than in the peralkaline glasses despite their having the same Na/Ca ratio. In the peralkaline glasses the formation of Na-Ca-Cl environments leads to a decrease in the number of network-modifying cations, which causes a polymerization of the glass network. No effect on the glass polymerization was observed in the peraluminous glasses. Some ^{35}Cl signal is also lost in the static spectra indicating that ~ 20% of Cl for a peralkaline glass and more than ~70% for a peraluminous glass must be in environments where there is a large enough electric field gradient that the resulting very broad line is unobservable. These environments could be simply Na-Ca-Cl with higher electric field gradients than those producing the observed ^{35}Cl signal or non-bridging Cl environments like for example Al-Cl. The Cl environment in the present mixed Na_2O-CaO aluminosilicate glasses appears to be more disordered than was to be expected from previous NMR spectroscopic studies on simpler glass compositions.

Keywords

Chlorine, aluminosilicate, glasses, phonolites, ^{35}Cl, ^{23}Na, ^{27}Al, ^{29}Si, NMR

INTRODUCTION

In natural magmas chlorine (Cl) concentration usually does not exceed 1 wt%, although alkali-rich magmas like phonolites can contain up to 1.2 wt% Cl (Carroll 2005; Aiuppa et al. 2009). Even though the abundance of Cl in natural magmatic systems is low compared to H_2O, the incorporation mechanism of Cl in silicate melts with compositions relevant to magmatic systems is important as the presence of Cl can lead to the formation of brines (e.g. Sourirajan and Kennedy 1962; Anderko and Pitzer 1993; Signorelli and Caroll 2000) as well as ore deposits (e.g. Helgeson 1969; Webster 1997a; Candela 1997). Chlorine also influences melt

rheology (Dingwell and Hess 1998; Zimova and Webb 2006; Baasner et al. 2013a). Baasner et al. (2013a) showed that incorporation of Cl into the system Na_2O-CaO-Al_2O_3-SiO_2 results in contrasting behavior with 1.1 mol% (0.6 wt%) *increasing* the viscosity in peralkaline melts by a factor of 10, whereas 0.6 mol% (0.3 wt%) Cl in peraluminous melts *decreases* viscosity by a factor of 3.

Even though the incorporation mechanism of Cl in silicate melts is the key to understand the behavior of Cl in magmatic systems, there are only a few studies about this topic. Stebbins and Du (2002) found from ^{35}Cl magic angle spinning (MAS) nuclear magnetic resonance (NMR) spectroscopy that in silicate and aluminosilicate glasses Cl is coordinated by mono- and divalent cations like Na or Ba rather than by Al and Si. These authors observed that in general the Cl environment is very similar in salts and glasses. For example in sodium silicate and aluminosilicate glasses Cl is coordinated by less than six (as for halides) but more than 4 Na cations (as in sodalite).

Sandland et al. (2004) concluded from ^{35}Cl MAS NMR spectroscopy that Cl in mixed Na_2O-CaO silicate glasses shows no strong preference for either Na or Ca. These authors also found that the presence of Al or H_2O does not significantly affect the Cl environment. Evans et al. (2008) investigated ^{35}Cl environment in aluminosilicate glasses containing monovalent (Na, K) as well as divalent (Mg, Ca) cations with x-ray absorption near edge structure (XANES) spectroscopy. They found that the salt-like Cl environments in magmatic melts are dominated by Ca and Mg and that alkali content, redox conditions and water only play a subsidiary role.

There are only two NMR studies of ^{35}Cl in silicate glasses, probably because spectra of ^{35}Cl in glasses are much more difficult to measure and interpret than that of other nuclei such as ^{19}F or ^{23}Na. The solubility of Cl in (alumino)silicate glasses is usually lower than 2 wt% for 0 - 200 MPa (Webster 1997b; Carroll 2005; Tanimoto and Rehren 2008) and, as ^{35}Cl is a

quadrupole nucleus with a spin of $I = 3/2$, a large quadrupole moment and a low Larmor frequency, its line shape, even at high magnetic fields under MAS conditions, is severely influenced by second order quadrupole broadening (e.g. Sandland et al. 2004). Literature reports a large variation of quadrupole coupling constants (C_q) for ^{35}Cl ranging from a few MHz up to 80 MHz (e.g. Johnson et al. 1969; Lucken 1969; Sandland et al. 2004; Gervais et al. 2005). Note, that linewidth is proportional to C_q^2 (e.g. Freude and Haase 1993). ^{35}Cl also has a large (> 1000 ppm) chemical shift range (Johnson et al. 1969; Sandland et al. 2004) further broadening the peak in disordered systems, thus the acquisition of ^{35}Cl spectra of glasses with an acceptable signal to noise ratio, even at magnetic fields of 14.1 T and higher, takes more than a day.

To date the Cl environment in mixed Na_2O-CaO aluminosilicate glasses as a function of the Al concentration has not been studied. In this work we investigate the incorporation mechanism of 0.6 - 1.9 mol% (0.3 - 1 wt%) Cl in peralkaline ($[Na_2O+CaO] > Al_2O_3$) and peraluminous ($[Na_2O+CaO] < Al_2O_3$) Na_2O-CaO aluminosilicate glasses with about 66 mol% SiO_2, which are a first approximation for phonolitic melts, using ^{35}Cl, ^{27}Al, ^{23}Na and ^{29}Si MAS NMR spectroscopy. The general differences between halogen-free peralkaline and peraluminous spectra and their relation to structure have been discussed previously by Baasner et al. (2014). The focus of this paper will be on the incorporation mechanism of Cl.

METHODS

Starting Materials

Peralkaline (NACS) and peraluminous (ANCS) Na_2O-CaO aluminosilicate glasses containing Cl alone or combined with F were synthesized from powdered oxides, carbonates, halides and ammonium halides. In addition, one Cl-bearing sodium silicate glass (NS) was synthesized.

97 The powder mixtures were decarbonated for 12 h at 1173 K at 1 atm and then melted at
98 1473 - 1923 K for several hours in a Pt crucible in an 1 atm furnace. The glasses were crushed
99 and remelted several times to achieve chemical homogenization. The sample ANCS 1.2Cl
100 was synthesized in a piston cylinder apparatus at 1923 K and 500 MPa for 3 h in a $Pt_{90}Rh_{10}$
101 capsule (detailed description in Baasner et al. 2013b). In order to achieve a higher Cl content
102 than in the other peraluminous samples produced at 1 atm, we synthesized this sample under
103 pressure to reduce the vaporizisation of Cl before it dissolves in the melt. Some of the
104 samples were doped with < 0.1 wt% CoO to enhance the spin lattice relaxation.

105 The compositions of the glasses were determined using a JEOL JXA-8900RL electron
106 microprobe with eight to ten measurements per sample using a 15 kV and 15 nA beam
107 defocused to 30 µm. Table 1a, b presents the compositions of the glasses in mol% oxides and
108 in atom% (at%). The notation in at% takes into account that there is one O^{2-} less for two Cl^- or
109 F^-. Table 1a also shows the $(Na_2O+CaO)/(Na_2O+CaO+Al_2O_3)$ ratio, which is referred as R
110 value (e.g. Thompson and Stebbins 2011) or the gamma value (e.g. Toplis et al. 1997; Webb
111 et al. 2007). Peralkaline glasses have an R > 0.5 indicating that there are enough Na and Ca
112 cations to charge balance Al-tetrahedra (Al coordinated by four oxygens) and that the
113 remaining Na and Ca cations exist as network-modifiers, which create mostly non-bridging
114 oxygens (NBO) at Si-tetrahedra (Si coordinated by four oxygens), which can be seen from
115 NMR spectroscopy (e.g. Allwardt et al. 2003; Lee 2004; Lee and Stebbins 2009).
116 Peraluminous glasses have an R < 0.5 indicating that there are not enough Na and Ca cations
117 to charge-balance all Al-tetrahedra, which leads to the formation of higher-coordinated Al
118 (Schmücker et al. 1997; Kohn et al. 1991) or triclusters (Toplis et al. 1997) and that there are
119 (nearly) no network-modifying cations that create NBO`s (Thompson and Stebbins 2011).

120 The Ca/[Ca+Na] ratio (Table 1b) in the peralkaline and the peraluminous samples is almost
121 the same (~ 0.15 and ~ 0.17) although it is slightly higher for peraluminous glasses as they

were produced in the 1 atm furnace at significantly higher temperatures than the peralkaline glasses, which caused some Na volatilization and a relative enrichment in Ca of the melt. The Cl concentration of the samples NS 2.2Cl and NACS 1.1Cl was confirmed with laser-ablation inductive coupled plasma mass spectrometry (LA-ICPMS).

NMR measurements

All NMR measurements in this study were performed at University of Warwick except for the very high field ^{35}Cl MAS data, which were collected at 81.599 MHz on an 830 MHz Bruker DRX (19.6 T) spectrometer at the National High Magnetic Field Laboratory, Tallahassee. ^{35}Cl MAS spectra were also collected at 58.726 MHz on a 600 MHz Bruker Avance II+ **(**14.1 T) or at 59.010 MHz on a 600 MHz Varian (14.1 T) spectrometer. At 14.1 T a 3.2 mm rotor with a spinning speed of 20 kHz was used and the spectra were collected using an echo sequence with pulse lengths of 1.75 (a solids 90°) and 3.5 μs (a solids 180°), an inter-pulse spacing of one rotor cycle (sample NACS 1.1Cl was also run with a 4 rotor cycle inter-pulse spacing for comparison), a recycle delay of 0.1 s and 36,000 - 2,300,000 acquisitions. Note, in our samples we are in the large C_q limit for ^{35}Cl, i.e. only the ½ -> -½ transition is irradiated (C_q > ~1.5 MHz), thus the pulse lengths required are 1/(I+1/2) of those for a liquid or sample with near zero C_q (e.g. NaCl). The inter-pulse spacing and the recycle delay were carefully tested to avoid saturation or any other distortion of the signal. In addition, static spectra of the samples NS 2.2Cl, NACS 1.1Cl, ANCS 1.0F 0.9Cl were collected at 14.1 T in a 10 mm static probe with an echo spacing of 250 μs, pulse lengths of 3.25 and 6.5 μs, a recycle delay of 0.1 s and 730,000 - 2,300,000 acquisitions. Different recycle delays were tested for NACS 1.1Cl and the signal intensity was the same within the noise level from 0.1s upwards. The spectra at 19.6 T were collected in a 1.8 mm rotor with a spinning speed of 30 kHz. The spectra were measured using an echo sequence with pulse lengths of 1.85 (a solids 90°) and

3.7 μs (a solids 180°), an inter-pulse delay of 4 rotor cycles, a recycle delay of 0.1 s and 70,000 - 4,800,000 acquisitions (total time 6 days). Solid NaCl was used as reference and was set to -46 ppm relative to 1 M aqueous NaCl solution.

^{23}Na MAS spectra were collected at 132.286 MHz on a 500 MHz Bruker Avance III (11.7 T) spectrometer. The samples were measured in a 2.5 mm rotor with a spinning speed of 26 kHz, a pulse length of 1.5 μs (a solids 90°), a recycle delay of 1 s and 60 - 660 acquisitions. Solid NaCl was used as reference that was set to -7 ppm relative to 1 M aqueous NaCl solution.

^{27}Al MAS spectra were collected at 130.301 MHz on a 500 MHz Bruker Avance III (11.7 T) and at 221.550 MHz on an 850 MHz Bruker Avance III (20 T) spectrometer. The samples at 11.7 T were measured in a 2.5 mm rotor with a spinning speed of 26 kHz, a pulse length of 0.75 μs, a recycle delay of 1 s and 1,600 - 16,000 acquisitions. The samples at 20 T were measured in a 3.2 mm rotor with a spinning speed of 20 kHz, a pulse length of 0.8 μs, a recycle delay of 2 s and 84 acquisitions. The peak of six-coordinated Al in yttrium aluminum garnet (YAG) was used as reference and was set to 0.7 ppm relative to 1 M aqueous $AlCl_3$ solution. In all experiments the pulse length corresponds to an angle less than a solids 90º.

^{29}Si MAS spectra were collected at 59.615 MHz on a 300 MHz Varian Infinity Plus (7 T) spectrometer. The samples were measured in a 7 mm rotor with a spinning speed of 4 kHz, a pulse length of 3.5 μs (45º), a recycle delay of 30 - 60 s and 172 - 2,544 acquisitions (spectra for the samples ANCS 0.6Cl and ANCS 1.2Cl were not measured due to failure of the spectrometer). Kaolinite was used as reference and was set to -91.5 ppm relative to tetramethylsilane (TMS, $Si(CH_3)_4$).

RESULTS

^{35}Cl MAS NMR

Figures 1 and 2 show the ^{35}Cl MAS NMR spectra of the Cl-bearing samples at 14.1 and 19.6 T. The spectrum of the Na_2O-SiO_2 glass has a quadrupole tail on the right hand side. In contrast, the lines of the peralkaline and peraluminous glasses are broader, lower in intensity, and approximately Gaussian with only a small quadrupole tail visible on the right hand side for some samples. The term "quadrupole tail" describes the asymmetric intensity distribution on the lower frequency flank of the peak, which is a common feature in NMR spectra of quadrupole nuclei (e.g. ^{35}Cl, ^{23}Na or ^{27}Al) in disordered solids when the nuclei exist in environments with a symmetry less than a perfect sphere or octahedron (e.g. Kirkpatrick 1988; Stebbins 1995). The signal to noise ratio of the ^{35}Cl spectra (Figs. 1 and 2) decreases from the sodium silicate glass to the peralkaline glasses to the peraluminous glasses, although the peraluminous samples were collected with the higher number of acquisitions. Compared to the sodium silicate glass and normalized to same amount of Cl atoms and number of acquisitions only ~ 60% of the ^{35}Cl MAS NMR signal was observed for the peralkaline glasses and only ~ 25% for the peraluminous glasses. The effect of different sample densities and rotor packing on the signal intensities is less than 10%. However the widths of the lines for peralkaline and peraluminous glasses are much broader than those of the sodium silicate glass, ~ 10 kHz and > ~ 15 kHz respectively. This suggests that a significant amount of the Cl exists in environments with a large enough electric field gradient that the intensity of the central band is reduced because significant intensity appears in the sidebands and/or the linewidth is too large to be narrowed by the MAS experiment (Massiot et al. 1990).

Figure 3 shows the spectra of the peralkaline glass NACS 1.9Cl and the peraluminous glass ANCS 1.2Cl at 14.1 T normalized to the same number of acquisitions and the same number of Cl atoms. For ANCS 1.2Cl compared to NACS 1.9Cl only about half of the ^{35}Cl signal was obtained. Fig. 3 also shows that there is a small broad, un-narrowed background underneath

195 the ^{35}Cl peak, which is similar for both spectra. The static NMR spectrum of the peralkaline
196 sample NACS 1.1Cl (Fig. 4) extents over ~ 94 kHz (600 to -1000 ppm) and ~ 80% of the
197 ^{35}Cl signal was detected compared with the sodium silicate glass (NS 2.2Cl). The static NMR
198 spectrum of the peraluminous glass ANCS 1.0F 0.9Cl shows an even broader ^{35}Cl peak that
199 extends over ~ 130 kHz (900 to -1300 ppm) with less than 30% of the ^{35}Cl signal compared to
200 the sodium silicate glass (Fig. A in the supplementary data). In general the static line shapes
201 are consistent with the parameters obtained from MAS NMR spectroscopy in Tables 2 - 4.
202 Thus the remaining Cl must be in environmentswith a large electric field gradient that results
203 in an extremely broad and unobservable line.

