

The characterization of boron sites in the glass structure of a calc-alkaline magma (Capraia Island, Italy)

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ABSTRACT. — A glass from a rhyolite belonging to the calc-alkaline magmatism of the island of Capraia, in the Neogene-Quaternary Tuscan Magmatic Province of Central Italy, has been examined by ¹¹B solid-state nuclear magnetic resonance spectroscopy, secondary electron imaging for surface morphology and electron microprobe analysis for glass chemistry. The glass is chemically homogeneous and does not show evidence of significant alteration processes, with a boron content of 126 ppm. The deconvolution of the ¹¹B MAS NMR spectrum reveals the occurrence of boron in both tetrahedral BO_{4/2}⁻ and trigonal BO_{3/2} structural units in which all the oxygens are bridging, even if, according to the glass chemistry and following the “aluminum priority model”, all the available charge balancing cations would be requested to form tetrahedrally coordinated aluminum. A possible explanation involves the role of residual H⁺ ions in the glass/melt which could behave as charge balancing cations for B in tetrahedral coordination or the occurrence of Al “triclusters” in the glass, making alkali ions available to charge balance. The lack of a significant amount of boron in trigonal BO_{2,2}O⁻ sites, characterized by non-bridging oxygen, might be interpreted as evidence of copolymerization of the boron structural units with

the glass network, occurring when boron is at trace element concentration such as in natural magmas of this composition.

RIASSUNTO. — Sono stati eseguiti spettri di risonanza magnetica nucleare con rotazione ad angolo magico relativi all'isotopo ¹¹B (¹¹B MAS NMR) su un campione di vetro relativo all'attività calco-alkalina all'isola di Capraia, appartenente alla magmatismo Neogenico-Quaternario che caratterizza l'Italia centrale. In aggiunta, sullo stesso campione di vetro sono state eseguite analisi chimiche tramite microsonda elettronica e immagini di superficie tramite microscopia elettronica, che mostrano una omogeneità chimica del vetro ed assenza di significativi effetti di alterazione.

La deconvoluzione degli spettri ¹¹B MAS NMR rivela la presenza di boro sia in coordinazione tetraedrica in strutture BO_{4/2}⁻ che trigonale in unità BO_{3/2}, nelle quali tutti gli ossigeni sono condivisi da strutture adiacenti. Una possibile spiegazione prevede il ruolo di ioni H⁺ nel bilanciamento delle cariche per il B in coordinazione tetraedrica. Gli spettri indicano l'assenza di boro in siti trigonali BO_{2,2}O⁻, e ciò potrebbe essere interpretato come una evidenza della co-polimerizzazione delle unità strutturali contenenti

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B all'interno della struttura del vetro nei casi in cui questo elemento sia presente a livello di elemento in traccia come nei magmi studiati.

KEY WORDS: ^{11}B NMR spectroscopy, boron speciation, silicate glasses, Capraia Island volcanites.

INTRODUCTION

Boron-containing silicate glasses are among the glassy systems that received much attention due to the large number of applications in ceramic technology and glass industry. Furthermore, the geochemistry of boron is frequently applied to Earth Sciences, in the study of the crust-mantle dynamics and in the sedimentary cycle (Leeman and Sisson, 1996).

One of the main characteristics of B-bearing systems in nature is that boron is associated to either hydrous magmas or aqueous fluid phases, as extensively addressed by Romano *et al.* (1995).

With the exception of three fluorides, the boron minerals are oxygen compounds in which boron is linked to oxygen or hydroxyl groups either trigonally ($\text{B}^{[3]}$) or tetrahedrally ($\text{B}^{[4]}$) (Hawthorne *et al.*, 1996), and the same should be expected to occur in B-bearing aluminosilicate melts. As the melt is rapidly cooled through the glass transition temperature (T_g), the liquid freezes into a set of configurations and becomes a mechanically rigid glass. The speciation of B in an Al-silicate glass has been described in terms of $\text{BO}_{4/2}^-$ tetrahedra and $\text{BO}_{3/2}$ planar triangles in which all the oxygens are bridging, and $\text{BO}_{2/2}\text{O}^-$ three-coordinated boron species containing non bridging oxygens.

