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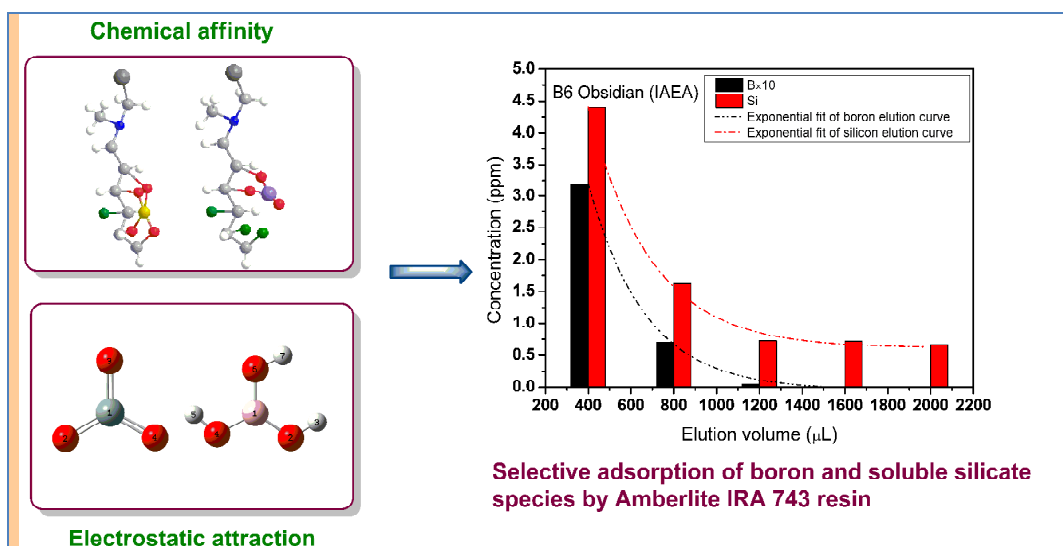
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Manuscript title: Effect of metasilicate matrices on boron purification by Amberlite IRA 743 boron specific resin and isotope analysis by MC-ICP-MS

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Effect of metasilicate matrices on boron purification by Amberlite IRA 743 boron specific resin and isotope analysis by MC-ICP-MS

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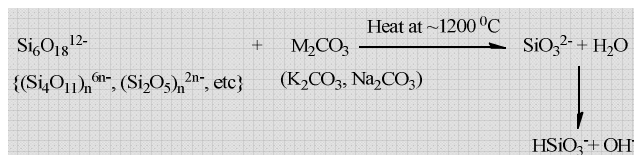
The selective adsorption of metasilicate species by N-methyl D-glucamine functional groups in Amberlite IRA 743 resin was observed, which is clarified as the formation of sugar-metasilicate complexes and possible physical adsorptions. The existence of metasilicate matrices causes obvious discrepancies in $\delta^{11}\text{B}$ values of silicate materials. It opens possibility to explore relevant procedures for the separation/purification of silicon from geological samples.

Boron isotopic composition is reported as $\delta^{11}\text{B}$ in per mil (‰) deviation from the boron isotope standard reference material (NIST SRM 951) as follows: $\delta^{11}\text{B} \text{ ‰} = 1000[(^{11}\text{B}/^{10}\text{B})_{\text{sample}}/(^{11}\text{B}/^{10}\text{B})_{\text{standard}} - 1]$. The facts that wide range of boron isotopic compositions in nature ($\delta^{11}\text{B}$, from -70 ‰ to +75 ‰),¹⁻³ and significant boron isotopic fractionations occurred in various geological processes, drive applications of boron isotope geochemistry to all areas of earth sciences from mantle geochemistry to surface environment.⁴ Such as, high-temperature and low-temperature geochemical processes,⁵⁻⁸ anthropogenic pollution sources and wastewater recharge monitoring,⁹⁻¹¹ paleo-ocean pH reconstruction and global biogeochemical cycles,¹²⁻¹⁶ etc. In recent years, valuable fundamental understanding on matter transfer and isotopic fractionation of boron during silicate weathering provided useful constrains for evaluating surficial environments¹⁷⁻¹⁸. Its geochemical properties of highly incompatible in mafic silicate minerals and highly soluble in moderate to high temperature fluids make the boron isotope interesting as a powerful tracer in magmatic-hydrothermal systems, e.g. dehydration reaction and metamorphism in subduction zones,¹⁹⁻²⁰ alteration of oceanic crust,²¹ and hydrothermal alteration of granite²².