204 Table 2 gives the peak maxima, the centers of gravity and the full width half maxima *FWHM*
205 of the ^{35}Cl MAS NMR spectra. The centers of gravity of the peralkaline glasses and the
206 sodium silicate glass are similar with ~ -155 ppm at 14.1 T and ~ -130 pm at 19.6 T, while the
207 centers of gravity of the peraluminous glasses are shifted to higher ppm values of ~ -140 ppm
208 at 14.1 T and ~ -115 ppm 19.6 T. In case of the spectra at 14.1 T, the spinning sidebands are
209 not completely separated from the central band, which contributes to an error of ±5 ppm for
210 the centers of gravity. The *FWHM* increases by a factor two or more at both fields from
211 sodium silicate to peraluminous glasses.

212 Figure 5 shows an overlay of the ^{35}Cl MAS NMR spectra of peralkaline and peraluminous
213 glasses at 14.1 T and 19.6 T normalized to same peak height. The increased width together
214 with a shift of the ^{35}Cl resonance to higher ppm values in the peraluminous glass compared to
215 the peralkaline glass can be clearly seen from both overlays.

216 Figure 6 shows the center of gravity δ_{cg} [ppm] as function of the inverse squared Larmor
217 frequency ν_o^{-2} [MHz^{-2}] for some of the Cl-bearing samples. Linear equations were used to fit
218 the data. The ordinates of the linear equations give the isotropic chemical shift δ_{iso} [ppm]
219 (Table 3). A mean quadrupole coupling constant C_q [MHz] (Table 3) can be calculated from

220 the slope of Eq. 1 (after e.g. Freude and Haase 1993; Schmidt et al. 2000a) using the
221 asymmetry parameter $\eta = 0.7$ (Stebbins and Du 2002)

222 $$\delta_{cg} = \delta_{iso} - \frac{1}{40} \cdot \frac{C_q^2 \cdot (1 + \eta^2 / 3)}{\nu_0^2}. \qquad (1)$$

223 For the peralkaline glasses the spectra of the samples NACS 1.1Cl and NACS 1.9Cl were
224 used for the plot in Fig. 6. For the peraluminous glasses the spectrum of ANCS 0.6Cl at
225 19.6 T and the spectrum of ANCS 1.2Cl at 14.1 T was used as the spectrum of ANCS 0.6Cl at
226 14.1 T had a very poor signal to noise ratio. The higher concentration of Cl in ANCS 1.2Cl
227 compared to ANCS 0.6Cl is not expected to have a significant influence on the results (e.g.
228 Stebbins and Du 2002; Sandland et al. 2004) as the concentration of Cl is low. The center of
229 gravity vs. inverse squared Larmor frequency plots for the other samples containing both, Cl
230 and F, are given in Figs. B and C in the supplementary data. Having data at only two fields,
231 along with the errors of the centers of gravity (± 5 ppm) and the unknown real value of the
232 asymmetry parameter η, results in significant uncertainty in these parameters (estimated as ~
233 ± 16 ppm for δ_{iso} and ~ ± 0.3 MHz for C_q) and the real errors might be higher. Therefore, we
234 also provide later in the text an alternate evaluation method using the program Quadfit (Kemp
235 et al. 2009).
236 An estimate of the width due to the quadrupole effect W_q and the width due to the chemical
237 shift distribution W_{csd} (Table 3) can be calculated after Schmidt et al. (2000a, b)

238 $$FWHM_1^2 = W_q^2 + W_{csd}^2 \qquad (2)$$

239 and

240 $$FWHM_2^2 = (B_1 / B_2)^2 W_q^2 + (B_2 / B_1)^2 W_{csd}^2. \qquad (3)$$

with $FWHM_1$ and $FWHM_2$ [Hz] being the full width half maxima of two spectra measured at a lower magnetic field B_1 [T] and a higher magnetic field B_2 [T]. Because of the low signal to noise ratio W_q and W_{csd} of the samples ANCS 0.6Cl and ANCS 1.0F 0.9Cl are not presented.

The sodium silicate glass and the peralkaline glass have, within error (±16 ppm), the same isotropic chemical shift of ~ -100 ppm, while the peraluminous glasses have a higher chemical shift of ~ -75 ppm. The mean C_q`s of the samples range from 2.3 - 3.1 MHz. The presence of F only has a minor influence, comparable with the error, on the chemical shift and C_q. The chemical shift dispersion, W_{csd}, for the sodium silicate glass is ~ 60 ppm, smaller than that of the peralkaline glasses, ~ 80 - 90 ppm (Table 3). The values for W_q are only 50% larger than those of W_{csd} at 14.1 T for both glasses. At 19.6 T W_{csd} is the dominant contribution to the linewidth, even though second-order quadrupole broadening is still affecting the signal, which is consistent with the relatively small C_q for ^{35}Cl observed here.

An alternate way of describing the effect of significant distributions in the parameters, if data at more than one field are available, is to use programs such as Quadfit to simulate the spectra (Kemp et al. 2009). Quadfit not only uses the parameter δ_{iso}, a mean $\overline{C}_q$, W_{csd} and a mean $\overline{\eta}$ for simulation, but also allows a distribution of C_q ($\Delta\overline{C}_q$) and η ($\Delta\overline{\eta}$). Using Quadfit to fit the spectra with a single quadrupole line, worked well for the NS glass (Fig. D in the supplementary data) but was not entirely successful for the peraluminous and peralkaline glasses. Figure 7 shows, as an example, the spectrum of NACS 1.1Cl at 14.1 T and 19.6 T simulated with Quadfit. There is some additional intensity (~ 10 - 20%) on the high frequency flank of the peralkaline and peraluminous spectra that could not be simulated. The presence of this feature in spectra of different samples from different magnetic fields suggests that there might be more than one type of Cl environment, although the signal to noise ratio of our spectra implies some uncertainty regarding this point. The parameters obtained from peak fitting of all spectra except ANCS 0.6Cl at 14.1 T (because of too low signal to noise) are

given in Table 4. The parameters suggest that for the sodium silicate, peralkaline and peraluminous glasses the mean chemical shifts, δ_{iso} are -80 ppm, -74 to -79 ppm, and -30 to -58 ppm respectively, whilst the distribution in chemical shifts W_{csd} increases from 37 ppm to ~ 75 ppm and to ~ 125 ppm. The mean quadrupole coupling constant $\overline{C}_q$ also increases from ~ 3.5 MHz in the sodium silicate and peralkaline glasses to ~ 4.2 MHz for the peraluminous glasses. For all glasses the distribution of the quadrupole coupling constant is large, $\Delta\overline{C}_q \geq 2.1$ - 3.0 MHz, with the peraluminous samples having the highest values. The mean asymmetry parameter $\overline{\eta}$ ranges from 0.5 to 0.8 with a distribution $\Delta\ \overline{\eta}\ \geq 0.2$. In summary, the values for the isotropic chemical shifts simulated with Quadfit are ~ 20- 30 ppm more positive and the quadrupole coupling constants ~ 1 MHz larger than those obtained using the method of Schmidt et al. (2000a, b), however both methods show the same trends: The peralkaline glasses have similar chemical shifts to the sodium silicate glass with the peraluminous glasses having a ~ 25 - 40 ppm higher chemical shift. Both the chemical shift dispersion and the distribution in quadrupole coupling constants increase markedly from sodium silicate to peralkaline to peraluminous glass.

^{23}Na MAS NMR

Figure 8 shows ^{23}Na MAS NMR spectra at 11.7 T. The peak shape is nearly Gaussian. The peak maxima, centers of gravity and the *FWHM* are given in Table 5. The peak parameters and the spectra of the halogen-free samples NACS and ANCS were taken from Baasner et al. (2014). The peak maximum of the halogen-free peralkaline glass has a higher shift, -17.0 ppm, and the *FWHM* is broader, 25.7 ppm, than that of the halogen-free peraluminous glass, -20.7 ppm and 20.7 ppm respectively. In the peralkaline as well as in the peraluminous glasses containing the highest Cl concentration the presence of Cl causes a small positive shift

290 in the peak maxima of up to 2 ppm while the centers of gravity and the *FWHM* remain
291 constant.

292

293 **^{27}Al MAS NMR**

294 The peak maxima, centers of gravity and the *FWHM* of the ^{27}Al MAS NMR spectra are given
295 in Table 6. The peak parameters and the spectra of the halogen-free sample NACS and ANCS
296 were taken from Baasner et al. (2014) including the calculation of δ_{iso} and C_q after Schmidt et
297 al. (2000a).

298 Figure 9 shows ^{27}Al MAS NMR spectra at 11.7 T of the halogen-free peralkaline sample
299 NACS and the Cl-bearing glass NACS 1.9Cl. The peaks have an obvious quadrupole tail on
300 the right hand side. All Al is four-coordinated (^{IV}Al) with a peak maximum at ~ 55 ppm, no
301 higher-coordinated Al (^{V}Al or ^{VI}Al) is observed and the spectrum of Cl-bearing glass NACS
302 1.9Cl is virtually identical to that of the halogen-free glass NACS.

303 Figure 10 shows ^{27}Al MAS NMR spectra at 20 T of the halogen-free peraluminous sample
304 ANCS and the Cl-bearing glass ANCS 1.2Cl. Despite the high field a quadrupole tail on the
305 right hand of the peaks is still visible. As found earlier for the halogen-free glass (Baasner et
306 al. 2014) most Al is ^{IV}Al with a peak maximum at ~ 57 ppm and a small (5 - 6% of the total
307 Al) fraction of ^{V}Al around 30 ppm in both spectra. A subtraction of the spectrum of ANCS
308 from ANCS 1.2Cl shows that the spectra are very similar although the amount of ^{V}Al might
309 be slightly higher (< 1%) in the Cl-bearing glass than in the Cl-free glass.

310

311 **^{29}Si MAS NMR**

Figure 11 shows ^{29}Si MAS NMR spectra at 7 T of the halogen-free and Cl-bearing peralkaline and peraluminous glasses. The lines have a Gaussian shape and the peak maxima, centers of gravity and *FWHM* are given in Table 7. The peak parameters and the spectra of the halogen-free samples NACS and ANCS were taken from Baasner et al. (2014). The halogen-free peraluminous sample ANCS has a lower chemical shift, -100.4 ppm, than the halogen-free peralkaline sample NACS, -96.3 ppm. The ^{29}Si peak in the peraluminous glasses is unaffected by the presence of Cl (and F), while in the peralkaline glasses Cl causes a small shift in the peak maximum of -0.9 ppm and -1.7 ppm in the centre of gravity. The ^{29}Si peaks in the spectra of NACS 1.1Cl and NACS 1.0F 0.9Cl are within error the same.

DISCUSSION

The values for mean isotropic chemical shift and quadrupole parameters derived from the methods of Schmidt et al. (2000a, b) and the program Quadfit (QF) show similar trends although the values are somewhat different. However the methods used to determine δ_{iso}, $C_{q,}$ W_{csd} and W_q for the ^{35}Cl spectra (Schmidt et al. 2000a, b) (Fig. 6) are intended for peaks that were produced by a single environment without a large dispersion in $C_{q,}$ although the ^{35}Cl lineshape for the peralkaline and peraluminous glasses indicates that this is not the case.

Sandland et al. (2004) suggested that in mixed Na_2O-CaO silicate glasses Cl exists in environments surrounded by either Ca or Na cations as well as in mixed cation environments. However the spectra of the peralkaline and peraluminous glasses are not well enough constrained to allow a meaningful fit to multiple peaks even though there is some evidence that a one site simulation with Quadfit is insufficient (see e.g. Fig.7). Stebbins and Du (2002) and Sandland et al. (2004) found that calcium (alumino)silicate glasses have a ~ 150 ppm higher ^{35}Cl isotropic chemical shift (52 to 102 ppm) than sodium (alumino)silicate glasses

(-65 to -89 ppm) and that mixed Na_2O-CaO silicate glasses have an intermediate shift. No data are available for mixed Na_2O-CaO aluminosilicate glasses. The present peralkaline mixed Na_2O-CaO aluminosilicate glasses have a similar ^{35}Cl chemical shift to sodium silicate glass, ~ -100 ppm (~ -76 ppm, QF) (Figs. 1, 2 and 4), suggesting that the ^{35}Cl sites are dominated by Na and that the Cl environments are very similar in both glass types, but with more disorder in the peralkaline glass. This was expected as in the peralkaline Na_2O-CaO aluminosilicate glasses with a Ca/[Ca+Na] ratio of 0.18 the Na concentration is much higher than the Ca concentration. The *FWHM* and W_{csd} of the ^{35}Cl MAS NMR signal is significantly broader in the peralkaline Na_2O-CaO aluminosilicate glasses than in the sodium silicate glass indicating a significantly larger chemical shift distribution, which could be either related to the incorporation of Ca cations in the Cl environment or due to the presence of Al. The latter is unlikely as the comparison of Al-bearing and Al-free glasses in previous studies showed that Al has no strong influence on the ^{35}Cl environment (Stebbins and Du 2002; Sandland et al. 2004). Sandland et al. (2004) observed no preference of Cl for Ca or Na cations in mixed Na_2O-CaO silicate glasses. However, the ^{35}Cl MAS NMR resonance of the peraluminous mixed Na_2O-CaO aluminosilicate glasses is shifted by ~ +25 ppm (~ +40 ppm QF) (Figs. 1, 2, 3 and 5) and the chemical shift distribution is ~ 50% larger than for the peralkaline glasses. In analogy to the data of Stebbins and Du (2002) and Sandland et al. (2004) this shift may indicate that more Ca cations relative to Na cations are incorporated in the Cl sites even though the samples have the same Ca/[Ca+Na] ratio. This suggests that Cl has a slight preference for Na cations compared to Ca cations in peralkaline samples. In the peraluminous glasses, where most Na and Ca cations are assumed to charge-balance Al-tetrahedra, the Na and Ca cations cannot arrange as freely as in the peralkaline glasses and presumably therefore, more Ca is incorporated in the Cl environment.