The question of the B speciation in natural melts/glasses is of particular interest for the understanding of a number of petrological processes, including the mineral/melt B partitioning and the effects on isotope-fractionation (Tonarini *et al.*, 2003).

In the study of boron speciation in synthetic glasses, ^{11}B magic-angle spinning (MAS) nuclear magnetic resonance (NMR) resulted particularly useful, yielding structured line-shapes which allow to distinguish the relative contribution of trigonal and tetrahedral boron units.

In the present study, ^{11}B MAS NMR spectroscopy was applied to a rhyolite glass from

the calc-alkaline magmatism of Capraia Island, characterized by a relatively high boron content, as most of the products of the Neogene-Quaternary magmatism in Central Italy.

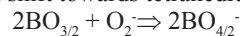
BORON SPECIATION IN ALUMINOSILICATE MELTS

In alkali silicate melts containing both boron and aluminum, the latter two cations appear to be in competition for the available alkali cations to stabilize their tetrahedral coordination within the silicate network. In the "aluminum priority model" it is postulated that the formation of tetrahedrally coordinated boron species is limited by the amount of charge-balancing alkali cations still available after subtracting that requested to form tetrahedrally coordinated aluminum sites.

The occurrence of predominately trigonally-coordinated boron in dry and anhydrous $\text{NaAlSi}_3\text{O}_8$ glasses at ambient pressure after the addition of variable amount of B_2O_3 was reported by Schmidt *et al.* (2004).

Raman spectroscopic studies by Konijnendijk and Stevels (1976) have shown that the progressive addition of Al_2O_3 to $\text{M}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$ glasses (where $\text{M}=\text{Na}$ or K) leads to a gradual disappearance of tetrahedral boron units accompanied by the formation of trigonal boron. Geisinger *et al.* (1988) have shown an increase in the proportion of $\text{B}^{[3]}$ from 29% to 60% from the pure borosilicate endmember melt (NaBSi_3O_8) to the corresponding aluminosilicate ($\text{NaAlSi}_3\text{O}_8$).

In the study on glasses in the ternary system $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{B}_2\text{O}_3$, Züchner *et al.* (1998) evidenced a shift towards tetrahedral boron in the reaction



with increasing Na content. This follows what was obtained by Youngman and Zwanziger (1995) and Zhong and Bray (1989) in the study of rubidium borate glasses and Youngman and Zwanziger (1996) in the study on potassium borate glasses.

These experiments indicate that the presence of aluminum destabilizes boron in tetrahedral coordination; nevertheless, even in sodium aluminoborate glasses with molar $\text{Al}/\text{Na} > 1$ moderate amounts of $\text{B}^{[4]}$ are evident from ^{11}B NMR spectra (Züchner *et al.*, 1998).

