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1 **Revision 1**

2 **^{17}O NMR evidence of Free Ionic clusters $\text{M}^{\text{n}+} \cdot \text{CO}_3^{2-}$ in silicate glasses: Precursors for**
3 **carbonate-silicate liquids immiscibility**

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23 Abstract

24 Carbon dioxide is a ubiquitous component of low-silica melts such as kimberlites or
25 melilitites. It is currently assumed that CO₂ molecules dissolving in low-silica melts as
26 carbonate groups (CO₃²⁻) induce a strong polymerization of the silicate network; however, the
27 exact molecular configuration of this dissolution mechanism is still debated.

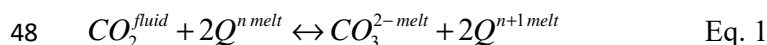
28 Using ¹⁷O MAS NMR spectroscopy, we have investigated the carbonate molecular
29 environment in a series of synthesized low-silica (31-41 wt.% SiO₂), CO₂-bearing (from 2.9
30 to 13.2 wt.% CO₂) silicate glasses analogous to melilitites and kimberlites. With the selective
31 {¹³C}- {²⁷Al}- and {²⁹Si}-¹⁷O J HMQC NMR method, we show that CO₂ dissolved in the
32 studied low-silica glasses is totally disconnected from the silicate network, forming Free Ionic
33 Clusters (FIC) Mⁿ⁺..CO₃²⁻ with Mⁿ⁺ a charge compensating cation.

34 The Mⁿ⁺..CO₃²⁻ FIC are considered as precursors to immiscibility in between carbonate and
35 silicate liquids. Observed in all studied compositions, we suggest that this immiscibility can
36 be produced from moderately to strongly depolymerized silicate melt compositions.

37 INTRODUCTION

38 Providing constraints on the CO₂ dissolution mechanisms in depolymerized silicate melts
39 contributes to our knowledge of kimberlite (Brooker et al. 2011; Russell et al. 2012), melilitite
40 (Keller et al. 2006; Bosshard-Stadlin et al. 2014) and carbonatite genesis (Mitchell 2005),
41 which are CO₂-enriched magmas. Carbonate – silicate liquid immiscibility is thought to be
42 one possible genetic mechanism for these peculiar magmatic systems (Brooker and
43 Kjarsgaard, 2011; Guzmics et al. 2015); however, the exact modalities of this mechanism
44 remain poorly constrained.

45 Early work on CO₂ dissolution in silicate melt (Mysen et al. 1976; Eggler 1978; Mysen and
46 Virgo 1980; Spera and Bergman 1980) suggested that CO₂ plays the role of polymerizing
47 agent of the silicate network structure according to the following reaction:



49 In this reaction, a CO₂ molecule scavenges available oxygen from a Qⁿ (a SiO₄ tetrahedron
50 unit with n bridging oxygen) unit to form a CO₃²⁻ group charge compensated by a network-
51 modifying cation (e.g. Ca²⁺). Raman spectroscopic studies (Mysen et al. 2011; Mysen 2012;
52 Moussallam et al. 2016) suggested that Eq. 1 proceeds to the right upon CO₂ dissolution
53 inducing a change in the proportion of the different oxygen species (i.e. Non-Bridging
54 Oxygen NBO and Bridging Oxygen BO). However, the exact molecular configuration of the
55 CO₃²⁻ groups is not identified. Several dissolution mechanisms have been invoked for CO₂
56 molecules in silicate melts. It has been suggested that CO₂ can form network carbonates (T-
57 CO₃²⁻-T with T = Si or Al) and NBO-CO₃²⁻ where a CO₂ molecule connects to an available
58 NBO of a tetrahedron (Brooker et al. 2001; Guillot and Sator 2011; Morizet et al. 2014). An
59 additional CO₂-dissolution mechanism has been proposed on the basis of molecular dynamic
60 simulations (Xue and Kanzaki 2013; Vuilleumier et al. 2015) and also inferred from Raman
61 spectroscopic studies (Mysen et al. 2011; Mysen 2012; Moussallam et al. 2016). In this
62 mechanism the CO₃²⁻ molecular groups are be present in the silicate network as Free Ionic
63 Clusters Mⁿ⁺..CO₃²⁻ where Mⁿ⁺ is a charge balancing cation (i.e. alkali or alkaline-earth). Each
64 type of CO₂-dissolution mechanism is a strong function of the glass chemical composition
65 (Brooker et al. 2001). For a given chemical composition, the melt physical and chemical
66 properties will be strongly affected by the type of CO₂-dissolution mechanism.