The comparatively small ^{35}Cl C_q values of 2 - 4 MHz (Tables 3 and 4) for the peralkaline, peraluminous and sodium silicate glasses are consistent with previous studies and indicate

that the Na-Ca-Cl environments are relatively symmetric (Stebbins and Du 2002; Sandland et al. 2004). The 2 ppm positive shift in the ^{23}Na spectra due to the presence of Cl in the peralkaline as well as in the peraluminous glasses (Fig. 8) is consistent with the formation of salt-like structural units similar to that in NaCl (Stebbins and Du 2002), which would lie with a shift of 0 ppm in the high frequency flank of the ^{23}Na resonance of the glasses. Overall, except for the higher amount of Ca that is incorporated in the Na-Ca-Cl environments in the peraluminous glasses compared to the peralkaline glasses, the environments seem to be similar. A similarity was quite unexpected as Stebbins and Du 2002 and Sandland et al. 2004 proposed that Cl bonds to network-modifying cations, which do not exist in significant quantities in peraluminous glasses (Stebbins and Xu, 1997; Thompson and Stebbins, 2011). However, the ^{35}Cl signal shows that a significant fraction of Cl atoms in the peraluminous glasses are in relatively symmetric Na-Ca-Cl environments. There are two possible explanations for this: first, Cl in peraluminous glasses could occupy interstitial positions in the glass network between charge-balancing cations at Al-tetrahedra. If one assumes that the charge-balancing Na and Ca cations are randomly distributed, this incorporation mechanism would explain the higher amount of Ca cations in the Cl environment although it might have a preference for Na cations like in the peralkaline glasses. Second, as recently shown by Thompson and Stebbins (2011) with ^{17}O NMR, peraluminous glasses are not necessarily completely free of non-bridging oxygens, which would allow a small quantity of network-modifying cations to exist and to build Na-Ca-Cl environments. However, a quantification of the non-bridging oxygens is not possible since no ^{17}O NMR data is available for our composition.

In the peralkaline glasses the ^{29}Si peak of the Cl-bearing glasses NACS 1.1Cl and NACS 1.0F 1.0Cl are shifted to lower frequencies compared to the halogen-free glass NACS (Fig. 11), which may indicate that Cl causes further polymerization of the glass-network (Engelhardt and Michel 1987). Si-Cl environments could not be responsible for the shift, because the

388 isotropic chemical shift for ^{29}Si in $SiCl_4$ is -18.5 ppm (Marsmann et al. 1983), which would
389 shift the signal to higher frequencies. This suggests that in peralkaline glasses the formation
390 of Na-Ca-Cl environments reduces the number of network-modifying Na and Ca cations and,
391 therefore, reduces the number of non-bridging oxygens, which leads to further polymerization
392 of the glass network. A further polymerization of the silicate-network would cause an increase
393 in viscosity, which was indeed observed by Baasner et al. (2013a) for peralkaline samples
394 with the same composition. An Al-Cl interaction, which could reduce the amount of Al-Si
395 bonds and thus could cause a negative shift of the ^{29}Si signal, seems unlikely to be prevalent
396 in case of the peralkaline samples, as such an interaction would cause a decrease in viscosity
397 by transforming charge balancing cations into network modifiers. In contrast, the ^{29}Si
398 spectrum of the peraluminous glass ANCS 1.0F 0.9Cl shows no difference due to the
399 presence of F and Cl compared to the spectrum of the halogen-free glass ANCS (Fig. 11).
400 Fluorine was found to cause a negative chemical shift of the ^{29}Si peak in peraluminous glasses
401 of -1 ppm for a concentration of 9.7 mol% F (Baasner et al. 2014), which is ten times as much
402 F as in ANCS 1.0F 0.9Cl. Thus, if Cl would have caused a shift in the spectrum of ANCS
403 1.0F 0.9Cl compared to ANCS, it would not be masked by an effect of F. In the fully
404 polymerized peraluminous glasses all Na and Ca cations are charge-balancing Al and nearly
405 all Si-tetrahedra are fully connected with bridging oxygens to other Si- or Al-tetrahedra (e.g.
406 Lee 2004; Lee and Stebbins 2009; Thompson and Stebbins 2011). Therefore, Cl in
407 peraluminous glasses should not have an influence on the Si environment by bonding to Na or
408 Ca as in the peralkaline glasses, since the Si-tetrahedra are already fully polymerized.

409 Cl as a monovalent anion could compensate one positive charge of a charge-balancing cation
410 by bonding to Na and Ca and, therefore, could create ^{V}Al in peraluminous glasses (e.g.
411 Thompson and Stebbins 2011). We only observed a slight increase of, at most, 1% in ^{V}Al in
412 the ^{27}Al spectrum of ANCS 1.2Cl compared to that of ANCS, although this increase could be
413 within the error (Fig. 10). However, a strong increase in ^{V}Al due to Cl in the peraluminous

glasses was not expected as the Cl concentration is small, 1.2 mol%, and less than 50% of the Cl exist in Na-Ca-Cl environments. Even if one assumes that one Cl anion could create one ^{V}Al, one would expect only an increase of 2% in ^{V}Al. Furthermore a recent study by Thompson and Stebbins (2011) showed that an excess of 1 mol% Al compared to charge-balancing cations in peraluminous glasses is likely to result in the formation of only 0.25 mol% ^{V}Al.

Compared to the sodium silicate glass only ~ 60% of the ^{35}Cl MAS NMR signal for the peralkaline glasses and ~ 25% for the peraluminous glasses normalized to the same number of acquisitions and molar concentration of Cl (Fig. 3) is observed. The values for C_q and the distribution in C_q are large enough to explain a significant proportion of the missing signal in terms of not spinning fast enough (Massiot et al. 1990; Table 4). However even in the static NMR spectrum (Fig. 4), which extends over ~ 94 kHz only ~ 80% of the ^{35}Cl signal was observed for the peralkaline glass NACS 1.1Cl and less than ~ 30% for the peraluminous glass (Fig. A in the supplementary data) compared to the sodium silicate glass NS 2.2Cl. The simplest explanation for the missing signal would be, that the ^{35}Cl concentration in the samples or the amount of the sample in the rotor is less than expected. However, we confirmed the Cl concentration measured with the electron microprobe with LA-ICPMS. A different filling of the rotors could cause only a difference in sample mass of ~ 5 to 10% (Baasner et al. 2013a; Baasner et al. 2013b). There are several possibilities that could produce an electric field gradient large enough to make the signal unobservable by NMR spectroscopy, e.g. a higher asymmetry and/or a higher diversity within the nearest neighbors of some of the Cl environments. Three structural configurations of Cl are conceivable that explain the missing signal: First, the Cl exists in asymmetric interstitial positions between Na and Ca cations, presumably charge-balancing cations that remain in their charge-balancing role and are, therefore, not as free to arrange as the network-modifying cations. Second, Al or Si cations are involved in the Cl environment like in $AlCl_3$ or $SiCl_4$, which both have a high

quadrupole coupling constant of more than 9 MHz (Sandland et al. 2004; Johnson et al. 1969) and, therefore, would not be observed. Third, Cl could, instead of replacing all oxygens around Al or Si, replace some or single bridging oxygens between Al- and Si-tetrahedra and then be additionally surrounded by other cations like Ca or Na, as was observed for F in aluminosilicate glasses (e.g. Schaller et al. 1992; Stebbins et al. 2000; Stebbins and Zeng 2000; Zeng and Stebbins 2000; Kiczenski and Stebbins 2002; Mysen et al. 2004; Stamboulis et al. 2005; Karpukhina et al. 2008; Baasner et al. 2014). However, it is unknown if the quadrupole coupling constant would be as high as for AlCl or $SiCl_4$. We observed no significant influence of Cl on the ^{27}Al or ^{29}Si environments in the peraluminous glasses (Figs. 10 and 11) that could show evidence for the second and third possibility. However, the amount of Cl is too small compared to that of Al and Si to definitely exclude Al-Cl or Si-Cl environments. Some signal is also missing in case of the peralkaline samples, which is also an argument against the existence of significant amounts of Al-Cl or Si-Cl environments. These environments would cause a depolymerization of the silicate network and a decrease in viscosity. However, Baasner et al. (2013a) found for peralkaline samples with the same composition that the addition of Cl increases viscosity and this increase appears to be too strong to leave space for significant amounts of Cl environments that cause a decrease in viscosity. Though, we cannot exclude minor fractions of Al-Cl or Si-Cl environments. We think that the first explanationfor the missing signal is the most likely, as our Quadfit simulations indicate (Table 4) that the quadrupole distribution of the Na-Ca-Cl environments is large, 2.1 - 3 MHz, in the aluminosilicate glasses. Since the simulation does not take spinning speed into account, it is likely that the quadrupole distribution is, in some cases, even larger than estimated. In this case the long quadrupole tail caused by the distribution, which is difficult to detect, would be underestimated. The observation of a missing ^{35}Cl signal in aluminosilicate glasses was not made in the previous studies of Stebbins and Du (2002) or of Sandland et al. (2004) who observed at least 90% of the ^{35}Cl signal in their aluminosilicate

466 glasses compared to silicate glasses. They investigated pure subaluminous Na_2O and
467 peralkaline to subaluminous CaO aluminosilicate glasses. The present samples are peralkaline
468 and peraluminous mixed Na_2O-CaO aluminosilicate glasses. Therefore, we can conclude that
469 the decrease in signal intensity is related to higher disorder in the Cl environment and is a
470 mixed cation effect that depends additionally on the aluminum content or on a deficit in
471 network-modifying Na and Ca cations.
472 The size of the electric field gradient and the large distribution of chemical shift for ^{35}Cl
473 combined with the low solubility of Cl in aluminosilicate melts (Caroll 2005) mean that the
474 information that can be obtained about the ^{35}Cl environment with MAS NMR is limited, even
475 at the highest available magnetic fields. Despite these analytical difficulties we were able to
476 show that the incorporation mechanisms of Cl in peralkaline and peraluminous
477 Na_2O-CaO-Al_2O_3-SiO_2 glasses are similar but not identical.
478

479 **IMPLICATIONS**

480 The NMR measurements in this study were conducted on silicate glasses and, thus, might be
481 not fully applicable to silicate melts at elevated temperatures. However, some consideration
482 about melt structure and melt viscosity can be made with caution, when the viscosity was
483 measured above and below the glass transition range on samples with a similar composition.
484 Baasner et al. (2013a) found an increase in viscosity due to the addition of Cl in peralkaline
485 Na_2O-CaO aluminosilicate melts with similar compositions to the present samples, which is
486 consistent with an increase in polymerization of the glass network indicated by the decrease in
487 chemical shift of the ^{29}Si peak when Cl is present. However, they also found that Cl decreases
488 viscosity in peraluminous Na_2O-CaO aluminosilicate melts. Theoretically, the formation of
489 Na-Ca-Cl sites as discussed in this study could decrease viscosity in peraluminous melts due
490 to reduction of charge-balancing cations and the resulting transformation of ^{IV}Al to ^{V}Al. ^{VI}Al
491 could decrease viscosity because the Al-O bond length is longer than in tetrahedral

coordinated ^{IV}Al (Tossel 1993) and, therefore, weaker. Indeed, several studies showed that in aluminosilicate melts, after the viscosity reached its maximum at the subaluminous join, it decreases with increasing peraluminousity (Riebling 1966; Toplis et al. 1997; Webb et al. 2007). We calculated how the removal of network-modifying cations in peralkaline melts as well as the removal of charge-balancing cations in peraluminous melts due the formation of Na-Ca-Cl environments would influence the R value ($Na_2O+CaO/[Na_2O+CaO+Al_2O_3]$) and then calculated the theoretical change in viscosity for melts in the system Na_2O-CaO-Al_2O_3-SiO_2 from Webb et al. (2007). From this simple approach the expected change in viscosity compared to the halogen-free melts is ~ -0.02 log units for the peraluminous sample ANCS 0.6Cl and ~ +0.20 log units for the peralkaline sample NACS 1.1Cl (1 log unit = a factor of 10 in viscosity in Pa s). In contrast the viscosity measurements of these samples by Baasner et al. (2013a) showed that compared to the halogen-free melts Cl decreases viscosity by 0.34 log units for ANCS 0.6Cl and increases viscosity by 0.96 log units for NACS 1.1Cl. In both cases the comparison of such estimates with real viscosity data of the present samples from Baasner et al. (2013a) showed that the measured effect of Cl on viscosity is larger than expected from simple structural considerations.

Baasner et al. (2014) investigated the incorporation of F in peralkaline and peraluminous glasses with the same composition as in the present study with MAS NMR spectroscopy. Their major findings were that F in peralkaline glasses exists in environments with Na and Ca as well as Al and Si, while in peraluminous glasses F only bonds to Al and Si. Our study here and also those of Stebbins and Du (2002) and Sandland et al. (2004) found no strong evidence for an important role of Al or Si in the incorporation mechanism of Cl in aluminosilicate glasses. Therefore, one can conclude that although F and Cl are both halogens their incorporation mechanisms are significantly different.

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FIGURE CAPTIONS

Figure 1. ^{35}Cl MAS NMR spectra of the Cl- and F-bearing peraluminous, peralkaline and sodium silicate glasses at 14.1 T. Spinning sidebands are marked with an asterisk. The spectra are normalized to the same peak height.

Figure 2. ^{35}Cl MAS NMR spectra of the Cl- and F-bearing peraluminous, peralkaline and sodium silicate glasses at 19.6 T. Spinning sidebands are marked with an asterisk. The spectra are normalized to the same peak height. The small peak at 75 ppm in the spectrum of NACS 1.1Cl is a contamination with an unknown material, which was not observed in the spectrum of NACS 1.1Cl at 14.1 T.

Figure 3. ^{35}Cl MAS NMR spectra of the Cl-bearing peraluminous (ANCS) and peralkaline (NACS) glasses at 14.1 T. Spinning sidebands are marked with an asterisk. The spectra are normalized to the same number of acquisitions and same number of Cl atoms.

Figure 4. Static ^{35}Cl NMR spectra of the sodium silicate glass NS 2.2Cl and the peralkaline glass NACS 1.1Cl at 14.1 T. The spectra are normalized to the same number of acquisitions and same number of Cl atoms (peak maxima for both samples ~ 90 ppm).

Figure 5. ^{35}Cl MAS NMR spectra of the Cl- bearing peraluminous (ANCS) and peralkaline glasses (NACS) at 14.1 T and 19.6T. Spinning sidebands are marked with an asterisk. The spectra are normalized to the same peak height. The baseline is the same for all spectra. The spectrum of ANCS 1.2Cl only appears to have a higher baseline because of spinning sidebands.

Figure 6. Center of gravity of ^{35}Cl MAS NMR central bands of the Cl-bearing peraluminous (ANCS 1.2 Cl (14.1 T)+ANCS 0.6Cl (19.6 T)), peralkaline (NACS 1.9Cl (14.1 T)+NACS 1.1Cl (14.1 T, 19.6 T) and sodium silicate glass as a function of inverse squared Larmor frequency ν^{-2}. The ordinate of the linear regressions gives the isotropic chemical shift δ_{iso} and the quadrupole coupling C_q constant is calculated from the slope. (see Table 3). The numbers over the data are the magnetic fields in Tesla.

Figure 7. ^{35}Cl MAS NMR spectra of the peralkaline glass NACS 1.1Cl at 14.1 T and 19.6 T (black lines) fitted with the program Quadfit (grey lines). Spinning sidebands are marked with an asterisk. The spectra are normalized to the same peak height.

Figure 8. ^{23}Na MAS NMR spectra of halogen-free and halogen-bearing peraluminous and peralkaline glasses at 11.7 T. The spectra are normalized to the same peak area. The small peak in the high frequency flank of the peak of NACS 1.9Cl is a contamination with the reference material NaCl.