A general review on boron isotope analysis method had been given by Aggarwal and Palmer²³. After decades of improvements/modifications on boron isotope analysis, the external reproducibilities better than ~ 0.2 ‰ could be achieved in few nano-grams of boron by negative thermal ionization mass spectrometry (NTIMS),²⁴ positive thermal ionization mass spectrometry (PTIMS),²⁵⁻²⁶ and multicollector inductively coupled plasma mass spectrometry (MC-ICP-MS)²⁷⁻²⁸. However, the further effort for improving extraction procedure of boron from silicate matrices has been emphasized on the basis of intercomparison study and laboratory observations,²⁹⁻³⁰ because of difficulties in full recovery of boron from silicate materials and possible contamination and isotopic fractionation associated with chemical extraction/purification procedures.

Currently, silicate geological samples were dissolved with HF digestion (abbreviated as A),³⁰ and alkali fusion approach (abbreviated as B)³¹ (Scheme 1) before being loaded into ion-exchange resins to purify boron and remove other matrices elements. By comparison, the relatively large spreads of $\delta^{11}\text{B}$ in silicate rocks were observed, where the $\delta^{11}\text{B}$ values by MC-ICP-MS are systematically $\sim +3$ ‰ higher than that by PTIMS for tourmalines under the same alkali fusion approach (B) (Figure 1a). The $\delta^{11}\text{B}$ values in rock and mineral reference materials (B4-Tourmaline, B6-Obsidian, IAEA) with high silica content (more than 34% SiO_2) obtained by MC-ICP-MS-A are agree well with PTIMS-B in the issued reference ranges,³¹ but are different from the determined values by MC-ICP-MS-B (Figure 1b). Therefore, it could be concluded that $\delta^{11}\text{B}$ values of silicate

minerals by MC-ICP-MS-B obviously deviate from the true values, which presumably would be attributed to matrices effect on boron isotope analysis by this approach.



Scheme 1. Illustration of the alkali fusion reaction of silicate minerals.

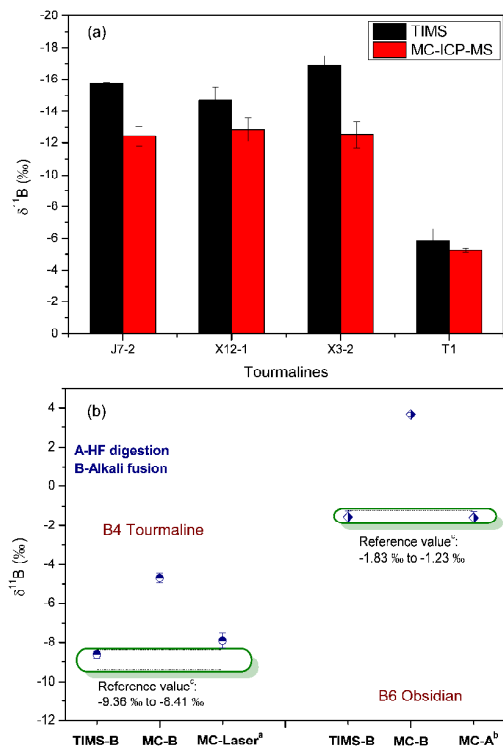


Figure 1. Distribution of $\delta^{11}\text{B}$ values in silicate materials measured by MC-ICP-MS and PTIMS after being followed different chemical procedures. The uncertainties bar (2σ) is within the symbol size. Fig 1(b): the $\delta^{11}\text{B}$ values of B4 and B6 in footnotes (a, b and c) are cited from references³⁰⁻³².

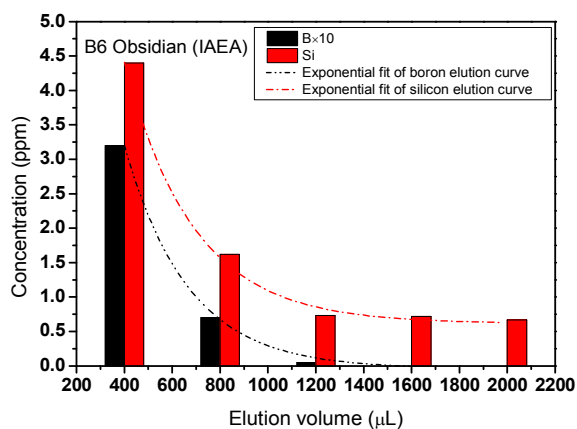


Figure 2. Elution curves of boron and silicon when separating boron from one silicate sample (IAEA B6-Obsidian) with the Amberlite IRA 743 resin.