67 In the present work, we show direct proof of the Mⁿ⁺..CO₃²⁻ FIC existence in low-silica
68 depolymerized melts. Based on ¹⁷O MAS NMR spectroscopy, we demonstrate that CO₃²⁻

69 molecular groups in low-silica melt are disconnected from the silicate network. Such a
70 dissolution mechanism represents the precursor of the immiscibility process between a silicate
71 melt and a carbonate melt.

72 EXPERIMENTAL METHOD

73 Several Fe-free glass compositions were investigated via ^{17}O NMR spectroscopy. The studied
74 compositions are depolymerized with SiO_2 content ranging from 30 to 40 wt.% (Table 1) and
75 a Non-Bridging Oxygen concentration per Tetrahedron (NBO/T) ratio of 1.2 to 3.2 calculated
76 from the chemical composition obtained from Electron Probe Micro-Analyses (EPMA, see
77 Table 1 and Supplementary material). Studied compositions are analogous to natural
78 kimberlites (Kjarsgaard et al. 2009) and melilitites (Keller et al. 2006).

79 The starting material was weighed into Pt capsules, which were then sealed by arc-welding.
80 Experiments were performed in piston-cylinder apparatus using $\frac{3}{4}$ inch talc-Pyrex high-
81 pressure assemblies between 0.5 and 1.5 GPa and at 1525°C. Details of the experimental
82 syntheses are provided in the Supplementary material.

83 ANALYTICAL METHOD

84 Major elements and CO_2 concentrations: EPMA and Raman spectroscopy

85 We performed micro-Raman analyses on a Jobin-Yvon LabRam 300 spectrometer equipped
86 with an Innova 300-5W Argon ion laser from Coherent© operating at a wavelength of 514 nm
87 to determine the CO_2 content dissolved in silicate glasses using the protocol proposed by
88 Morizet et al. (2013). A detailed description of the Raman analyses and the CO_2
89 determination from them is provided in Supplementary material.

90 NMR spectroscopy

91 All Solid State ^{17}O NMR were conducted on a Bruker 850 MHz Avance III Wide Bore
92 spectrometer operating at a frequency of 115.3 MHz and referenced against liquid H_2O at 0
93 ppm. The ^{17}O spectra were acquired using Full Hahn-echo and $\{^{27}\text{Al}, ^{13}\text{C}, ^{29}\text{Si}\}$ J-HMQC
94 (Heteronuclear Multiple-Quantum Correlation) pulse sequences (Amoureux et al. 2007;
95 Keeler 2010). The details of the analytical conditions are given in the Supplementary material.
96 The J-HMQC experiment uses the so-called scalar coupling (“J”) which arises from the
97 electrons involved in the bond between two nuclei and allows the creation of Heteronuclear
98 Multiple-Quantum Coherences. In an $\{X\}$ - ^{17}O J-HMQC experiment where oxygen is the
99 observed nuclei and X the indirect one, the resulting ^{17}O spectrum displays only the oxygen
100 environments that are chemically bound to X.

101 RESULTS AND DISCUSSION

102 The ^{17}O MAS and $\{X\}$ - ^{17}O J-HMQC NMR spectra are shown in Figure 1 for several samples:
103 XE-2 (Figure 1A), HK-1 (Figure 1B), HK-M (Figure 1C) and RB8E-12 (Figure 1D). Several
104 oxygen environments are witnessed in the ^{17}O MAS NMR spectra: $\sim+50$ ppm assigned to ^{17}O
105 nuclei in BO configuration associated with Si or Al tetrahedra; $\sim+100$ ppm assigned to ^{17}O
106 nuclei in NBO configuration (Stebbins et al. 1999; Lee and Stebbins 2003; Kelsey et al. 2008)
107 and $\sim+160$ ppm assigned to ^{17}O nuclei in CO_3^{2-} environments (Morizet et al. 2017). The peak
108 at $\sim+100$ ppm is less apparent in Mg-bearing compositions (HK and XE) whereas it is
109 prominent in Mg-free Ca-rich RB8E composition consistent with the peak assignment to Ca^{2+}
110 NBO (Thompson and Stebbins 2011). The presence of Mg^{2+} surrounded by oxygen atoms
111 units is proposed at $\sim+50$ -70 ppm (Allwardt and Stebbins 2004) but not clearly visible here
112 due to strong overlap with the BO-(Si,Al) signal at $\sim+50$ ppm.
113 The selective heteronuclear $\{X\}$ - ^{17}O J-HMQC NMR pulse sequence probes local
114 environments of oxygen atoms bound to X atoms. Hence, it should be pointed out that

