The partial ^1H NMR spectra of Al–OH and molecular H_2O in hydrous aluminosilicate glasses: Component-Resolved analysis of ^{27}Al–^1H cross polarization and ^1H spin-echo MAS NMR spectra

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ABSTRACT

The Component-Resolved methodology was applied to ^1H spin-echo and ^{27}Al–^1H cross polarization (CP) MAS NMR data of aluminosilicate glasses. The method was able to resolve two components with different T_2 relaxation rates, hydroxyl groups (OH) and molecular water (H_2O_{mol}), from the spin-echo data and to determine partial spectra and the relative abundances of OH and H_2O_{mol}. The algorithm resolved two to three components with different ^{27}Al–^1H CP dynamics from the ^{27}Al–^1H cross polarization data; the obtained partial NMR spectra for Al–OH are in excellent agreement with those obtained previously from the difference spectra between spectra with various contact times and confirm previous quantitative results and models for the Al–OH, Si–OH and H_2O_{mol} speciation (Malfait and Xue, 2010).

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1. Introduction

As the most abundant volatile component, water has a strong influence on the type, rate and outcome of most magmatic processes. Because of this importance, the speciation of water in aluminosilicate glasses and melts has been the subject of intense spectroscopic study. As a result, it is now generally accepted that water is present in silicate glasses and melts as molecular water (H_2O_{mol}) and hydroxyl groups (OH); OH is the more abundant species in samples with a low water content, whilst H_2O_{mol} the most abundant species at higher water content [1–4]. However, the nature of the hydroxyl groups in aluminosilicate glasses has long been controversial: dissolution mechanisms in which water depolymerizes the melt through the formation of Si–OH and Al–OH groups, as well as dissolution mechanisms in which water leaves the degree of melt polymerization unchanged, have been proposed [5–11]. Recently, cross polarization (CP) experiments from ^{27}Al and ^{29}Si to ^1H have unambiguously demonstrated the presence of Si–OH and Al–OH groups [10,11], confirming the depolymerization mechanism and some (semi-)quantitative data on the relative abundance of the different types of OH groups (e.g. Si–OH, Al–OH, Mg–OH) has become available [9–17].

In a previous study [11], we determined the partial ^1H NMR spectrum for H_2O_{mol} from spin-echo MAS NMR spectra collected at different echo delays. In addition, we determined the partial ^1H NMR spectrum for Al–OH from ^{27}Al–^1H CP MAS NMR data and used this partial spectrum to quantify the Al–OH content for a set of hydrous glasses along the SiO_2–$NaAlSiO_4$ join from their quantitative ^1H MAS NMR spectra. With this approach, we were able to tightly constrain the relative abundances of Si–OH and Al–OH. The shapes of the partial Al–OH spectra were defined as the difference spectra between ^{27}Al–^1H CP spectra collected at various contact times. However, this approach has been criticized because, in order to properly scale the CP spectra before taking the difference spectra, we had to a priori impose a spectral region (typically the range > 7 ppm) with zero intensity for Al–OH.

Recently, Hedin et al. [18] demonstrated the suitability of the Component-Resolved (CORE) method to extract partial NMR spectra from a CP dataset without a priori assumptions about the shape of these partial spectra. The method is based on simultaneously fitting a set of spectra as linear combinations of the partial spectra associated with a limited number of species. Programs based on this principle have been available for over 3 decades [19] and have been applied to a wide range of spectroscopic methods, including spectrophotometry [20,21], pulsed-gradient spin-echo NMR spectroscopy [22–25] and Raman spectroscopy [26–29].

In the present study, we have applied the CORE methodology to our ^{27}Al–^1H cross polarization and ^1H spin-echo MAS NMR data

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in order to determine the partial ^{1}H NMR spectrum of Al–OH groups and H_2O_{mol} in aluminosilicate glasses, without any a priori assumptions about its lineshape. The results confirm our previously determined partial spectra for H_2O_{mol} and Al–OH and underscore the suitability of combining partial NMR spectra, extracted from cross polarization or spin-echo datasets, with quantitative NMR spectra to determine the relative abundances of species with overlapping partial spectra.

2. Experimental

In this study, we are applying a new fitting strategy to previously published ^{27}Al–^{1}H CP and ^{1}H spin-echo MAS NMR data for variable contact or delay times for a set of well characterized hydrous glasses along the SiO$_2$-NaAlSiO$_4$ join [11]; a full description of the sample synthesis and characterization and NMR methodology can be found there and will only be briefly summarized here. Hydrous glasses (0.5–2 wt% water) were prepared by loading the appropriate amount of deionized water and 100 mg of anhydrous glass into Pt capsules (3 mm outer diameter, ca. 2 cm long). The welded capsules were suspended from a Mo wire in the hot zone of an internally heated pressure vessel and held at 1773 K and 200 MPa for 4 h. The samples were isobarically quenched by dropping the capsules to the cold zone (ca. 333 K) of the pressure vessel (estimated quench rate: 200–500 K/s). The water content of the recovered glasses was determined by quantitative ^{1}H MAS NMR, using adamantane (C$_{10}$H$_{16}$) as a standard (measured under identical conditions); the results and synthesis conditions are listed in Table 1, as well as the estimated glass transition temperature and OH/H$_2$O$_{mol}$ ratio [30,31].