Figure 9. ^{27}Al MAS NMR spectra of the Cl-free and Cl-bearing peralkaline (NACS) glasses at 11.7 T. The spectra are normalized to the same peak height. The residual results from subtracting the spectrum of NACS from that of NACS 1.9Cl.

Figure 10. ^{27}Al MAS NMR spectra of the Cl-free and Cl-bearing peraluminous (ANCS) glasses at 11.7 T. The spectra are normalized to the same peak height. The residual results from subtracting the spectrum of ANCS from that of ANCS 1.2Cl.

Figure 11. ^{29}Si MAS NMR spectra of the halogen-free and halogen-bearing peraluminous and peralkaline glasses at 7 T. The spectra are normalized to the same peak height.

Table 1a. Electron microprobe (EMP) analysis as oxide components of the glass samples. [a]

	SiO_2 [mol%]	2 σ [mol%]	Al_2O_3 [mol%]	2 σ [mol%]	CaO [mol%]	2 σ [mol%]	Na_2O [mol%]	2 σ [mol%]	F [mol%]	2 σ [mol%]	Cl [mol%]	2 σ [mol%]	R[c]	Ca/[Ca+Na]
Peralkaline														
NACS[b]	65.52	1.42	11.94	1.02	5.53	0.36	17.02	0.57	-	-	-	-	0.65	0.14
NACS 1.0F 1.0Cl[b]	65.77	0.27	11.95	0.10	5.50	0.10	15.79	0.17	0.99	0.15	1.02	0.04	0.64	0.15
NACS 1.1Cl[b]	66.86	0.42	11.82	0.13	5.75	0.16	15.57	0.37	-	-	1.10	0.06	0.64	0.16
NACS 1.9Cl[b]	65.55	0.31	11.95	0.16	5.81	0.10	16.69	0.17	-	-	1.92	0.06	0.65	0.15
Peraluminous														
ANCS[d]	65.94	1.63	19.20	1.07	4.19	0.39	10.67	0.25	-	-	-	-	0.44	0.16
ANCS 1.0F 0.9Cl[b]	66.48	0.80	19.73	0.55	3.84	0.12	8.95	0.25	1.01	0.19	0.88	0.02	0.39	0.18
ANCS 0.6Cl[d]	66.31	0.55	20.45	0.31	3.75	0.11	9.49	0.51	-	-	0.64	0.05	0.39	0.16
ANCS 1.2Cl[b]	67.01	0.35	18.55	0.13	4.03	0.13	10.41	0.21	-	-	1.18	0.13	0.44	0.16
Sodium silicate														
NS 2.2Cl[b]	78.09	1.10	0.44	0.05	0.04	0.03	21.43	0.67	-	-	2.20	0.50	-	-

a - Standards were: Wollastonite = Si, Ca; Anorthite = Al; Albite = Na, Topaz = F; Halite = Cl.; Sanidine = K, Cobalt oxide = Co. In all samples contaminations of K_2O (< 0.1 mol%) from the SiO_2 and Al_2O_3 chemicals were observed.

b - Doped with < 0.12 mol% CoO.

c - R= $(Na_2O+CaO)/(Na_2O+CaO+Al_2O_3)$ in mole fraction is an measure of the degree of polymerization of the melt by taking into account the number of sodium and calcium that is either used for charge-balancing aluminum or creating non-bridging oxygens in the melt (e.g. Thompson and Stebbins, 2011). If R > 0.5 the glass is peralkaline and if R < 0.5 the glass is peraluminous.

d - Published in Baasner et al. (2013a)

738 Table 1b. Electron microprobe (EMP) analysis of the glass samples.[a]

	Si [at%]	2 σ [at%]	Al [at%]	2 σ [at%]	Ca [at%]	2 σ [at%]	Na [at%]	2 σ [at%]	F [at%]	2 σ [at%]	Cl [at%]	2 σ [at%]	O[c] [at%]	Ca/[Ca+Na]
Peralkaline														
NACS[b]	20.58	0.45	7.50	0.64	1.74	0.11	10.69	0.36	-	-	-	-	59.49	0.14
NACS 1.0F 1.0Cl[b]	20.79	0.09	7.55	0.06	1.74	0.03	9.98	0.10	0.31	0.05	0.32	0.012	59.31	0.15
NACS 1.1Cl[b]	21.00	0.13	7.42	0.08	1.81	0.05	9.78	0.23	-	-	0.34	0.019	59.65	0.16
NACS 1.9Cl[b]	20.54	0.10	7.49	0.10	1.82	0.03	10.46	0.11	-	-	0.60	0.018	59.08	0.15
Peraluminous														
ANCS[d]	19.73	0.49	11.49	0.64	1.25	0.12	6.38	0.15	-	-	-	-	61.14	0.16
ANCS 1.0F 0.9Cl[b]	19.93	0.24	11.83	0.33	1.15	0.04	5.37	0.15	0.30	0.06	0.26	0.006	61.16	0.18
ANCS 0.6Cl[d]	19.65	0.16	12.12	0.18	1.11	0.03	5.62	0.30	-	-	0.19	0.014	61.31	0.16
ANCS 1.2Cl[b]	20.08	0.10	11.12	0.08	1.21	0.04	6.24	0.13	-	-	0.36	0.040	60.99	0.16
Sodium silicate														
NS 2.2Cl[b]	25.86	0.37	0.29	0.04	0.01	0.01	14.20	0.44	-	-	0.73	0.165	58.91	-

739 a - Standards were: Wollastonite = Si, Ca; Anorthite = Al; Albite = Na, Topaz = F; Halite = Cl.; Sanidine = K, Cobaltoxide = Co. In all samples
740 contaminations of K (< 0.03 at%) from the SiO_2 and Al_2O_3 chemicals were observed.
741 b - Doped with < 0.04 at% Co.
742 c - Calculated from stoichiometry by taking in account that two F^{-1} replace one O^{-2} in the glass.
743 d - Published in Baasner et al. (2013a)
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Table 2. ^{35}Cl peak maximum, center of gravity and full width half maximum *FWHM* of the ^{35}Cl MAS NMR spectra at different fields [a].

	Peak maximum [ppm]		Center of gravity [ppm]		*FWHM* [ppm]	
	14.1 T	19.6 T	14.1 T	19.6 T	14.1 T	19.6 T
Peralkaline						
NACS 1.0F 1.0Cl	-132	-112	-149	-128	151	109
NACS 1.1Cl	-131	-117	-155	-129	145	104
NACS 1.1Cl[b]	-130	-	-161	-	161	-
NACS 1.9Cl	-123	-	-163	-	165	-
Peraluminous						
ANCS 1.0F 0.9Cl	-119	-104	-143	-115	191	182
ANCS 0.6Cl	-152	-130	-123	-113	303	139
ANCS 1.2Cl	-123	-	-149	-	246	-
Sodium silicate						
NS 2.2Cl	-137	-109	-156	-129	103	74

a - The errors of the peak maximum and center of gravity are ±5 ppm for the 14.1 T spectra and ±3 ppm for the 19.6 T spectra. The error in *FWHM* is less than ±16 ppm for the peralkaline samples, but ±25 ppm for the peraluminous samples because of the low signal to noise ratio.

b - measured on the Varian spectrometer 14.1 T

Table 3. ^{35}Cl isotropic chemical shift δ_{iso}, width due to quadrupole broadening W_q, width due to chemical shift distribution W_{csd} and quadrupole coupling constant C_q obtained from spectra ^{35}Cl MAS spectra at 14.1 T and 19.6 T evaluated after Schmidt et al. (2000a, b).

	δ_{iso}[a] [ppm]	C_q[b] [MHz]	W_q[c] [ppm] 14.1 T	W_{csd}[c] [ppm] 14.1 T
Peralkaline				
NACS 1.0F 1.0Cl	-105	2.3	123	89
NACS 1.1Cl + NACS 1.9Cl[d]	-95	2.8	131	79
Peraluminous				
ANCS 1.0F 0.9Cl[f]	-74	3.1	-	-
ANCS 0.6Cl + ANCS 1.2Cl[ef]	-75	3.0	-	-
Sodium silicate				
NS 2.2Cl	-101	2.6	84	60

a - The maximum error in δ_{iso} is ±16 ppm.

b - C_q was calculated estimating an asymmetry parameter $\eta = 0.7$. The maximum error in C_q is ±0.3 MHz taking into account that η could range from 0 to 1.

c - The maximum error in W_q and W_{CSD} is less than ±12.5% for a max. error of 16 ppm in *FWHM*.

d - The evaluation was done based on the measurements of the sample NACS 1.1Cl at 14.1 T and 19.6 T and the sample NACS 1.9Cl at 14.1 T.

e - The spectrum of ANCS 0.6Cl at 14.1 T was not included in the evaluation for δ_{iso} and C_q because of its poor/low signal to noise ratio. The evaluation was done based on the measurement of ANCS 1.2Cl at 14.1 T and ANCS 0.6Cl at 19.6T.

f - W_q and W_{CSD} are not presented for the peraluminous spectra because of their low signal to noise ratio.

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Table 4. ^{35}Cl chemical shift δ_{iso}, width due to chemical shift distribution W_{csd} and quadrupole coupling constant $\overline{C}_q$, the quadrupole distribution $\Delta\overline{C}_q$, the asymmetry parameter η and the distribution of the asymmetry parameter $\Delta\eta$ of the curves fitted to the ^{35}Cl MAS NMR spectra at different magnetic fields B with the program Quadfit[a].

	δ_{iso} [ppm]	W_{CSD} [ppm]	$\overline{C}_q$ [MHz]	$\Delta\overline{C}_q$ [MHz]	$\overline{\eta}$	$\Delta\overline{\eta}$.
ANCS 1.0F 0.9Cl	-45	125	4.2	3.0	0.8	0.2
ANCS 0.6Cl	-58	125	4.3	3.0	0.8	0.2
ANCS 1.2Cl	-30	125	4.2	3.0	0.8	0.2
NACS 1.0F 1.0Cl	-79	72	3.3	2.1	0.8	0.2
NACS 1.1Cl	-77	82	3.7	2.7	0.5	0.2
NACS 1.9Cl	-74	82	3.5	3.0	0.7	0.2
NS 2.2Cl	-80	37	3.5	2.5	0.5	0.3

a - Various approaches to fit the spectra suggest that the errors of the parameter are ±5 ppm for δ_{iso} ±10 ppm for W_{csd}, 0.2 for $\overline{\eta}$, 0.1 for $\Delta\overline{\eta}$ and ±0.2 MHz for $\Delta\overline{C}_q$ and $\Delta\overline{C}_q$.

Table 5. ^{23}Na peak maximum, center of gravity and full width half maximum *FWHM* of the ^{23}Na MAS NMR spectra at 11.7 T[a].

	Peak maximum [ppm]	Center of gravity [ppm]	*FWHM* [ppm]
NACS[b]	-17.0	-16.9	25.7
NACS 1.0Cl 1.0F	-16.0	-16.6	24.4
NACS 1.1Cl	-16.3	-16.8	24.7
NACS 1.9Cl	-14.9	-16.7	25.2
ANCS[b]	-20.7	-19.2	20.7
ANCS 0.9Cl 1.0F	-20.6	-20.8	20.9
ANCS 1.2Cl	-18.8	-19.2	20.9

a - The errors of peak maximum, center of gravity and *FWHM* are ± 0.5 ppm.
b - from Baasner et al. (2014)

Table 6. ^{27}Al peak maximum, center of gravity and full width half maximum *FWHM* of the ^{27}Al MAS NMR spectra at different magnetic fields [a].

	Magnetic field [T]	Peak maximum [ppm]	Center of gravity [ppm]	*FWHM* [ppm]
NACS[b]	11.7	55.54	51.18	16.90
NACS 1.1Cl	11.7	55.36	52.54	16.96
NACS 1.9Cl	11.7	55.28	51.71	16.81
ANCS[b]	11.7	52.55	43.91	23.21
ANCS1.2Cl	11.7	52.82	41.57	23.89
ANCS[b]	20.0	57.03	54.30	15.04
ANCS 1.2Cl	20.0	57.17	54.21	15.25

a - The errors of peak maximum, center of gravity and *FWHM* are ±0.25 ppm for the 11.7 and 20 T spectra.
b - from Baasner et al. (2014)

798
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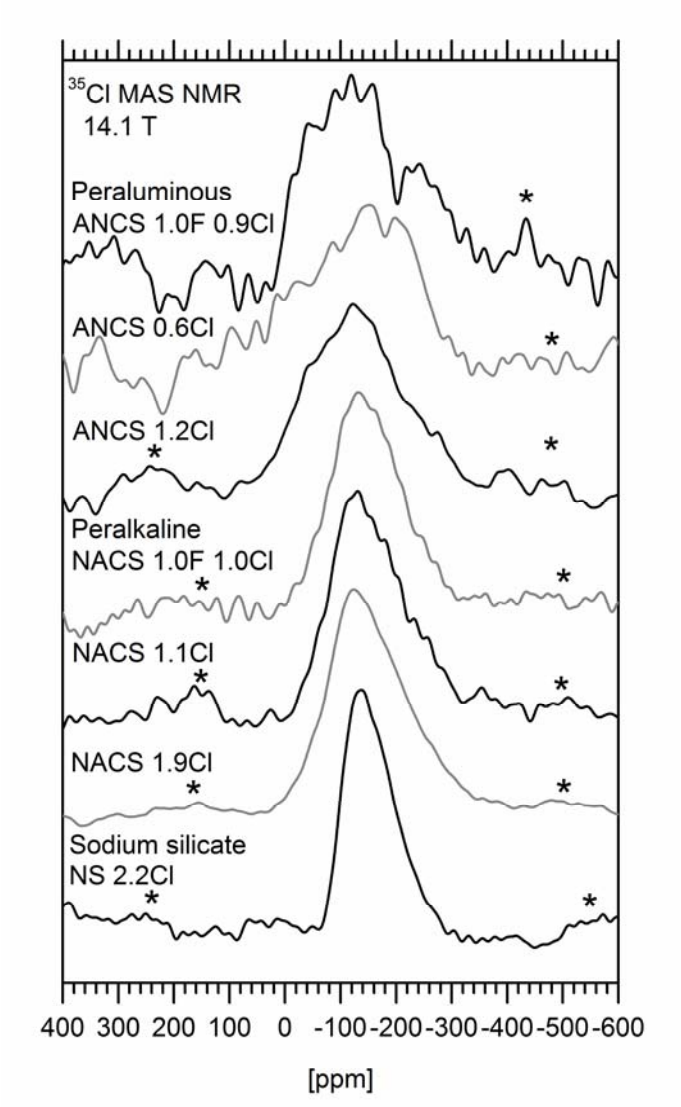
800
801 Table 7. ^{29}Si isotropic chemical shift δiso, center of gravity and full width half
802 maximum (*FWHM*) of the ^{29}Si MAS NMR spectra at 7 T[a].