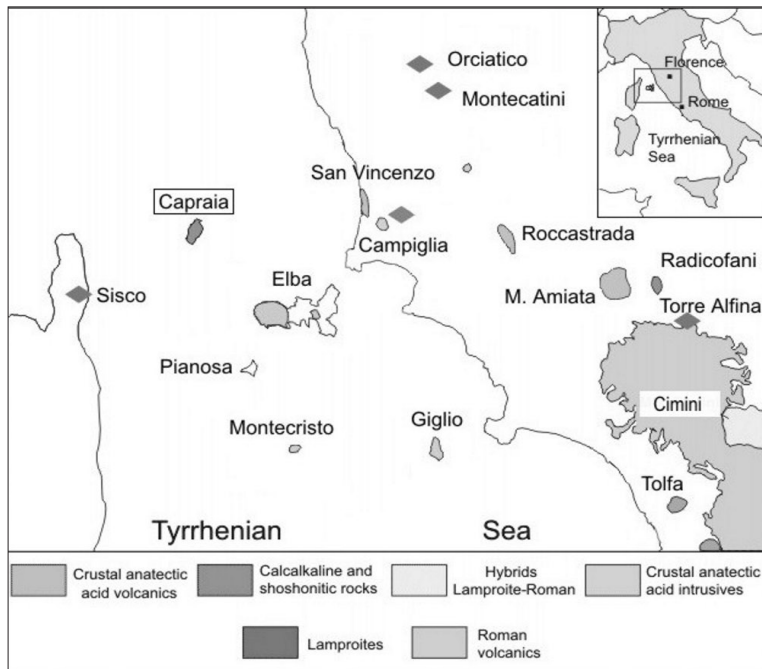


Fig. 1 – Location of the Capraia Island among the igneous rocks of the Tuscan and North-Western Roman Magmatic Province.

The question whether BO_3 planar triangles and BO_4 tetrahedra can link either together or with the SiO_4 and AlO_4 tetrahedra in the structure of silicate glasses is still open. Geisinger *et al.* (1988), in a study on binary alkali borate glasses along the join NaAlSiO_8 - NaBSi_3O_8 , interpreted NMR data as excluding the presence of $\text{Si-O-B}^{[3]}$, $\text{Si-O-B}^{[4]}$ and $\text{B}^{[3]}-\text{O}-\text{B}^{[4]}$ linkages, thus strengthening the hypothesis that boron acts as a network-modifier cation. On the other hand, Martens and Müller-Warmuth (2000) interpreted ^{11}B NMR spectra in binary and ternary sodium borosilicate glasses as an indication of random co-polymerization of $\text{SiO}_{4/2}$ with trigonal and tetrahedral boron structural units.

According to Züchner *et al.* (1998) a preferential conversion of $\text{BO}_{3/2}$ to $\text{BO}_{2/2}\text{O}^-$ occurs above a threshold of alkali content. This was confirmed by Youngman and Zwanziger (1996) and Zhong and Bray (1989), who observed the decrease of the fraction of tetrahedrally-coordinated boron above a threshold of potassium concentration and formation of non-bridging oxygen.

According to Schmidt *et al.* (2004) and Schmidt (2004) the presence of water strongly increases the fraction of $\text{B}^{[4]}$ in albite glass, and the increase in the fraction of tetrahedrally-coordinated boron in anhydrous glasses at high pressure was reported by Schmidt *et al.* (2004). However, the effects of the complex compositions of natural glasses where boron is at ppm levels have been investigated.

OUTLINE OF THE MAGMATISM AT CAPRAIA ISLAND

The volcanic rocks of Capraia Island, in the northern Tyrrhenian Sea (Fig. 1), belong to the Tuscan Magmatic Province (Marinelli, 1967), characterized by a variety of intrusive and extrusive crustal and mantle-derived magmas (Innocenti *et al.*, 1992) associated with the extensional phases which occurred after the Miocene compressional regime related to the sardinia-corsica rotation and Apennine orogenesis (Keller and Pialli, 1990). The development of fractures allowed the magma uprising and the overlapping of lava flows and

pyroclastic activity which characterize Capraia, with rocks having high-K calc-alkaline affinity. K-Ar dating allowed to distinguish two main cycles of volcanic activity, with emission of rocks ranging in composition from high-K andesites to dacites and rhyolites (Poli and Perugini, 2003) between 7.25 Ma and 7.59 Ma in the eastern and central areas, and the emplacement of shoshonites in the southern sector of the Island at about 4.5 Ma (Aldighieri *et al.*, 1998). The studied glass was separated from a rhyolitic lava flow (Cava dello Zurlotto Unit) belonging to the first volcanic cycle which outcrops in the eastern coast of the Island, characterized by a glassy texture with phenocrysts of K-feldspar, amphibole, clinopyroxene, biotite, Fe-Ti oxides and apatite.