115 chemical bonds involving nuclei other than the considered one (X) will not contribute to the
116 ^{17}O NMR signal in the $\{\text{X}\}$ - ^{17}O J-HMQC spectrum. Serendipitously, the $\{^{13}\text{C}\}$ - ^{17}O J-HMQC
117 spectra show a single line located at $\sim+160$ ppm confirming that this peak is associated with
118 CO_3^{2-} molecular groups. More importantly, the absence of signal at $\sim+50$ or $+100$ ppm
119 indicates that the CO_3^{2-} is connected neither to an available NBO nor to a BO. This is also
120 confirmed by the $\{^{29}\text{Si}\}$ - ^{17}O J-HMQC spectra, which do not exhibit a signal at $+160$ ppm but
121 only at $+50$ and $+100$ ppm; this is consistent with ^{17}O atoms in BO and NBO configuration,
122 respectively. The absence of common ^{17}O signals in the $\{^{29}\text{Si}\}$ - ^{17}O J-HMQC and $\{^{13}\text{C}\}$ - ^{17}O J-
123 HMQC spectra shows that there is no oxygen atom simultaneously bound to silicon and
124 carbon atoms (within the detection level of $\sim 5\%$) thereby precluding the existence of T- CO_3^{2-} -
125 T and NBO- CO_3^{2-} carbonate units. This CO_2 -dissolution mechanism has been proposed on the
126 basis of FTIR results (Brooker et al. 2001), inferred from Molecular Dynamic simulations
127 (Vuilleumier et al. 2015) and indirectly suggested from the change in the network structure
128 upon CO_2 -dissolution (Mysen et al. 2011; Mysen 2012; Moussallam et al. 2016). Our results
129 are consistent with the MD results from Vuilleumier et al. (2015) suggesting that FIC
130 represents 75% of the dissolved CO_3^{2-} molecular groups and 25% corresponding to network
131 carbonate units (T- CO_3^{2-} -T with T = Si or Al; Brooker et al. 2001). In the FIC $\text{M}^{n+} \cdot \text{CO}_3^{2-}$,
132 M^{n+} is a charge balancing cation which can be Mg^{2+} , Ca^{2+} and Na^+ to a lower extent (Na_2O is
133 ~ 5 wt.%) for the currently investigated compositions. Although, Morizet et al. (2017) showed
134 that CO_3^{2-} groups dissolve preferentially in the vicinity of Ca^{2+} cations, we do not exclude the
135 possibility for $\text{Mg}^{2+} \cdot \text{CO}_3^{2-}$ being formed considering that Mg^{2+} could play a role comparable
136 to Ca^{2+} (Cormier and Cuello 2013).

137 At this point, we wish to raise the level of confidence in the above discussion. Indeed, one
138 could argue that the ^{17}O signal from Si-O-C linkages could be absent from the $\{^{29}\text{Si}\}$ - ^{17}O J-
139 HMQC spectrum if the associated $J(^{29}\text{Si}-^{17}\text{O})$ coupling value strongly differs from those