	δ_{iso} [ppm]	Center of gravity [ppm]	*FWHM* [ppm]
NACS[b]	-96.3	-96.2	17.1
NACS 1.0Cl 1.0F	-97.2	-97.9	17.1
NACS 1.1Cl	-97.2	-97.9	17.5
ANCS[b]	-100.4	-100.4	17.9
ANCS 0.9Cl 1.0F	-100.8	-101.1	18.0

803 a - The errors of δ_{so}, center of gravity and *FWHM* are ± 0.4 ppm.
804 b - from Baasner et al. (2014)
805
806
807
808
809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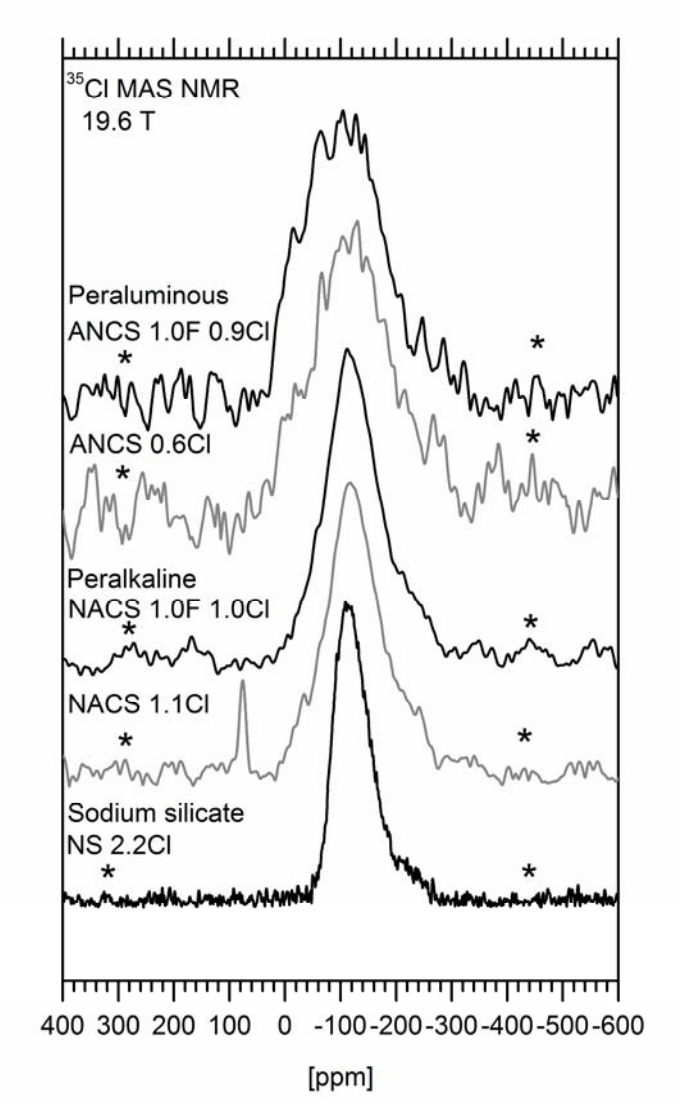
14.1 T
Peraluminous
ANCS 1.0F 0.9Cl
ANCS 0.6Cl
ANCS 1.2Cl
Peralkaline
NACS 1.0F 1.0Cl
NACS 1.1Cl
NACS 1.9Cl
Sodium silicate
NS 2.2Cl
400 300 200 100 0 -100 -200 -300 -400 -500 -600
[ppm]

Figure 1.



813

814 Figure 2.

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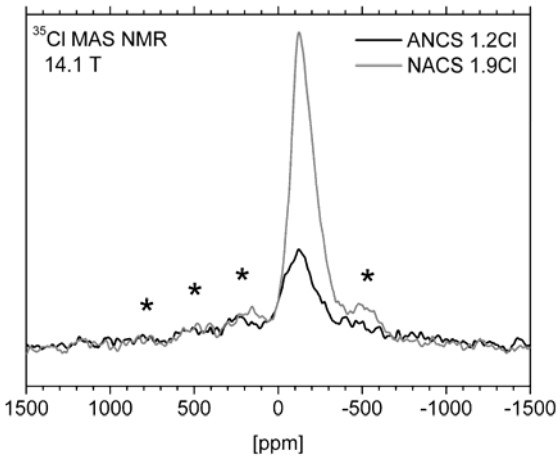
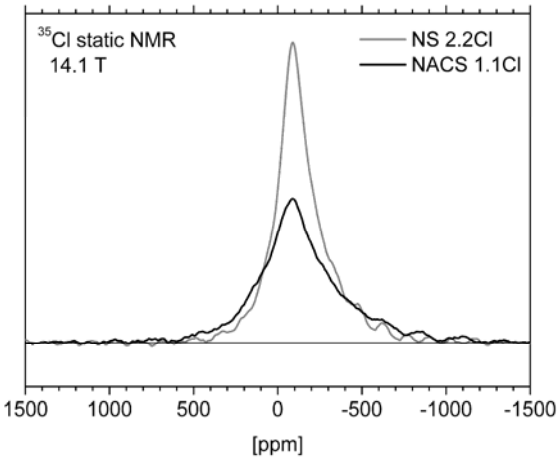


816

817 Figure 3.



818

819 Figure 4.

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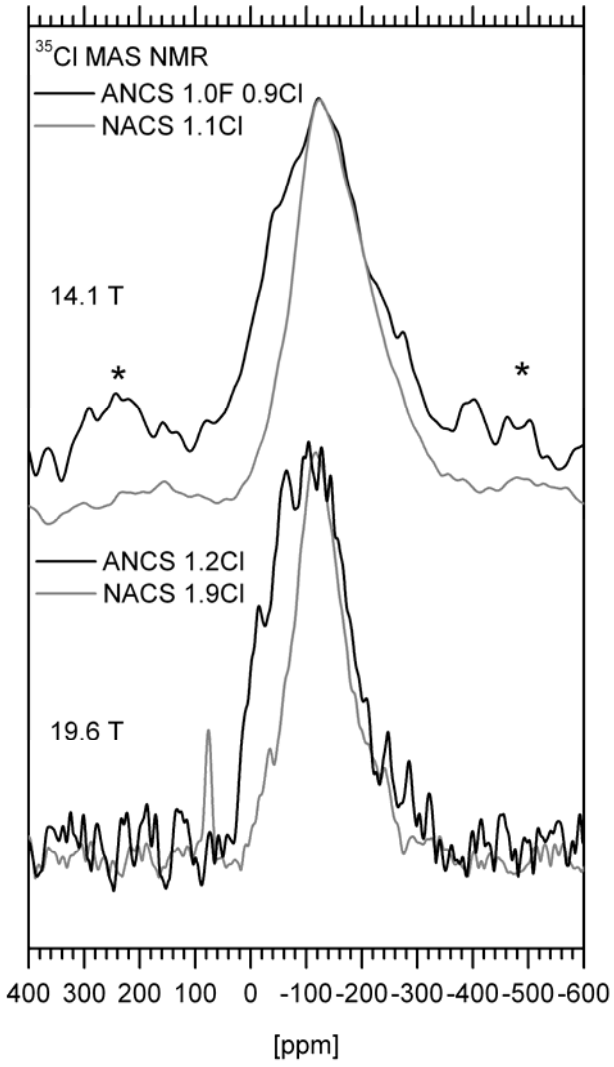
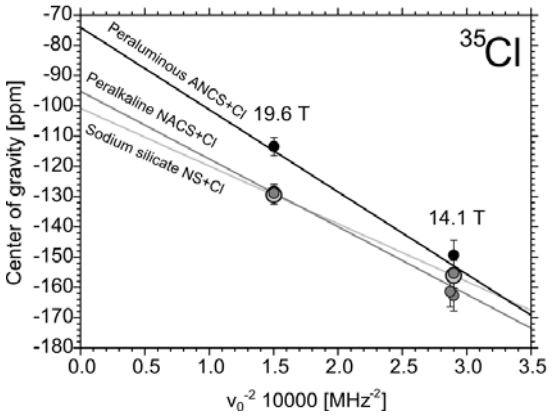


821

822 Figure 5.

823



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825 Figure 6.

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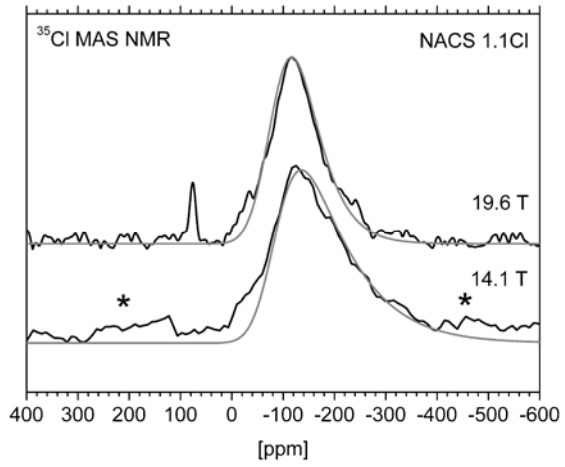

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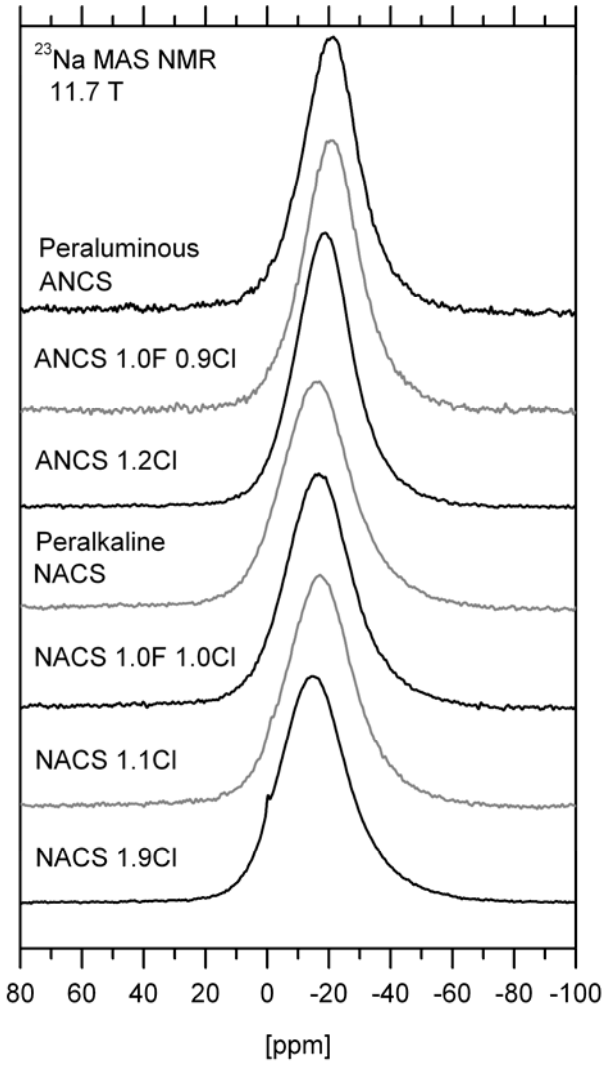
828 Figure 7.



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830 Figure 8.

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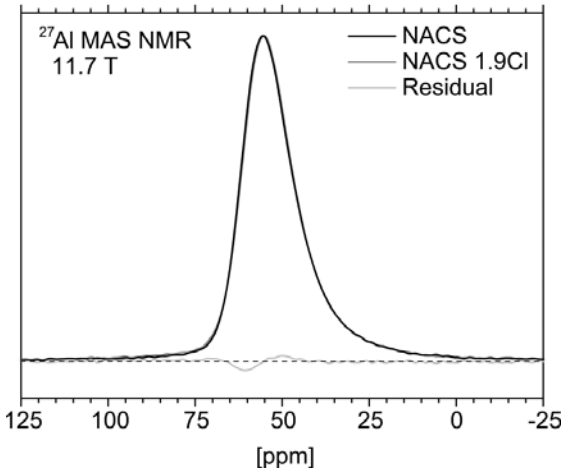
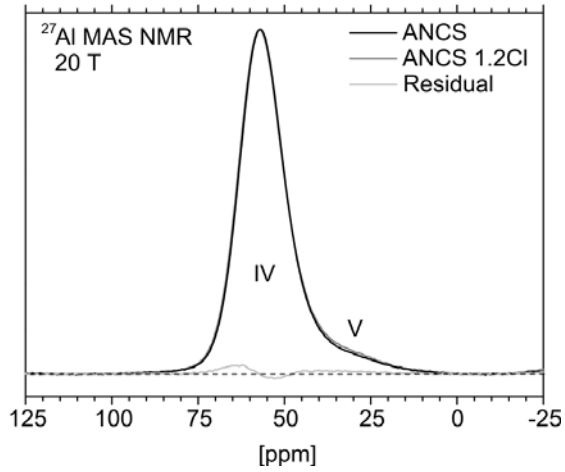


832

833 Figure 9.



834

835 Figure 10.

836

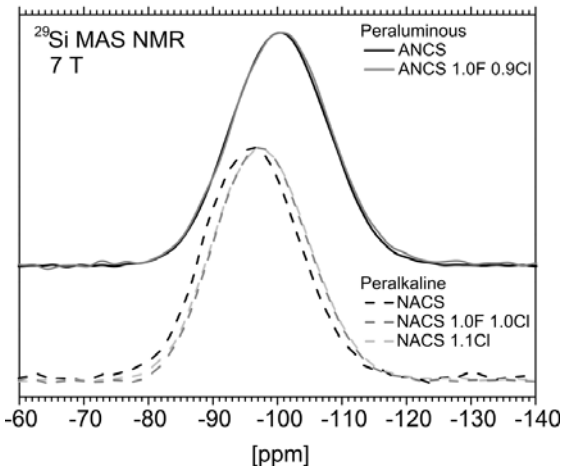

29Si MAS NMR
7 T
Peraluminous
ANCS
ANCS 1.0F 0.9Cl
Peralkaline
NACS
NACS 1.0F 1.0Cl
NACS 1.1Cl
-60 -70 -80 -90 -100 -110 -120 -130 -140
[ppm]

Figure 11.

SUPPLEMENTARY DATA

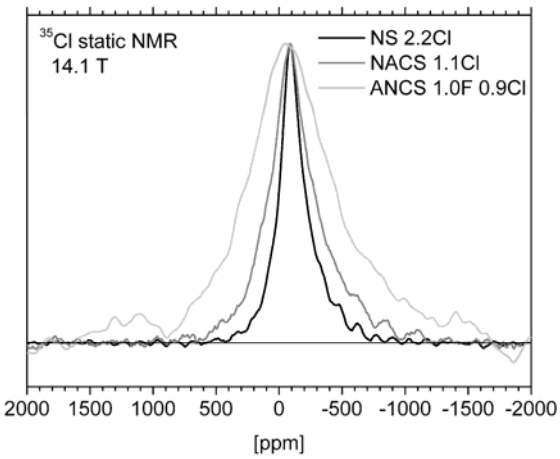


Figure A. Static ^{35}Cl NMR spectra of the sodium silicate glass NS 2.2Cl, the peralkaline glass NACS 1.1Cl and the peraluminous glass ANCS 1.0F 0.9Cl at 14.1 T. The peak maxima are at -90 ppm for the sodium silicate and the peralkaline glass and -50 ppm for the peraluminous glass. The spectra are normalized to the same peak height.