EXPERIMENTAL PROCEDURES

The sampled rhyolite flow was crushed and quartered, and the glass separated from the host rock by a Frantz Isodynamic magnetic separator and careful hand-picking under a binocular. Only the most optically clean fragments were selected. The amorphous character of the glasses was ascertained by the lack of any sharp peak during X-ray powder diffraction (XRD) analyses (Siemens diffractometer, $\text{CuK}\alpha$ line).

Secondary electron imaging (SE-SEM) was obtained using a LEICA STEREOSCAN 430i.

The major and minor element composition of the glass was determined by electron microprobe using both wavelength and energy dispersion techniques (WDS-EDS) with a CAMECA SX50 running with an accelerating voltage of 15 KV, a beam current of 15 nA, a counting time of 100 s and a defocused beam size of 10 μm . For major and minor elements, analytical uncertainties are within 1% and 10%, respectively.

^{11}B MAS NMR experiments were performed using a Bruker AMX300WB spectrometer working at a resonance frequency of 96.3 MHz for ^{11}B , equipped with a CPMAS probe using 4 mm rotors. The spinning speed was 8 kHz, the pulse length used was 1.5 μsec corresponding to a 15 degree pulse, the recycle delay was 4 s and 12000 scans were acquired. Chemical shifts are referred to an external $\text{BF}_3\text{Et}_2\text{O}$ standard. The NMR spectrum

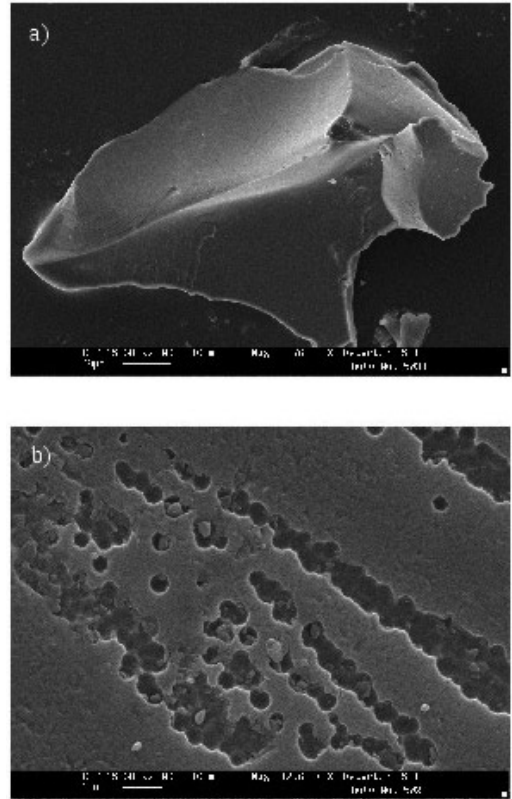


Fig. 2 – Back-scattered scanning electron photomicrographs showing the dense nature of the rhyolite glass (a) and the rare evidence of pitted surfaces and corroded morphology (b).

was fitted with a home-made software using a non-linear least-squares fitting routine.

RESULTS

SE-SEM imaging shows that the sample is characterized by dense glass (Fig. 2a). Most of the glass does not show any evidence of surface alteration; pitted and corroded surfaces (Fig. 2b) with less than 1 μm holes are rare.

