Stable Boron isotopes

Natural boron in the environment

Boron is a highly volatile semi-metal and a group 13 element in the periodic table of elements. It naturally occurs in oxides and hydroxides and it exists in high concentrations in liquids as boron acid and in their mineral salts (borates) (e.g. colemanite or sodium borate). With respect to the silica based earth the concentration of boron is with ~0.3 ppm rather low. However, in the upper crust it´s concentration is higher and makes up to ~15 ppm. Due to weathering, the boron ends up in the ocean where it occurs with a concentration of around 4.5 ppm.

Borates are used in the glass and ceramic industry, as well as for the production of flux and solder. Furthermore, perborate is used as bleaching agent in the detergent industry. Due to the ability of borate to form easily soluble chemical compounds it often reaches the groundwater through leakage water of disposal sites or contaminated sites. Besides, a higher borate concentration appears in sewage sludge and in agricultural fertilizers. Therefore, they can be utilized as a non-fecal wastewater indicator in waste disposals as well as for the detection of agricultural pollution.

Groundwater in Germany usually shows boron concentrations between 0.01 and 0.1 mg/L. These values are much lower than the limit value set by the drinking water ordinance (1 mg/L boron).

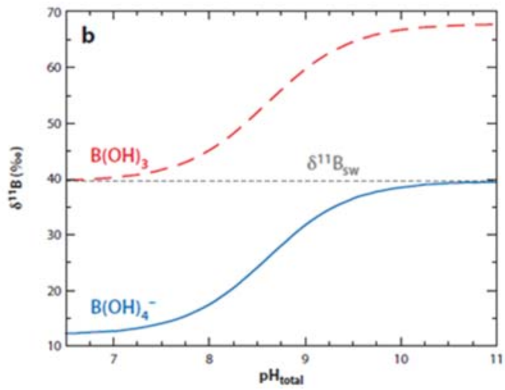
Boron isotopes

Boron has an atomic mass of 10.81 u and has two stable isotopes: the light ^{10}B with an abundance of 20 % and the heavier ^{11}B with an abundance of 80 %.

Stable Isotopes are always indicated as a ratio of two isotopes of one element. The change of the boron isotope ratio, which occurs due to fractionation of the boron atoms after a chemical reaction or a physical transition is stated in the δ-notation (1) and refers to a standard:

$$\delta^{11}B\ (‰) = \left(\left(\frac{{}^{11}B/{}^{10}B_{sample}}{{}^{11}B/{}^{10}B_{standard}} \right) - 1 \right) \times 1000 \qquad (1)$$

The natural fractionation of boron in the ocean attributes to the distribution between the complexes $B(OH)_4^-$ (borate ion) and $B(OH)_3$ (boric acid). The heavy ^{11}B fits preferably in the trigonal $B(OH)_3$. Experimentally based solutions yielded a fractionation factor of α=1.0272 for this equilibrium reaction (2). These days it is commonly assumed that the ocean has a $\delta^{11}B$-value of 39.61 ‰, which is constant over large geological timescales. This is due to the high residence time of boron in the ocean.



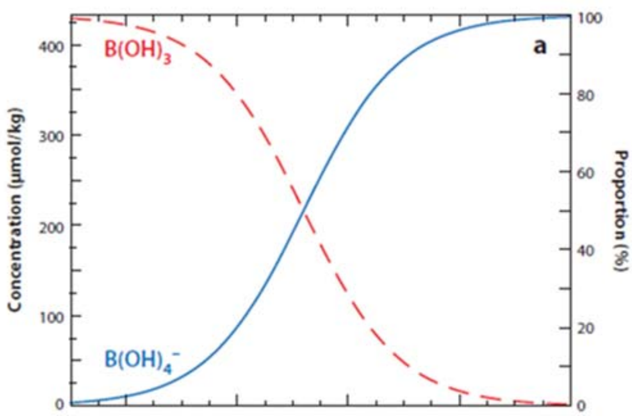
$$^{10}B(OH)_3 + {}^{11}B(OH)_4^- = {}^{11}B(OH)_3 + {}^{10}B(OH)_4^- \quad (2)$$

Due to different isotope properties, such as the high relative mass difference (~10 %), the isotope ratios have a large, natural range between -30 ‰ and +50 ‰. Therefore, boron isotopes can be an important parameter for geochemical processes.

Nowadays the common technique to measure and analyse boron isotopes is the thermion mass spectrometry (TIMS). Using this technique, the samples are vaporized, thermally ionized and accelerated. The ions are separated in a magnetic field and registered on so-called Faraday-Cups.

Boron as a proxy for the atmospheric CO_2 concentration

The boron acid/borate ratio in the ocean depends on the pH. If the pH value of the ocean is lower, more CO_2 is dissolved and the lime/carbonic acid equilibrium is shifted in the direction of the educts (3) and hence, boron acid is the dominant species in the ocean. The reaction is affected by pressure, temperature and salinity.



$$CO_2 + H_2O \leftrightarrow H^+ + HCO_3^- \leftrightarrow 2H^+ + CO_3^{2-} \quad (3)$$

For lower CO_2 concentrations in the ocean, the equilibrium reaction shifts to the products and the borate ion is the dominant species in the ocean.

Based on the latest published scientific researches only borate ions are capable of being substituted into $CaCO_3$ of the calcite generating foraminifera (4). Knowing that the lighter ^{10}B fits preferably in the borate ion it is possible to draw conclusions regarding to the pH value of the ocean.

$$CaCO_3 + B(OH)_4^- \rightarrow Ca(HBO_3) + HCO_3^- + H_2O \quad (4)$$

In summary it is possible to determine the pH value of the ocean prevailing during the formation of foraminifera by measuring their $\delta^{11}B$ value. The concentration of boric acid as well as the concentration of CO_2 is derived from the measured pH value. Consequently, a quantitative assertion about the CO_2 concentration of the atmosphere can be traced back. However, it is necessary to consider other parameter results, such as vital effects of foraminifera or the increased input of boron at estuaries. Additionally, the parameters pressure, temperature and salinity have to be taken into account for all measurements.

The research of boron isotopes becomes increasingly relevant since the climate change leads to an increasing CO_2 concentration in the atmosphere and hence, to ocean acidification which highly affects marine as well as terrestrial ecosystems.

Boron as a tracer for anthropogenic groundwater pollution

Due to the fact that boron is an omnipresent accompanying element of nitrate and thus arrives in the groundwater through anthropogenic pollution, it can be useful to measure boron isotopes to get information about anthropogenic pollution sources. In natural environments boron isotope ratios only change in large, for the measurements negligible timescales, so that they normally show the same or similar $\delta^{11}B$ ratios as the pollution source. Therefore, it is possible to differentiate between anthropogenic and geogenic boron sources. Based on the large, naturally occurring range of $\delta^{11}B$ values it is partly possible to distinguish natural fertilizers from mineral fertilizers and sewage water input.

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