

^{11}B MAS NMR of natural borate minerals

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Borate minerals form in a wide variety of geologic environments and their derivatives have many large-scale industrial applications. However, various analytical obstacles make boron itself difficult to study. ^{11}B MAS NMR has long been applied to this task, but previous efforts have largely failed to resolve crystallographically distinct sites with the same coordination number. This shortcoming limits attempts to correlate NMR parameters with local structure and hence, the utility of NMR as a probe of detailed structural aspects. We find that the use of ultrahigh-field NMR enhances the resolution of both three- and four-coordinate boron in some cases, providing new analytical opportunities.

A collection of natural borate minerals was analyzed by ^{11}B MAS NMR spectroscopy at 14.1 and 21.1 T. The ^{11}B MAS NMR spectrum of ulexite ($\text{CaNaB}_5\text{O}_9(\text{OH})_6 \cdot 5\text{H}_2\text{O}$) shows only a single three-coordinate boron site at 14.1 T, despite having two such sites in the crystal structure (Figure 1). At 21.1 T, two BO_3 sites are apparent and can be fit to obtain distinct NMR parameters. Similarly, the ^{11}B MAS spectrum of howlite ($\text{Ca}_2\text{B}_5\text{SiO}_9(\text{OH})_5$) at 14.1 T exhibits a complex pattern in the four-coordinate region, but all four crystallographically inequivalent sites can be detected in the 21.1 T spectrum (Figure 2). This resolution permits peak assignments according to the local geometry and/or connectivity.

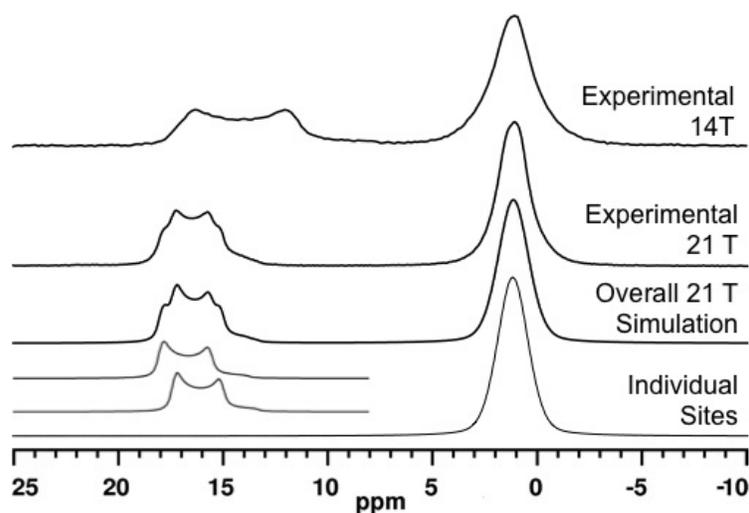


Figure 1: ^{11}B MAS NMR spectra of ulexite (Qinghai Province, China) at 14.1 T and 21.1 T, along with lineshape calculations of the 21.1 T data.

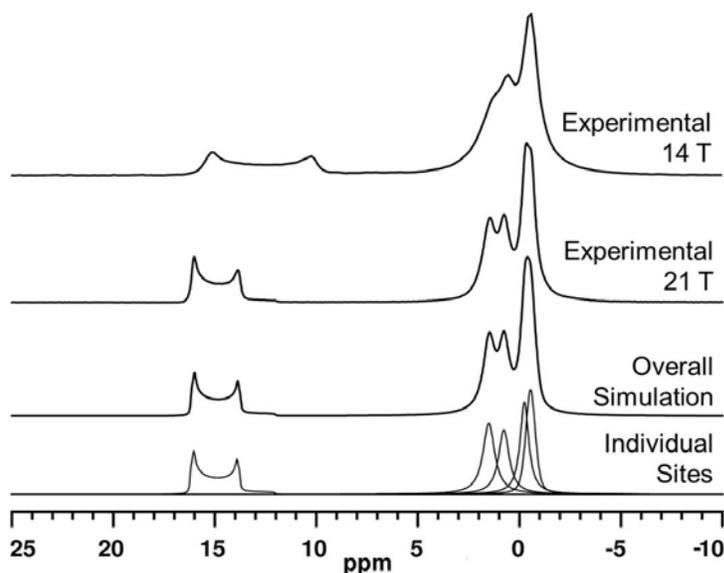


Figure 2: ^{11}B MAS NMR spectra of howlite (Fischell's Brook, Newfoundland) at 14.1 and 21.1 T, along with lineshape calculations of the 21.1 T data.

Crystallographic site resolution offers the potential for more detailed correlations between NMR data and structural parameters. Figure 3 shows the correlation between δ_{iso} and the average B-O bond length for the three-coordinate boron sites in calcium- and magnesium-bearing borate minerals. While there are undoubtedly many factors contributing to the observed shifts, this plot reveals a convincing trend that may prove useful in structural studies. Furthermore, accurate measurements of quadrupolar coupling constants can be used in conjunction with high-level theoretical calculations to refine the positional coordinates of water and hydroxyl protons inferred from x-ray diffraction. Such "NMR crystallography" is only possible with highly precise and accurate data.

These and other ultrahigh-field NMR studies [1,2] represent an important starting point for the establishment of further structural correlations with great promise for mineralogy.

References

- [1] A.J. Lussier, F.C. Hawthorne, Y. Abdu, S. Herwig, V.K. Michaelis, P.M. Aguiar, S. Kroeker, *Mineralogical Magazine* **75** (2011) 65-86.
- [2] A.J. Lussier, Y. Abdu, F.C. Hawthorne, V.K. Michaelis, P.M. Aguiar, S. Kroeker, *Canadian Mineralogist* **49** (2011) 63-88.

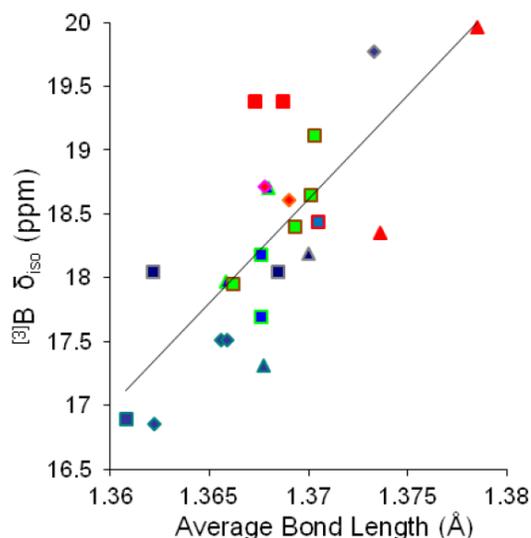


Figure 3: ^{11}B NMR isotropic chemical shifts for three-coordinate boron sites in a selection of natural minerals plotted as a function of the average B-O bond length.