140 occurring for ^{29}Si - $^{17}\text{O}(\text{BO})$ or ^{29}Si - $^{17}\text{O}(\text{NBO})$ linkages. A simple way to rule out this
141 possibility is to show that the full ^{17}O spectrum can be totally reconstructed as the sum of the
142 3 selective $\{\text{X}\}$ - ^{17}O J-HMQC spectra. The reconstructions of the ^{17}O MAS NMR spectra from
143 the deconvolution of the $\{\text{X}\}$ - ^{17}O J-HMQC spectra are shown in Figure 2 for three ^{17}O MAS
144 NMR spectra: Mg-free RB8E-12 (Figure 2A) and Mg-bearing XE-2 and HK-1 (Figure 2B and
145 C). The deconvolution procedure was conducted as follows: each $\{\text{X}\}$ - ^{17}O J-HMQC NMR
146 spectrum was fitted with Gaussian lines; one line for the $\{^{13}\text{C}\}$ - ^{17}O J-HMQC, one line for the
147 $\{^{27}\text{Al}\}$ - ^{17}O J-HMQC and two lines for the $\{^{29}\text{Si}\}$ - ^{17}O J-HMQC corresponding to the BO-Si
148 and NBO-Si environments, respectively. The parameters obtained are reported in Table 1.
149 Since the $\{^{27}\text{Al}\}$ - ^{17}O J-HMQC spectrum was not acquired for all the samples due to the
150 requirement of very long acquisition times, we used the δ_{iso} and FWHM from the XE-2
151 deconvolution for HK spectra; and the average δ_{iso} and FWHM obtained from RB8E-12 and
152 RB8E-13 for RB8E-7 spectrum. In Figure 2A, we show that the performed deconvolution
153 adequately reproduces the ^{17}O MAS NMR spectrum for the Mg-free RB8E-12 sample. The
154 high carbon content of this sample excludes the possibility of a lack of ^{17}O signal of
155 significant intensity in the $\{^{29}\text{Si}\}$ - ^{17}O J-HMQC spectrum. For Mg-bearing compositions, the
156 ^{17}O MAS NMR spectra are not perfectly reproduced by the deconvolution. Regardless of the
157 glass composition (XE-2 and HK), the residuals of the simulation exhibit a signal located at
158 $\sim +70$ ppm not accounted for. Considering that this residual NMR signal is only observed in
159 Mg-bearing glass composition, the signal could be attributed to oxygen atoms in MgO_x
160 configuration. This assignment would be consistent with the results of Hung et al. (2016)
161 which identified ^{17}O resonance for MgO_x oxygens in Ca/Mg orthosilicate glasses at +60 ppm.
162 Considering that the NMR signal of the CO_3^{2-} environments is reproduced adequately by a
163 single line at $\sim +160$ ppm, the majority of the CO_3^{2-} groups are FIC in the investigated glass
164 compositions.

165 IMPLICATION FOR CARBONATE – SILICATE LIQUID IMMISCIBILITY

166 Numerous implications arise from the present results; however we only focus on two of them:
167 1) the immiscibility between carbonate and silicate liquids and 2) the impact of FIC on the
168 carbonated melt transport properties. It is reasonable to consider that the $M^{n+}..CO_3^{2-}$ FIC
169 constitutes a carbonate subnetwork intimately mixed within a silicate subnetwork. For
170 instance, Kubicki and Stolper (1995) showed that the molecular energy involved for ion pairs
171 complexes (similar to FIC $M^{n+}..CO_3^{2-}$) is low as compared to any other type of carbonates
172 dissolved in silicate melt. Therefore, the energy barrier to dissociate the carbonate subnetwork
173 from the silicate subnetwork is lower in the case of FIC.

174 Network-modifying cations have varying coordination numbers in a silicate melt (e.g. 5 to 8
175 for Ca^{2+} ; Cormier and Cuello 2013). Upon CO_2 dissolution, the network-modifying cation
176 will share less of its positive charges to the silicate network in order to compensate the
177 negative charges of the CO_3^{2-} groups; resulting in a network-modifying cation that is less
178 connected to the silicate network. In particular, Vuilleumier et al. (2014) showed that the Ca-
179 O distance in molten $CaCO_3$ is on average 2.35 Å, suggesting that Ca^{2+} is more closely
180 connected to the carbonate subnetwork than to the silicate subnetwork. Consequently, we
181 believe that the presence of FIC $M^{n+}..CO_3^{2-}$ could be viewed as a possible precursor to
182 immiscibility. For instance, removal of the carbonate network from the silicate network is a
183 proposed mechanism to form calciocarbonatite from a melilitite parental melt (Guzmics et al.
184 2015).

185 We suggest that this immiscibility could also proceed from kimberlite owing to the fact that
186 FIC groups are observed in the investigated HK composition analogous to kimberlite melt.
187 However, the molecular configuration $M^{n+}..CO_3^{2-}$ FIC poses the problem of the way CO_2
188 degasses from depolymerized silicate melts. The CO_2 migration into the fluid phase imposes a

189 molecular structure reconfiguration to dissociate the $M^{n+}..CO_3^{2-}$ groups and causes the
190 network-modifying cation to remain in the silicate melt, thus depolymerizing the silicate
191 network structure. This difficulty could explain the absence of degassing in kimberlitic melt
192 upon decompression as witnessed by Moussallam et al. (2015).

193 Finally, it turns out that the identified CO_2 -dissolution mechanism can also affect the physical
194 properties of carbonated melts (e.g. magma transport and electrical conductivity).