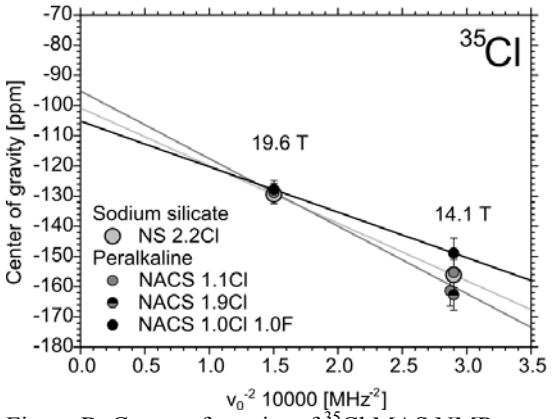


Figure B. Center of gravity of ^{35}Cl MAS NMR central bands of the Cl-bearing peralkaline and sodium silicate glasses as a function of inverse squared Larmor frequency ν^{-2}. The ordinate of linear regressions gives the isotropic chemical shift δ_{iso} and the quadrupole coupling C_q constant was calculated from the slope (see Table 3). The numbers on top of the data are the

magnetic fields in Tesla. One linear equation was fitted to the combined data of NACS 1.1Cl at 14.1 T, 19.6 T and NACS 1.9Cl at 14.1 T.

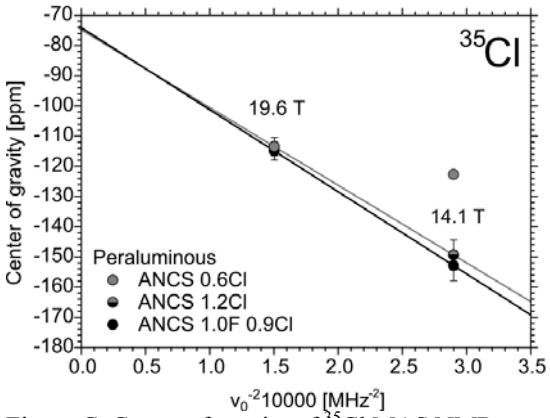
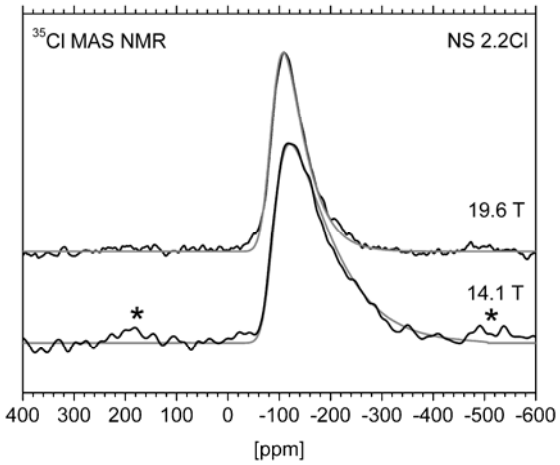


Figure C. Center of gravity of ^{35}Cl MAS NMR central bands of the Cl-bearing peralkaline and sodium silicate glasses as a function of inverse squared Larmor frequency ν^{-2}. The ordinate of the linear regressions gives the isotropic chemical shift δ_{iso} and the quadrupole coupling C_q constant was calculated from the slope (see Table 3). The numbers on top of the data are the magnetic fields in Tesla. The center of gravity of ANCS 0.6Cl at 14.1 T was not used for further evaluation as the signal to noise ratio of the spectrum was too low and its usage in evaluation delivered an unusual low $C_q \sim 1.5$ MHz, which is not consistent with the general quadrupole peak shape in the spectra in this study and previous studies (e.g. Sandland et al., 2004). Instead a linear equation was fitted to the center of gravity of ANCS 1.2Cl at 14.1 T and the center of gravity of ANCS 0.6Cl at 19.6 T.



882

883 Figure D. ^{35}Cl MAS NMR spectra of the sodium silicate glass NS 2.2Cl at 14.1 T and 19.6 T

884 (black lines) fitted with the program Quadfit (grey lines). The fit is $\overline{C}_q$ = 3.5 MHz,

885 $\Delta\overline{C}_q$ = 2.5 MHz, $\overline{\eta}$ = 0.5, $\Delta\overline{\eta}$ = 0.3. Spinning sidebands are marked with an asterisk. The

886 spectra are normalized to the same peak height.

887

888
889 Table A. Expected MAS relative intensities after Massiot et al. (1990) for a range of
890 quadrupole coupling constants C_q and an asymmetry parameter $\eta = 0.8$ for different magnetic
891 fields (values in T) and spinning speeds (values in kHz).

C_q [MHz]	Intensity 14.1 T 20 kHz	Intensity 19.6 T 30 kHz
2.6	0.75	0.94
3.5	0.38	0.80
4.1	0.19	0.65
4.3	0.16	0.58