In order to reveal the possible reasons behind the experimental phenomena, the boron purification procedure of silicate materials was checked out in this work. As large amount of SiO_3^{2-} or HSiO_3^- ions exist in sample solution after the alkali fusion reaction (Scheme 1), the concentrations of boron and silicon were monitored in the elution step when following the purification procedure with the Amberlite IRA 743 boron specific resin. As shown in Figure 2, two ions are eluted synchronously from the resin with similar rates, clearly indicating the Amberlite IRA 743 boron specific resin could effectively adsorb SiO_3^{2-} and HSiO_3^- ions either.

To verify the effect of soluble metasilicate matrices on the boron isotope analysis by MC-ICP-MS, the $^{11}\text{B}/^{10}\text{B}$ variations in the boron isotope reference material of NIST 951 are compared when adding Si into 200 ppb of NIST 951 solution to reach the molar ratios of B/Si from 1.0 : 0.1 to 1.0 : 20 (Figure 3). As we expected, the $^{11}\text{B}/^{10}\text{B}$ values of NIST 951 with the B/Si ratio of 1.0 : 0.1 are consistent with the certified value of 4.04362 ± 0.00137 ,³³ and negatively shift at the lower Si/B ratios, and then are $\sim +2.6\%$ higher than the true value when the Si/B ratios are higher than 2.0 : 1.0. It is coincident with previous conclusion that the high amount of matrices makes the mass bias more unstable and susceptible and induced significant deviation in $^{11}\text{B}/^{10}\text{B}$ during boron isotope analysis by MC-ICP-MS³⁴.

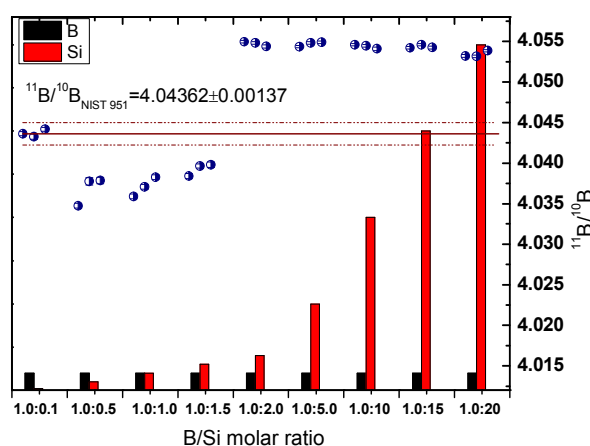


Figure 3. Variations in $^{11}\text{B}/^{10}\text{B}$ values of NIST 951 with increasing the B/Si ratios from 1.0 : 0.1 to 1.0 : 20. The data of $^{11}\text{B}/^{10}\text{B}$ were referred to the Right y-axis.

The Amberlite IRA 743 boron specific resin is a unique chelating resin specifically designed to effectively remove boric acid and borate from solution. As a basic anion exchange resin, the styrene-divinylbenzene macroporous matrices with N-methyl D-glucamine functional groups ensure the selective adsorption of boron from bulk solutions³⁵⁻³⁷. The boron absorbability of this resin increased with increasing solution pH and reached to the maximum at pH~9.0, and the combination of distribution and ^{11}B MAS NMR measurement indicated the formation of a 1 : 1 tetradentate complex of boron species with N-methyl D-glucamine functional groups,³⁸ and the high load capacity of boron was attributed to the specific chemical affinity and physical adsorption (e.g. van der Waal forces, electrostatic attraction, and hydrogen bonding) on the basis of investigation on adsorption thermodynamic and kinetic mechanism³⁹. Besides, it was found that several coordination of sugars to silicon existed via oxygen based entirely on ^{13}C and ^{29}Si NMR⁴⁰⁻⁴¹, because certain sugars react readily with basic silicic acid to form soluble sugar-silicate chelating complexes⁴². These studies strongly support a long-standing supposition that sugar-like molecules play a significant role in the biological uptake and transport of silicon and in mineral digenesis⁴⁰.

On the basis of discussions given above, possible binding structures for complexes of boron and silicon with N-methyl D-glucamine functional groups in the Amberlite IRA 743 resin are shown in Figure 4a,b, where the

formations of 1 : 1 tetradentate complex of borate with N-methyl D-glucamine group and sugar-silicate complex clarify the selective adsorption of boron and silicate species by the resin from parent solutions. In addition, the possible driving forces for physical adsorption among the functional groups and two aqueous species also were examined. The molecular geometries of boric acid and metasilicate species were optimized at the B3LYP level of density functional theory (DFT)⁴³, where the lan12dz basis was used for silicon atom, and the G-31G** basis set was used for boron and oxygen atoms⁴⁴. All DFT calculations were performed with GAUSSIAN 03 packages⁴⁵. It turns that H_3BO_3 and SiO_3^{2-} has the trigonal geometry with the approximate sizes (Figure 4c), which satisfies alternative adsorption of boron/metasilicate species on the Amberlite IRA 743 resin via electrostatic attraction.