For the quantitative ^{1}H MAS NMR spectra, the DEPTH sequence, which contains three back-to-back pulses ($\pi/2$–π–π) with a phase cycle of 16, was used to minimize spurious resonances from the probe [32]. The remaining background was removed by subtracting the FID for an empty rotor. For the ^{1}H DEPTH experiments, recycle delays of five times the spin lattice relaxation time (T1) were used to ensure full relaxation of the magnetization (8 s < T1 < 66 s, depending on water content) and 16 to 64 scans were averaged for each sample. The ^{1}H spin-echo data were collected with the rotor-synchronized spin-echo pulse sequence ($\pi/2$–τ–π–τ–acquisition, 50 μs < τ < 12.8 ms). The ^{27}Al–^{1}H CP spectra were collected with a low RF field strength for the contact pulses for ^{27}Al (2.8 kHz, unless otherwise noted), yielding a small value for the adiabatic passage parameter and subsequent high sensitivity [15,33]. The power for the proton channel was ramped (by 5.3 kHz) to improve the stability of

the Hartmann-Hahn matching condition and spin-temperature inversion was included in the phase cycle to eliminate the signal from direct polarization. All spectra were collected with a spinning rate of 20 kHz. All spectral and data processing was done in Matlab, using matNMR subroutines for linear prediction, apodization, Fourier transformation and the phasing of the spectra [34] and the lsqnonlin solver from the Matlab Optimization Toolbox for the fitting routines. The algorithms that were written to implement the fitting strategy outlined below are available in the Supplementary Information.

3. Fitting strategy

3.1. General principle

The CORE method is based on simultaneously fitting a set of NMR spectra as linear combinations of the partial spectra associated with a limited number of species and depends on the following assumptions:

- Each NMR spectrum is a linear combination of the partial spectra of a limited number of species; in matrix form, this can be written as

$$A_{ij} = C_{ik} \times \varepsilon_{kj} \qquad (1)$$

where i,j,k are the spectrum index, chemical shift values and species, respectively; A_{ij} is the matrix of CP or spin-echo intensities as a function of chemical shift and contact time or spin-echo delay time C_{ik} is the matrix of the coefficients, related to the spin-echo decay or CP dynamics for each species, and ε_{kj} contains the partial NMR spectrum for each species,

Table 2
Principal Component Analysis.

Sample	Eigenvalues of the covariance matrix					
	PC1	PC2	PC3	PC4	PC5	PC6
	^{1}H spin-echo data					
nas033zH2	97.878	2.037	0.072	0.006	0.005	0.002
	^{27}Al-^{1}H cross polarization data					
nas008zH1c	96.232	3.068	0.535	0.142	0.017	0.005
nas016zH1	96.332	3.552	0.078	0.032	0.005	0.002
nas025zH1	93.168	6.745	0.053	0.022	0.007	0.005
nas033zH1	96.389	3.549	0.048	0.007	0.005	0.003
nas042zH1	97.955	1.995	0.030	0.010	0.007	0.004
nas050zH1b	99.508	0.380	0.042	0.031	0.025	0.015

Table 1
Hydrous glasses: composition, synthesis conditions, glass transition temperature (T_g) and water speciation.

Sample	Anhydrous composition[a]				^{1}H NMR	Synthesis conditions			Literature estimates	
	Na$_2$O (wt%)	Al$_2$O$_3$ (wt%)	SiO$_2$ (wt%)	Al/(Al+Si) (molar ratio)	H$_2$O$_{tot}$ (wt%)	P (MPa)	T$_{melt}$ (K)	t_{melt} (h)	T_g[b] (K)	OH/H$_2$O$_{tot}$[c]
nas008zH1c	4.2	6.9	89.0	0.083	0.93	200	1773	4.5[d]	822	0.82
nas016zH1	8.1	13.3	78.6	0.167	0.79	200	1773	4.0	838	0.84
nas025zH1	11.8	19.4	68.7	0.250	0.93	200	1773	4.0	822	0.81
nas033zH1	15.3	25.2	59.5	0.333	0.62	200	1773	4.0	861	0.88
nas033zH2	15.3	25.2	59.5	0.333	1.97	200	1773	4.0	749	0.61
nas042zH1	18.7	30.7	50.7	0.417	0.84	200	1773	4.5[d]	832	0.82
nas050zH1b	21.8	35.9	42.3	0.500	0.54	200	1773	4.0	874	0.89

[a] Composition as prepared, confirmed by electron microprobe (Malfait and Xue [11]).
[b] Estimated from Morizet et al. [30] for T_g corresponding to the Cp maxima.
[c] Estimated from Ohlhorst et al. [31] for a T_g derived from Morizet et al. [30] and H$_2$O$_{tot}$ from NMR.
[d] Capsules did not drop on first run (4 h), but did drop after a second run of 30 min.