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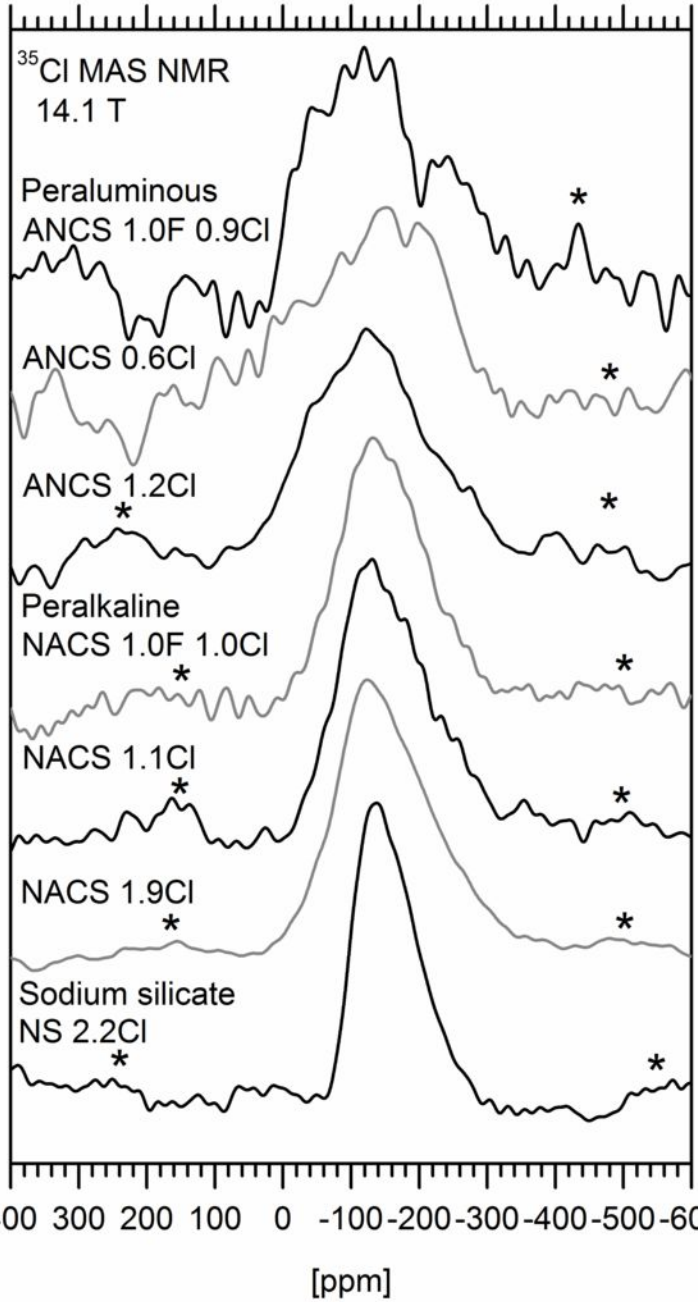
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Peraluminous
ANCS 1.0F 0.9Cl
ANCS 0.6Cl
ANCS 1.2Cl
Peralkaline
NACS 1.0F 1.0Cl
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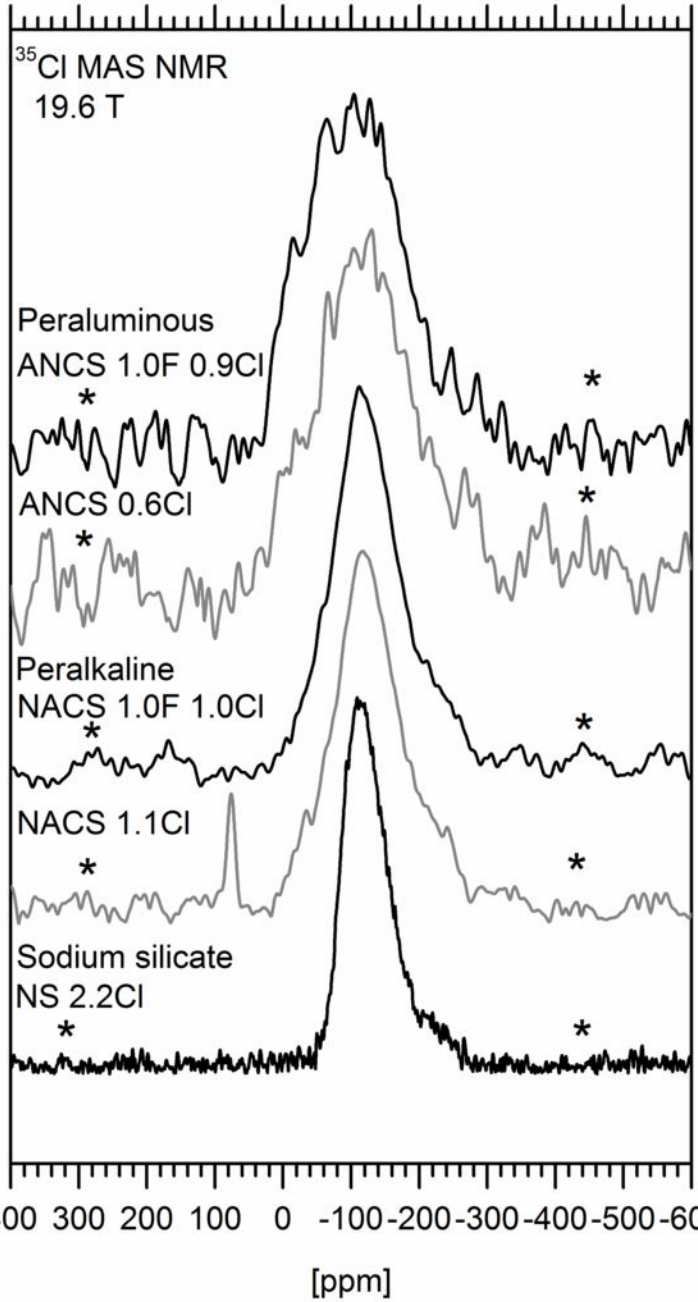
NACS 1.9Cl
Sodium silicate
NS 2.2Cl
400 300 200 100 0 -100 -200 -300 -400 -500 -600
[ppm]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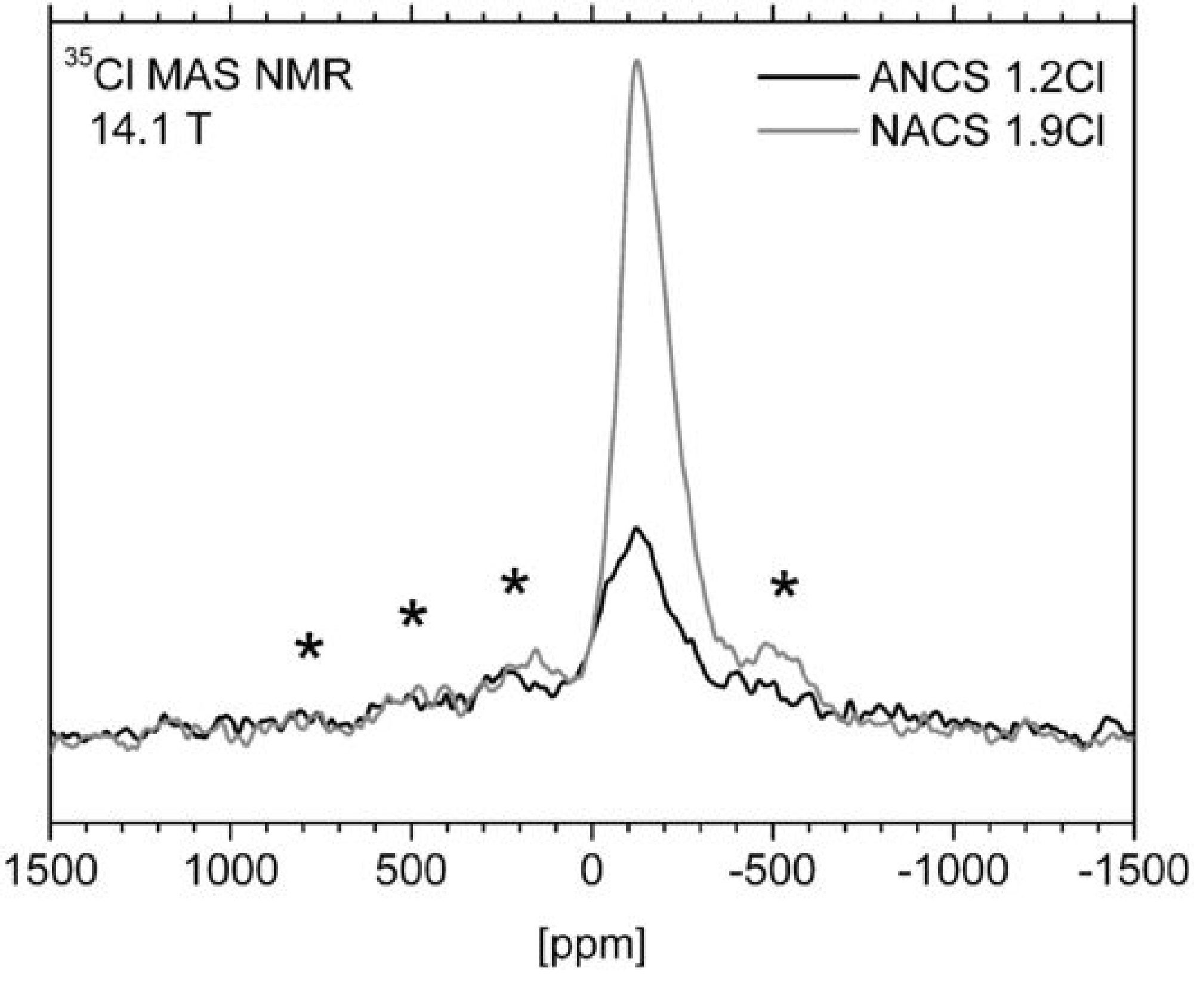
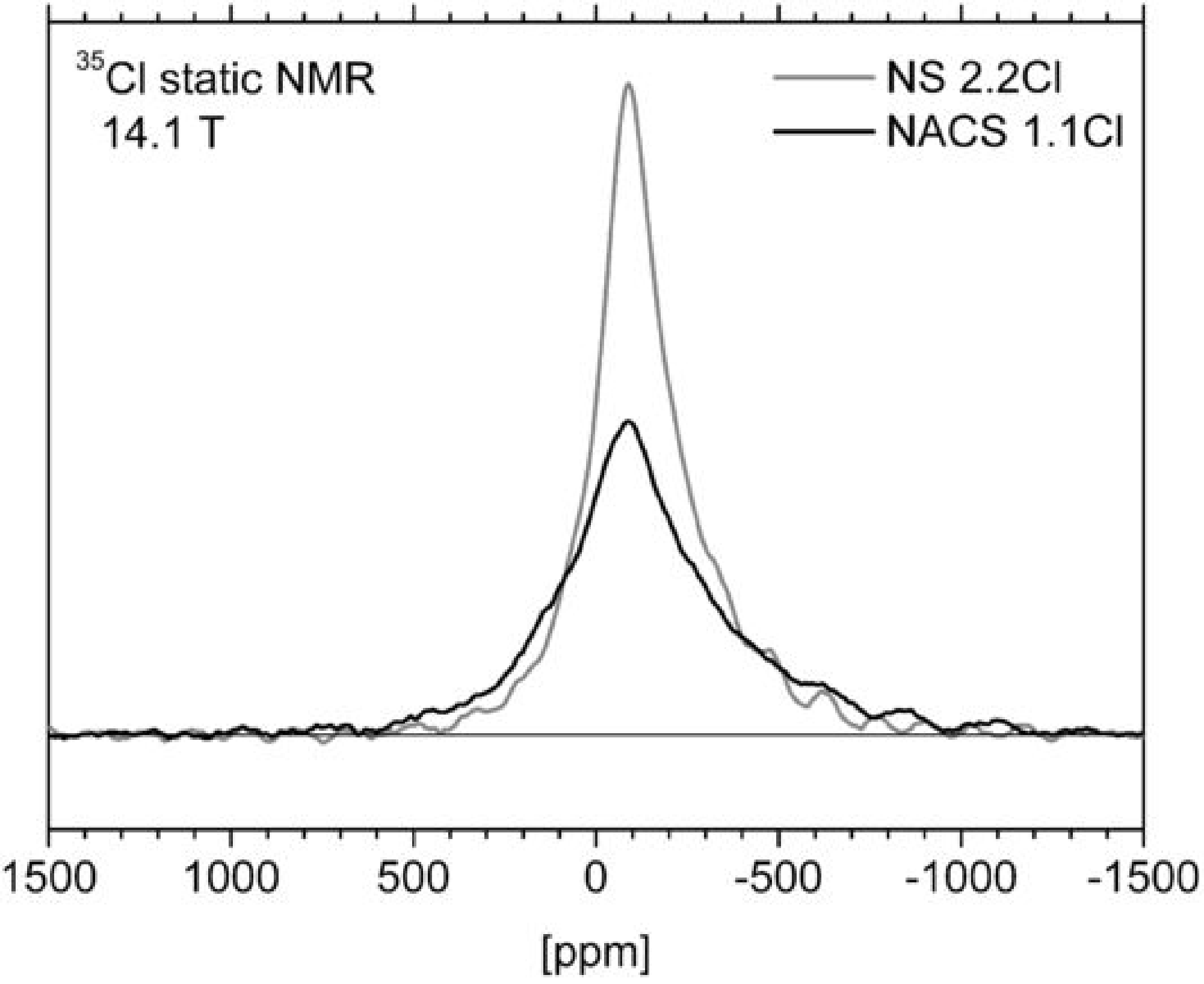
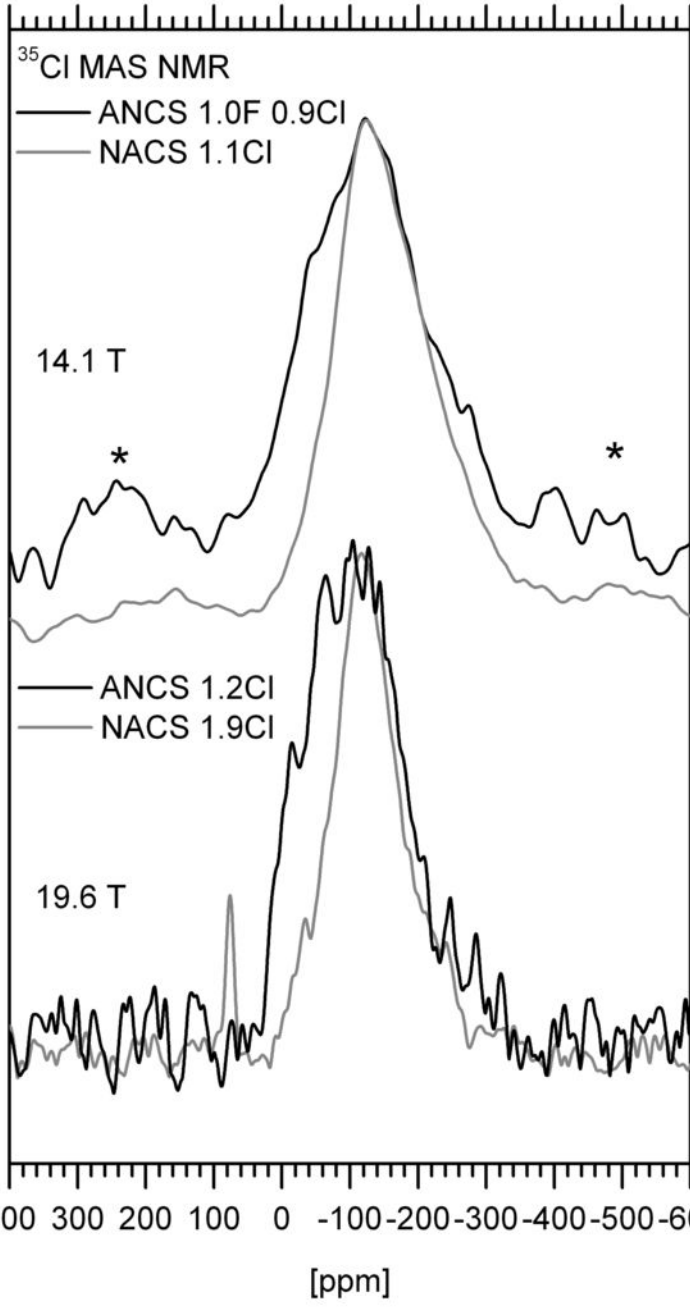
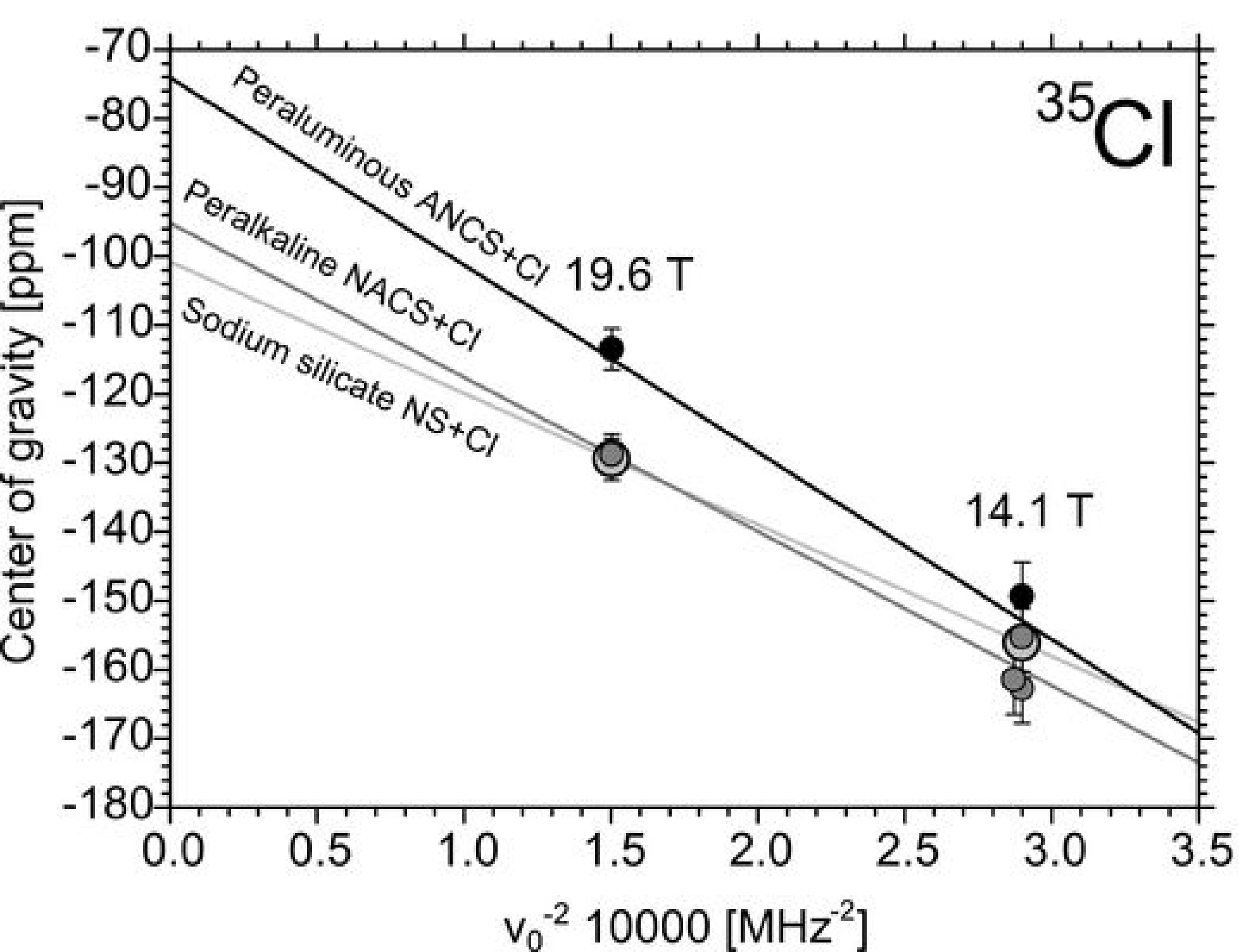
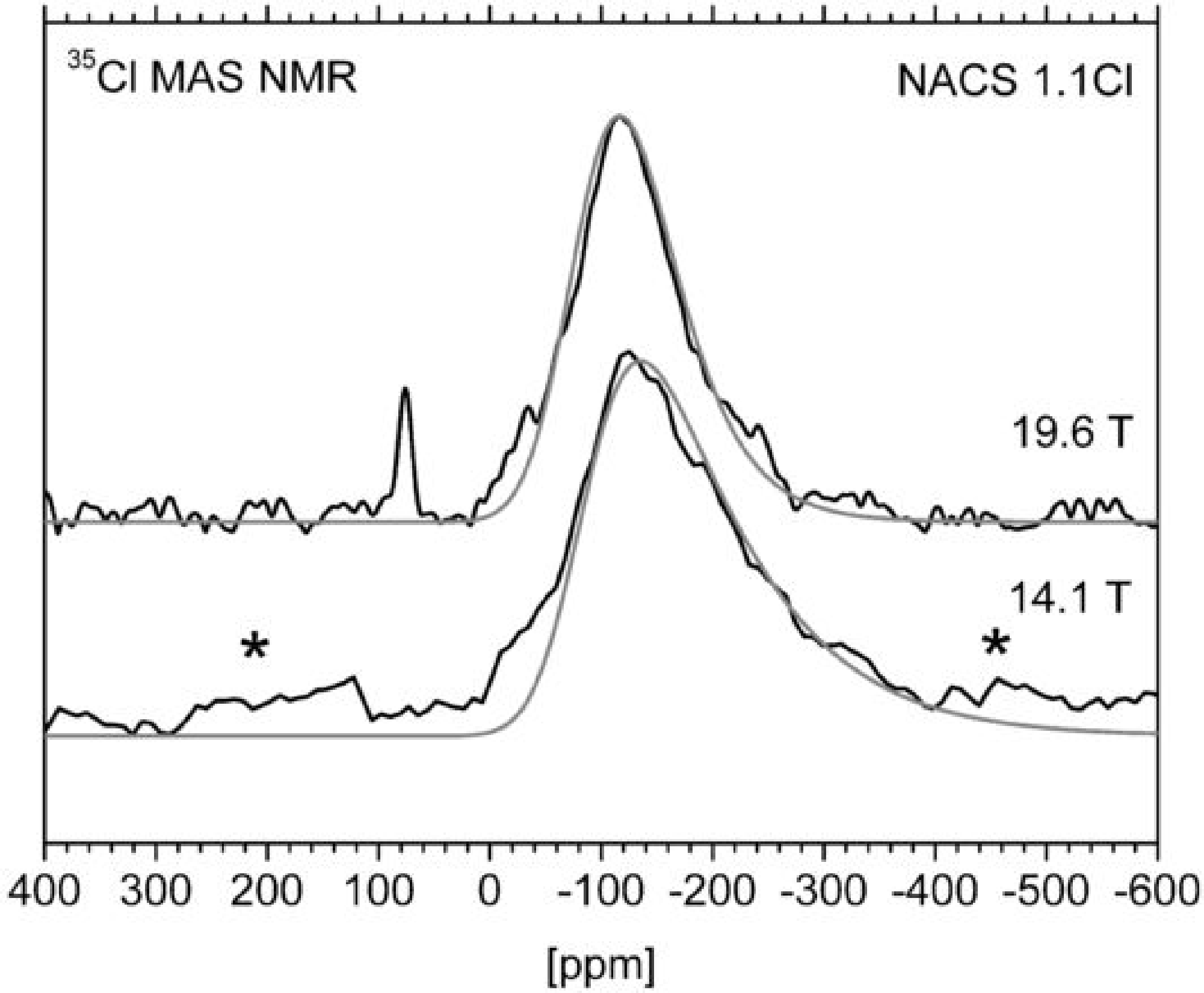
19.6 T
Peraluminous
ANCS 1.0F 0.9Cl
ANCS 0.6Cl
Peralkaline
NACS 1.0F 1.0Cl
NACS 1.1Cl
Sodium silicate
NS 2.2Cl
*
400 300 200 100 0 -100 -200 -300 -400 -500 -600
[ppm]

