

## Boron isotope composition of crop plants

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Boron (B) and its isotopes have been used for a long time in geo- and environmental sciences to study mixing and fractionation processes as well as sources of anthropogenic contamination. The authentication of food using isotope compositions of specific reservoir- and process-sensitive elements is a relatively new and growing application in isotope chemistry. Unlike some well-established stable and radiogenic isotope systems (C-N-O-S-Sr-Pb) the use of B isotopes to trace the origin of food is almost unexplored. However, due to the essential role of B for embryonic development and organogenesis in plants and animals and the enormous range of isotope compositions found in nature B is a very interesting tracer to verify the origin and possible cultivation methods of various types of crop plants.

Our first B isotope data of vegetables, corn and fruits cover most of the natural variation of about 100‰ in  $\delta^{11}\text{B}$ . These highly variable B isotope compositions reflect regionally varying contributions of the natural background (geology, hydrology, soil) as well as anthropogenic processes during cultivation (fertilization/irrigation).

Most of the crop plants investigated show  $\delta^{11}\text{B}$  values between -5 and +20 ‰. Those values likely reflect the geogenic background of the rocks and soils where the crops were cultivated. Corn samples from Europe (EU TRACE project) show a total range in  $\delta^{11}\text{B}$  from -2 to +22 ‰. However, within specific growing areas the range of  $\delta^{11}\text{B}$  values for corn samples is much smaller (~10 ‰). To date the isotopically most extreme samples are a pepper sample from Israel (+35 ‰  $\delta^{11}\text{B}$ ) and a cabbage reference material from NIST (-24 ‰  $\delta^{11}\text{B}$ ). The high, seawater-like,  $\delta^{11}\text{B}$  value of the Israeli pepper may reflect irrigation with waters derived from the Dead Sea (~50-60 ‰  $\delta^{11}\text{B}$ ) or salinar aquifers. The low  $\delta^{11}\text{B}$  value of the NIST cabbage may reflect fertilization of a boron-loving crop with fertilizers coming from non-marine evaporate deposits.

In addition to the direct tracing of reservoirs and processes using the  $\delta^{11}\text{B}$  of crop plants, B isotope fractionation during incorporation, transport and integration of B in the plants is an unexplored field to study the function and transport mechanisms of B in biological systems.

## An empirical comparison of expected versus observed REE distribution in mantle pyroxene

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The stability of clinopyroxene (Cpx) over a wide range of P – T conditions makes this rock-forming mineral an important constituent of the sub-arc environment, both in the subducting slab and the overlying mantle wedge. Because of its relatively high partition coefficients for many lithophile elements, Cpx exerts considerable control over arc magma chemistry.

However, because Cpx chemistry is variable, partitioning of elements depends on the exact type of pyroxene present. Subduction related Cpx constantly undergo thermodynamically induced crystallo-chemical transformations in response to increasing P-T conditions, commonly resulting in elevated Al, particularly Al in tetrahedral coordination (Al<sub>IV</sub>), or the Ca-Tschermak component (CaTs). Experimental results pertaining to the distribution coefficient (D) of REE in these high Al Cpx phases [1] show that for heavy (H)REE in high Al Cpx the distribution coefficient is greater than unity. In the depleted mantle wedge, Cpx can become very Cr-rich and Ca-poor, chemical changes that also affect the M2-site dimensions.

Here we endeavoured to test empirically the correlation between crystallographic parameters (which ultimately reflect composition) and the REE distribution in a suite of mantle and eclogitic Cpx. For the first time we present unit cell dimensions and fractional atomic coordinates derived from structural XRD data for the very same grains on which trace element compositional data were acquired by LA-ICP-MS.

The data show (within experimental error) remarkable agreement between the average metal – oxygen (M2-O) bond-length obtained from XRD data minus the ionic radius of O and the optimal ionic radius inferred from REE distribution in an Onuma diagram [2]. This suggests that, indeed, the recorded REE distribution in the Cpx is a direct consequence of the atomic crystallographic arrangement that permits a trace cation into the lattice site [3], which in turn is a physical manifestation of the major element chemistry. This results in Onuma diagram apices ranging from Pr to Er.

Consequently, as shown experimentally for high Al Cpx [1] the major element chemistry has an influence on which trace cations are preferentially retained in the solid phase both in direct slab melting and fluid-induced sub-arc mantle melting.

[1] Blundy, Robinson & Wood (1998) *EPSL* **160**, 493 – 504.

[2] Onuma *et al.* (1968) *EPSL* **5**, 47-51. [3] Brice (1975) *J Cryst. Growth* **28**, 249-253.