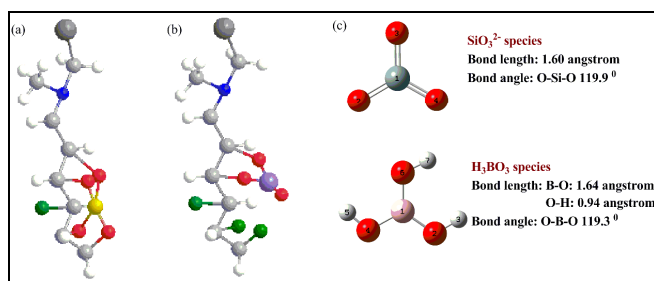


Figure 4. (a) Binding structure for 1 : 1 tetradentate complex of borate with N-methyl D-glucamine group in Amberlite IRA 743 resin; (b) possible structure of sugar-silicate complex formed between metasilicate anions and functional groups in the resin; (c) the optimized geometries and sizes of H_3BO_3 and SiO_3^{2-} species at the B3LYP level of density functional theory (DFT). In the complexes structures of Figure 4a, b: the polystyrene chain of the resin and hydroxyl group are indicated in dark gray and green, and atoms of C, H, N, O, B and Si are illustrated in light gray, white, blue, red, yellow and purple respectively.

So far, the relevant association constants of sugar-silicate complex have not been given. Taking the overall formation constant (K) of $10^{4.0 \pm 0.1}$ for the complex of boron species with N-methyl D-glucamine into account,⁴⁶ the relative fraction of boron with solution pH is calculated based on the equilibrium chelating and dissociation reactions. In general extraction procedure, boron was adsorbed on the resin at $\text{pH} > 8$, and eluted with 0.1 M HNO_3 or HCl ($\text{pH} \sim 1$). The adsorption-elution process of boron from metasilicate matrices solution by the Amberlite IRA 743 resin is schematically shown in Figure 5, clearly explaining how the borate and metasilicate species attach on the resin at the neutral or weak basic pH condition and are eluted into fluid phase under acidic pH condition.

Conclusions

In conclusion, the selective adsorption of metasilicate species by N-methyl D-glucamine functional groups in Amberlite IRA 743 resin was clarified by understanding the possible binding structure of sugar-metasilicate complex and the driving forces of physical adsorption between metasilicate and the functional groups in the resin. It explains the obvious deviation in $\delta^{11}\text{B}$ values of silicate geological samples measured by MC-ICP-MS when boron was extracted by alkali fusion approach and purified by the Amberlite IRA 743 resin. Therefore, it must be of great interest to understand the thermodynamic/kinetic mechanism of metasilicate species by polymer supported N-methyl D-glucamine functional groups in our near future work, which opens possibility to explore relevant procedures for the separation/purification of silicon from geological samples instead.

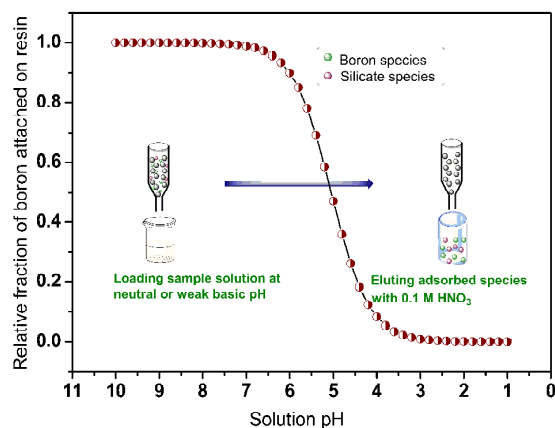
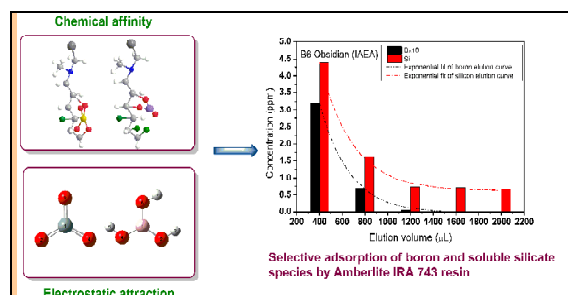


Figure 5. Adsorption-desorption processes of boron and metasilicate species on the Amberlite IRA 743 resin with changing solution pH.

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Graphical abstract



Notes and references

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