195 Interconnection between FIC molecular groups could explain the high electrical conductivity
196 observed in CO_2 -bearing silicate melt (Sifré et al. 2014). There is an intimate mixture between
197 a carbonate subnetwork having an extremely low viscosity and a silicate subnetwork with a
198 higher viscosity (Morizet et al. *in press*). Through immiscibility, the carbonate liquid will
199 migrate towards the surface due to its low viscosity and density (Vuilleumier et al. 2014),
200 whereas the silicate liquid, which becomes enriched in SiO_2 , is stalled at depth due to the
201 increased viscosity (Giordano et al. 2008). Therefore, the direct proof of the existence of FIC
202 gives legitimacy to the development and application of the immiscibility theory in a wide
203 range of processes taking place in the Earth's interior.

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210

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318 **Figure caption:**

319 Figure 1. ¹⁷O MAS and {¹³C}- {²⁷Al}- {²⁹Si}-¹⁷O J-HMQC NMR spectra of CO₂-
320 bearing silicate glasses: XE-2 (A), HK-1 (B), HK-M (C) and RB8E-12 (D). Three oxygen
321 environments are identified with MAS spectra: FIC Mⁿ⁺..CO₃²⁻, Ca²⁺ NBO-Si and BO-(Si,Al).
322 The NMR spectra for the other synthesized glasses can be found in Supplementary material.

323 Figure 2. ^{17}O MAS spectrum deconvolution obtained from Gaussian lines derived
324 from {X}- ^{17}O J-HMQC spectra. The deconvolution of the ^{17}O NMR spectra for the other
325 synthesized glasses can be found in Supplementary material.

Revision 1

Table 1: Experimental conditions, chemical compositions of the investigated synthetic Fe-free silicate glasses.

Sample	HK-1	HK-2	HK-M	RB8E-7	RB8E-12	RB8E-13	XE-2	Natural Kimberlite [§]	Natural Melilitite [§]
Pressure (GPa)	1.5	0.5	1.5	0.5	1.0	1.0	1.5		
Glass chemical composition in wt.%									
SiO ₂	40.2	40.1	31.8	33.3	30.3	30.1	40.6	30.4	36.5
Al ₂ O ₃	4.3	4.4	3.5	8.7	8.1	8.6	14.8	2.3	7.7
MgO	21.9	21.3	21.9	0.0	0.1	0.2	12.6	29.7	11.8
CaO	22.0	22.3	22.0	41.8	39.8	36.0	17.8	9.6	14.2
Na ₂ O	4.5	4.5	3.5	5.7	4.8	5.0	4.8	0.1	4.3
CO ₂ [*]	7.1	2.9	13.2	6.5	12.6	7.7	4.2	6.40	0.52
H ₂ O [†]	0.8	1.0	1.3	0.7	1.5	1.3	1.0	7.10	1.06
NBO/T from stoichiometry [‡]	2.6	2.5	3.2	2.1	2.2	1.9	1.2	3.60	1.66
NMR parameters									
Free Ca ²⁺ ..CO ₃ ²⁻									
δ _{iso}	154.2	157.3	155.7	164.9	164.6	166.0	157.8		
FWHM	42.0	41.3	44.2	34.7	30.7	33.6	45.3		
BO-Si									
δ _{iso}	54.4	57.4	55.2	61.0	51.6	53.4	48.7		
FWHM	24.4	29.3	24.3	23.3	24.3	22.3	25.5		
BO-Al									
δ _{iso}	42.5	42.5	42.5	47.8	45.5	47.5	42.5		
FWHM	25.8	25.8	25.8	25.6	25.7	25.5	25.8		
NBO-Si									
δ _{iso}	95.9	96.7	96.0	106.5	106.8	106.2	99.3		
FWHM	31.4	33.1	23.7	24.6	25.2	24.0	47.1		

^{*} The glass CO₂ content has been determined using Raman spectroscopy and the method described in Morizet et al. (2013). With the derived CO₃/HF ratio obtained from the deconvolution of the Raman spectra (see Supplementary material), it is possible to determine the CO₂ content using the linear relationship wt.% CO₂ = 13.5 x CO₃/HF. The typical error on the CO₂ content using Raman method is 10% in relative to the value.

[†] The H₂O content was determined by FTIR spectroscopy on a doubly polished glass plate. Contribution for OH⁻ and H₂O^{mol} vibrational peaks at 4500 and 5200 cm⁻¹ were summed to obtain the H₂O^{tot}. The error does not exceed ±0.2 wt.% H₂O and corresponds to the standard deviation obtained on the replicated measurements.