Major and minor element microprobe analyses for different glass fragments are given in Table 1; the data indicate that the glass is chemically quite homogeneous. The boron content, measured

TABLE 1
Chemical composition of glass fragments from the Capraia rhyolite flow

sample	# 1	# 2	# 3	# 4	# 5	# 6	# 7	# 8	# 9	# 10	# 11	# 12	# 13	# 14	# 15	# 16	# 17
SiO ₂	72.65	73.09	73.38	73.12	72.96	72.84	73.45	73.22	72.54	73.17	72.27	72.91	73.43	73.57	72.67	72.41	72.98
TiO ₂	0.18	0.15	0.07	0.17	0.06	0.07	0.11	0.10	0.07	n.d.	n.d.	0.14	0.13	n.d.	0.24	0.18	0.13
Al ₂ O ₃	12.97	13.12	12.84	12.99	13.11	13.16	13.01	13.13	12.91	13.15	12.70	12.84	13.09	12.97	12.97	12.93	12.99
FeO	1.02	0.95	0.76	0.72	0.79	0.85	0.73	0.80	0.95	0.75	0.68	1.14	0.70	0.83	1.16	1.01	0.86
MgO	0.12	0.22	0.10	0.13	0.19	0.18	0.12	0.12	0.09	0.12	0.09	0.21	0.06	0.19	0.17	n.d.	0.14
CaO	1.02	1.01	0.98	1.07	1.01	1.01	0.96	0.97	0.95	1.01	1.03	0.96	0.98	1.11	1.02	1.05	1.01
K ₂ O	4.82	4.73	4.83	4.94	4.74	4.61	4.74	4.75	4.87	4.72	4.93	4.81	4.71	4.70	4.80	4.79	4.78
Na ₂ O	3.01	3.06	3.08	3.01	3.14	3.09	3.03	3.13	3.11	3.11	3.08	3.06	3.01	2.07	3.05	3.08	3.01
Total	95.87	96.54	96.18	96.18	96.05	95.92	96.34	96.33	95.50	96.16	94.95	96.27	96.22	95.49	96.17	95.59	95.90

by isotopic dilution analysis was 126 ppm on an average of the studied glasses.

The ¹¹B MAS NMR spectrum for the Capraia glass is shown in Figure 3, where the spectrum obtained from the fitting procedure and the contributions of tetrahedral and trigonal groups to line-shape are also shown. The spectrum is well structured, but the signal-to-noise ratio is relatively low due to the relatively low boron concentration. The different B structural units show peculiar NMR line-shapes due to their different symmetry and hence different quadrupolar interaction parameters, i.e. the quadrupolar coupling constant (C_Q) and asymmetry parameter (η). In fact, following their symmetry properties, only BO₃ units are significantly broadened by quadrupolar effects, while this effect is negligible for BO₄ compared to dipolar broadening; B^[4] species hence yield almost gaussian line-shapes under MAS conditions whereas B^[3] species show line-shapes determined by the second order quadrupolar effects, with BO_{2/2}O⁻ characterized by a large asymmetry parameter due to the lack of D_{3h} symmetry. Initial values for the fitting parameters (i.e. isotropic chemical shift and quadrupolar interaction parameters) were found by preliminary simulations and then let free to vary in the fitting procedure. The occurrence of a near-Gaussian component is evident from the spectrum, and ascribed to boron in tetrahedral coordination (BO_{4/2}) (Jäger *et al.*, 1995). The presence of a second component is also evident; the fitting yields values of 0.20 ± 0.05 for η and 2.7 ± 0.1 MHz for the