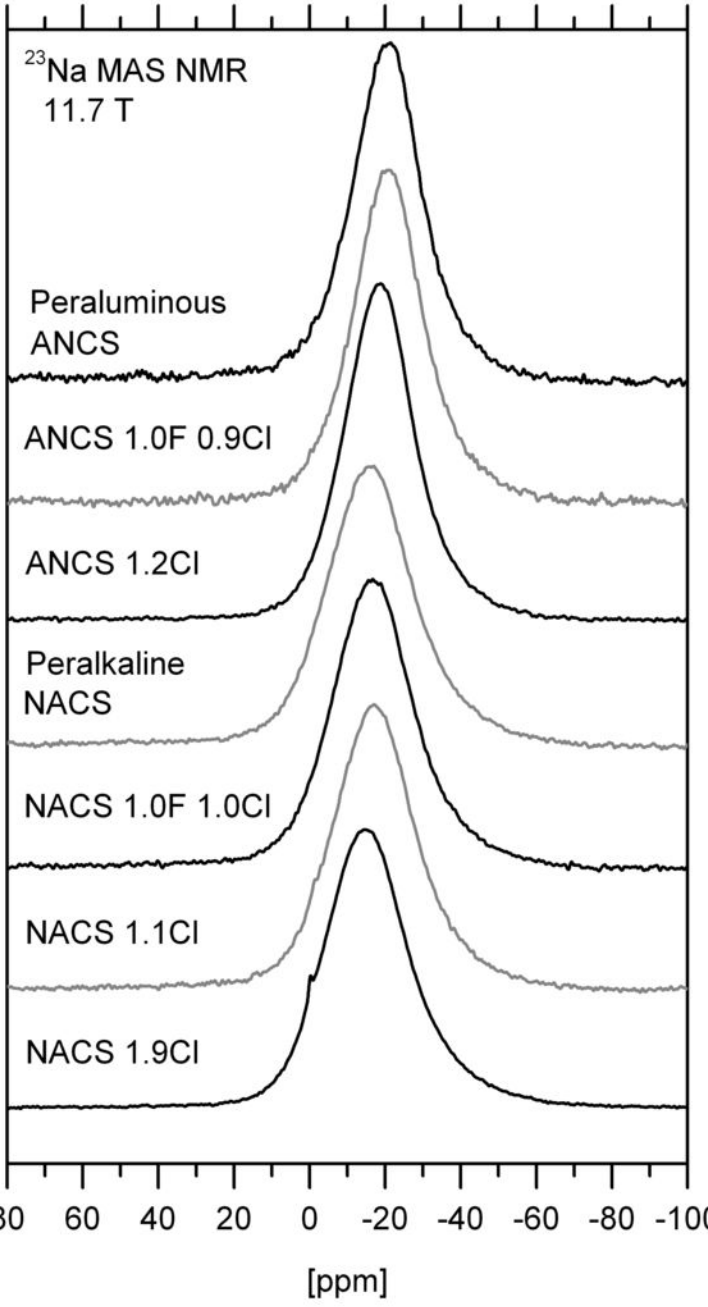

35Cl MAS NMR
14.1 T
ANCS 1.2Cl
NACS 1.9Cl
*
*
*
*
1500
1000
500
0
-500
-1000
-1500
[ppm]

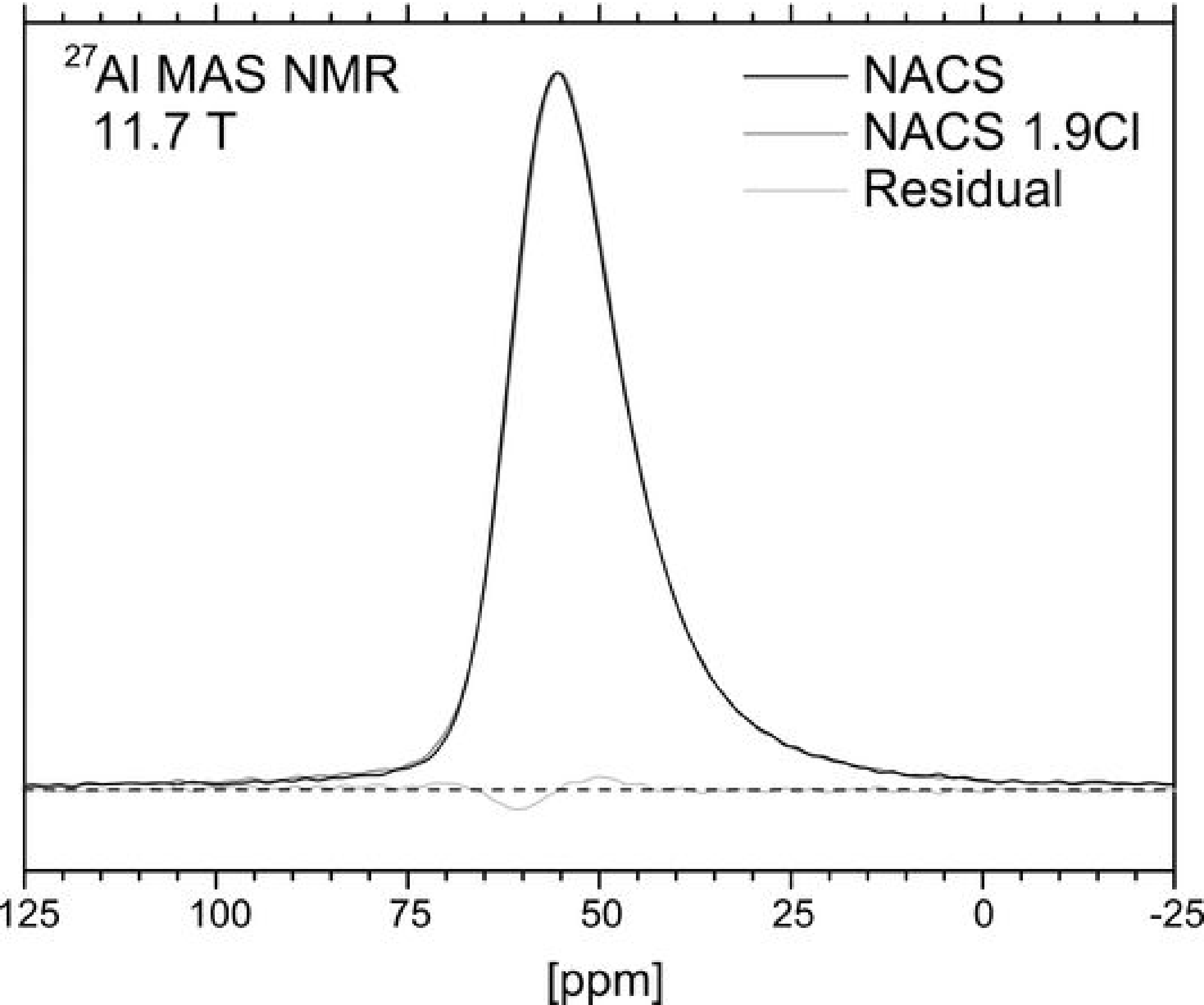

35Cl static NMR
14.1 T
NS 2.2Cl
NACS 1.1Cl
1500
1000
500
0
-500
-1000
-1500
[ppm]

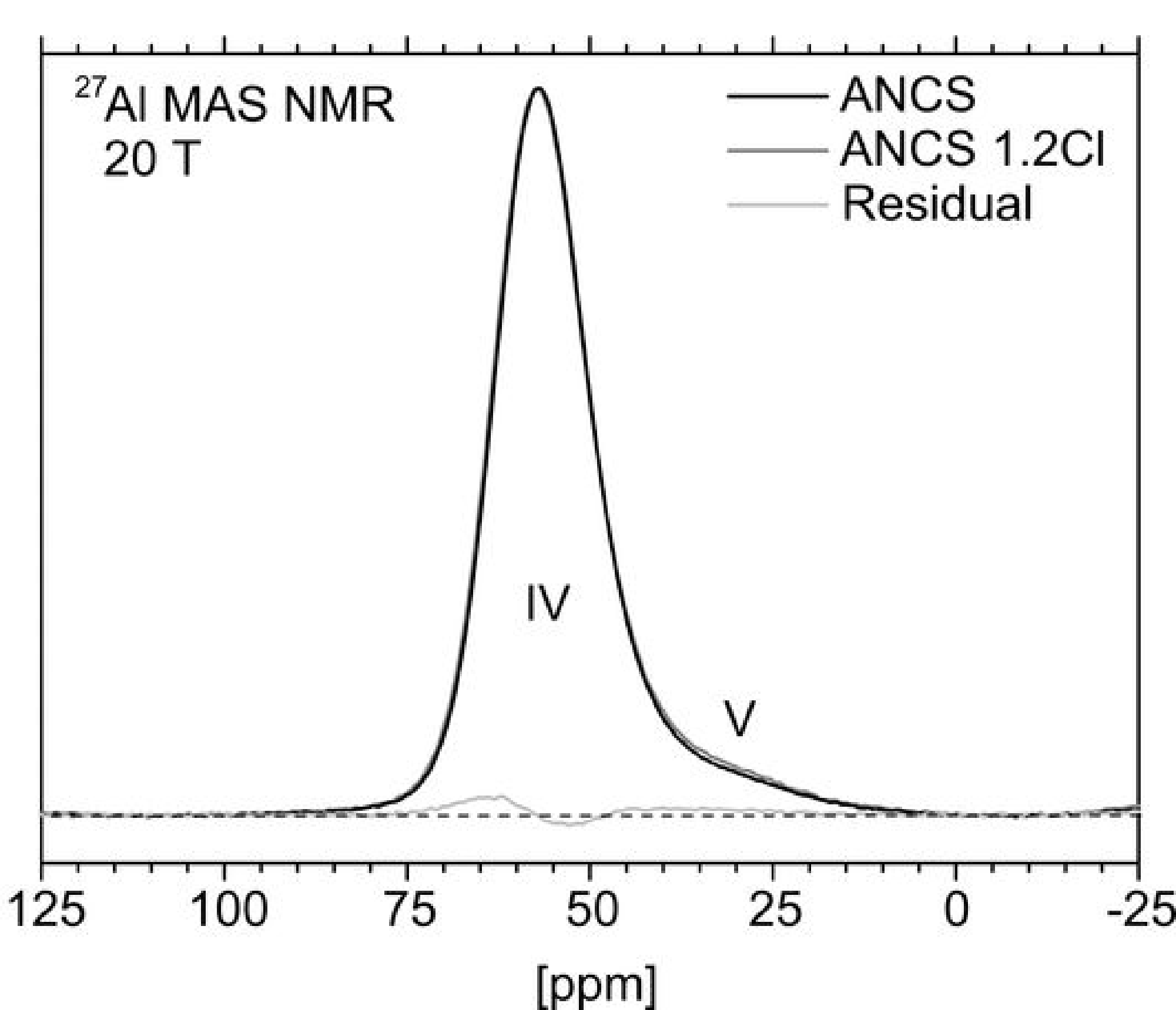

35Cl MAS NMR
ANCS 1.0F 0.9Cl
NACS 1.1Cl
14.1 T
*
*
ANCS 1.2Cl
NACS 1.9Cl
19.6 T
400 300 200 100 0 -100 -200 -300 -400 -500 -600
[ppm]

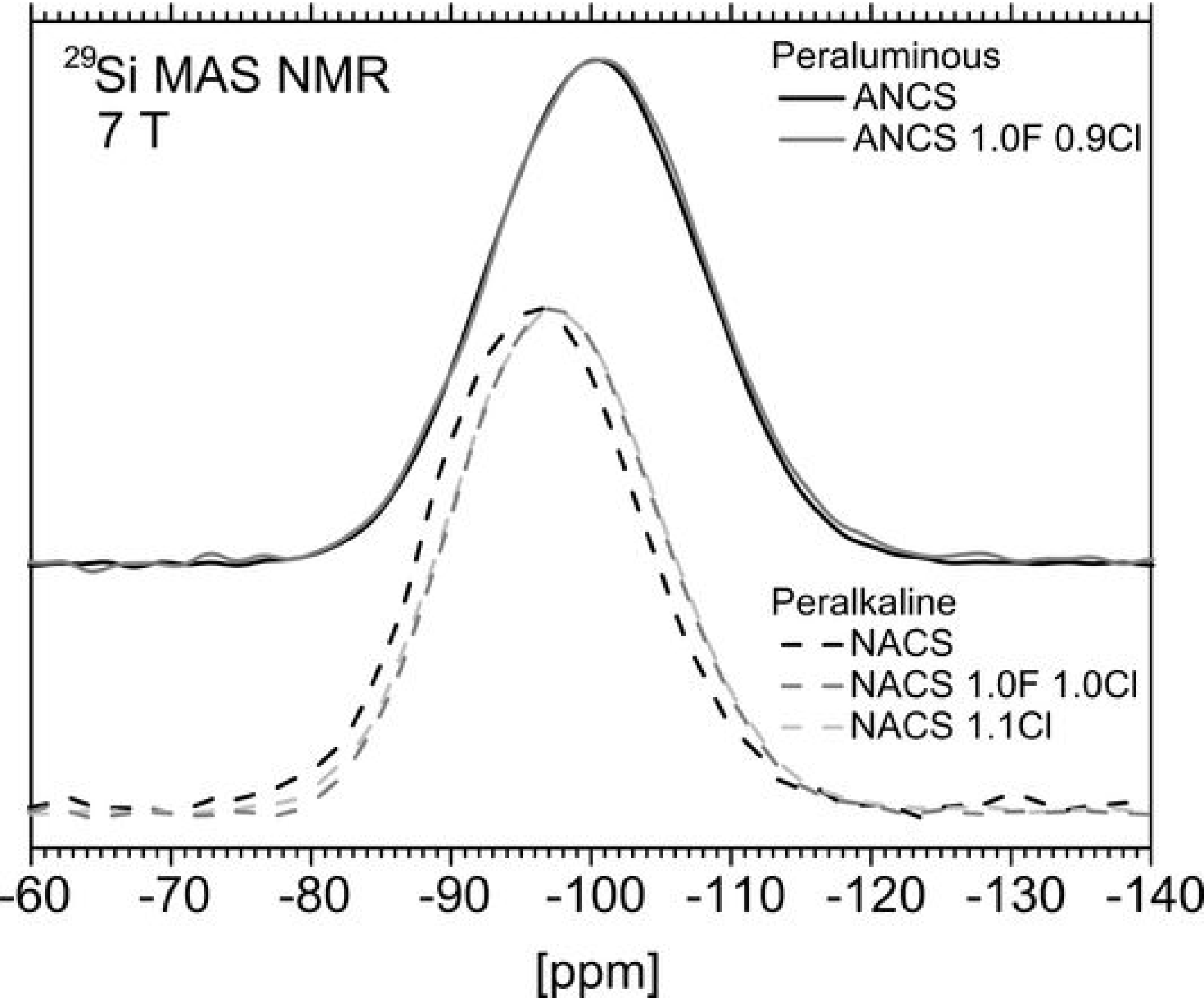

-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
Center of gravity [ppm]
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
v_0^{-2} 10000 [MHz^{-2}]
^{35}Cl
Peraluminous ANCS+Cl
Peralkaline NACS+Cl
Sodium silicate NS+Cl
19.6 T
14.1 T


35Cl MAS NMR
NACS 1.1Cl
19.6 T
14.1 T
*
*
400
300
200
100
0
-100
-200
-300
-400
-500
-600
[ppm]


^{23}Na MAS NMR
11.7 T
Peraluminous
ANCS
ANCS 1.0F 0.9Cl
ANCS 1.2Cl
Peralkaline
NACS
NACS 1.0F 1.0Cl
NACS 1.1Cl
NACS 1.9Cl
80 60 40 20 0 -20 -40 -60 -80 -100
[ppm]


27Al MAS NMR
11.7 T
NACS
NACS 1.9Cl
Residual
125
100
75
50
25
0
-25
[ppm]


^{27}Al MAS NMR
20 T
ANCS
ANCS 1.2Cl
Residual
IV
V
125
100
75
50
25
0
-25
[ppm]


^{29}Si MAS NMR
7 T
Peraluminous
ANCS
ANCS 1.0F 0.9Cl
Peralkaline
NACS
NACS 1.0F 1.0Cl
NACS 1.1Cl
-60
-70
-80
-90
-100
-110
-120
-130
-140
[ppm]