[‡] The NBO/T describing the average polymerization was calculated on a stoichiometric basis using the chemical composition measured by EPMA.

[§] An average typical natural composition of kimberlite and melilitite were obtained from Kjarsgaard et al. (2009) and Keller et al. (2006), respectively. Additional oxides (TiO₂, FeO and K₂O for the most important) have not been reported but are nominally present: ~0.4 wt.% for TiO₂, ~10.0 wt.% FeO and ~2.0 for K₂O.

Figure 1

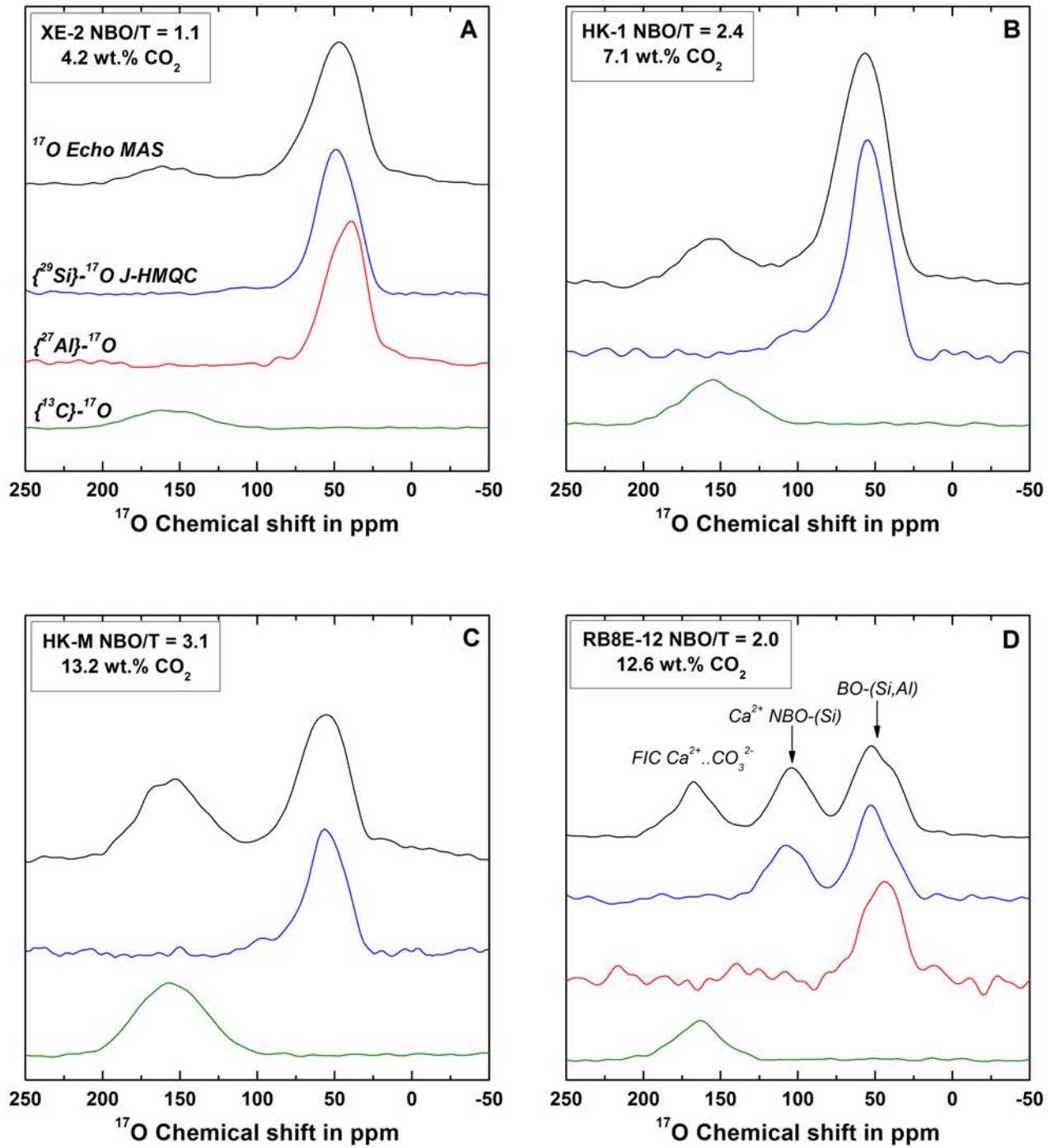


Figure 2