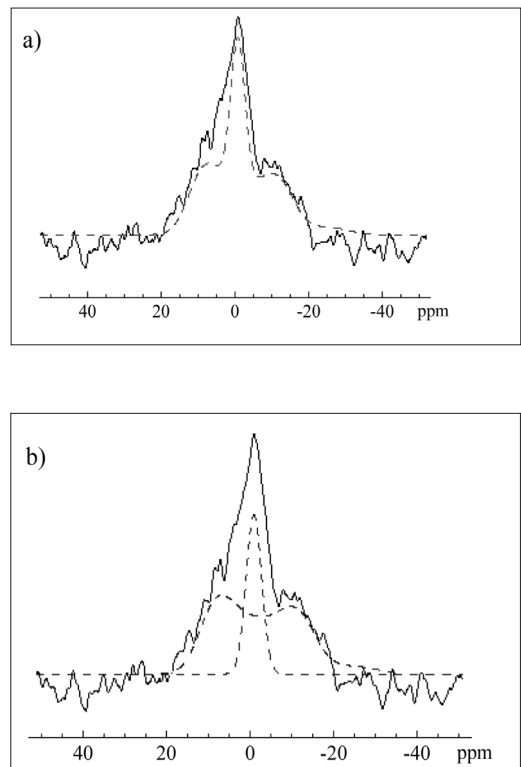


Fig. 3 – ¹¹B MAS NMR spectra for the Capraia rhyolite glass with overlapping (a) the deconvolution curve and (b) the contribution of the two different components to the spectrum drawn as dashed lines.

quadrupolar coupling constant. This component is attributable to boron in trigonal coordination, and in particular, given the low value of η , to $\text{BO}_{3/2}$ units (Züchner *et al.*, 1998). The addition of a third component, associated to trigonal boron in $\text{BO}_{2/2}\text{O}^-$ groups, does not improve the fitting. The relative contribution of $\text{B}^{[4]}$ and $\text{B}^{[3]}$ species in the glass is 26.5% and 73.5 %, respectively.

Charge-balancing of Al^{3+} by M^{n+} cations (where $\text{M} = \text{Ca}, \text{Na}, \text{K}, \text{Mg}$) is supposed to stabilize Al in tetrahedral coordination. On a stoichiometric basis, all the studied glasses are characterized by an “excess” of Al after the proper charge-balancing cation partitioning. In the assumption that Al is mostly in tetrahedral coordination and that the M^{n+} cations are preferentially used by Al with respect to B in the competition for tetrahedrally coordinated species, no charge-balancing cations would remain available to form $\text{B}^{[4]}$, and boron would be expected to occur only in trigonal coordination. The possibility of distorted tetrahedral $\text{BO}_{3/2}\text{O}^-$ sites deriving from the interaction of trigonal $\text{BO}_{3/2}$, which acts as a Lewis acid, and electron rich OH groups (more likely than H_2O) yielding OH terminations (Holtz *et al.*, 1993) and break-up of Si-O-B or Al-O-B copolymerization by non-bridging oxygens, seems unlikely on the basis of the spectral fitting parameters which are typical of undistorted tetrahedral $\text{BO}_{4/2}$ units. Another possibility is that H^+ ions act as charge balancing ions allowing the tetrahedral coordination of boron which thus copolymerizes sharing all oxygen atoms. The B tetrahedral coordination could be related to the occurrence of triclusters in the glass structure (Al_3O or Al_2SiO ; Romano *et al.*, 2000) where Al remains in tetrahedral coordination, making some charge-balancing cations such alkalis available for $\text{B}^{[4]}$.

CONCLUSIVE REMARKS

The major element chemistry indicates that the studied glass is characterized by an “excess” of Al with respect to charge-balancing cations. Therefore, on the basis of the competition for charge-balancing cations between tetrahedrally coordinated aluminum and boron, it would be expected that AlO_4 units preferentially form and that boron occurs only in trigonal coordination.

On the contrary, the ^{11}B MAS NMR spectrum indicates the occurrence of a significant amount of $\text{B}^{[4]}$ in the glass structure, together with a higher amount of trigonal structural units, with all the oxygens bridging.

This suggests that, at least in calc-alkaline magmas and when at trace-level concentration, boron copolymerizes sharing oxygens. In this case, it can be hypothesized that H^+ ions act as charge balancing ions, interacting with oxygens and allowing the tetrahedral coordination of boron, or the occurrence of Al in triclusters in the glass could be postulated.

It must however be noted that the formation of $\text{BO}_{4/2}$ units for a given composition is likely to depend not only from the stoichiometry or degree of hydration of the melt, but also on a number of parameters including the thermal history of the glass, which cannot be easily quantified in a natural system.

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