

## **A neutron diffraction study of the hydrous borate inderborite, $\text{CaMg}[\text{B}_3\text{O}_3(\text{OH})_5]_2(\text{H}_2\text{O})_4 \cdot 2\text{H}_2\text{O}$**

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### **ABSTRACT**

The crystal chemistry of inderborite, a B-rich mineral ( $\text{B}_2\text{O}_3$  ~41 wt%) with ideal formula  $\text{CaMg}[\text{B}_3\text{O}_3(\text{OH})_5]_2 \cdot 6\text{H}_2\text{O}$  or  $\text{CaMg}[\text{B}_3\text{O}_3(\text{OH})_5]_2(\text{H}_2\text{O})_4 \cdot 2\text{H}_2\text{O}$  from the Inder Deposit, Kazakhstan, was re-investigated by a multi-methodological approach (single-crystal X-ray and neutron diffraction, electron probe micro-analysis in wavelength-dispersive mode, laser ablation multi-collector inductively mass spectrometry). The experimental findings show that the real chemical formula of inderborite from the Inder Deposit is virtually identical to the ideal one: the fraction of potential isomorphic substituents is insignificant. Boron is, therefore, the only industrially relevant element occurring in this mineral. The in situ B isotope composition of the Inder inderborite shows enrichment in the heavy  $^{11}\text{B}$  isotope, giving a weighted mean  $\delta^{11}\text{B}_{\text{NIST951}}$  of  $+35.15 \pm 0.49$  ‰ ( $2\sigma$ ,  $N = 6$ ). Such a positive  $\delta^{11}\text{B}$  value falls within the range of values in which the source of boron is ascribable to marine reservoirs rather than to terrestrial ones.

X-ray (at 293 K) and neutron (at 20 K) structure refinements confirm that the principal building block unit of the structure is a  $[\text{B}_3\text{O}_3(\text{OH})_5]^{2-}$  ring, consisting of two  $\text{BO}_2(\text{OH})_2$  tetrahedra (B-ion in  $sp^3$  electronic configuration) and one planar-triangular  $\text{BO}_2\text{OH}$  group (B-ion in  $sp^2$  electronic configuration). In the  $[\text{B}_3\text{O}_3(\text{OH})_5]^{2-}$  ring, all the oxygen atoms that are not shared between two boron atoms are protonated. The building units share corners with the  $\text{CaO}_2(\text{OH})_4(\text{OH}_2)_2$  polyhedra and  $\text{Mg}(\text{OH})_4(\text{OH}_2)_2$  octahedra, forming hetero-polyhedral sheets parallel to (100). Subsequent hetero-polyhedral sheets are mutually connected only by H-bonding interactions, even mediated by the zeolitic (“interstitial”)  $\text{H}_2\text{O}$  molecules. Ten out of 11 independent oxygen sites in the structure of inderborite are involved in H-bonds as donors or acceptors, and this reflects the pervasive effect of the H-bonding network. The role played by the complex H-bond network is expected to be substantial on the stability of the crystalline edifice, having effects within the single hetero-polyhedral sheet, between subsequent sheets, and in the bonding with the interstitial zeolitic  $\text{H}_2\text{O}$  molecules. Finally, the potential utilizations of inderborite, as a B-bearing mineral, are discussed.

**Keywords:** Inderborite, borates, mineral commodity, X-ray diffraction, neutron diffraction, crystal chemistry, hydrogen bonding