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To cite this version:

Wolfram Kloppmann, Emmanuelle Petelet-Giraud, Catherine Guerrot, Lise Cary, Hélène Pauwels. Extreme Boron Isotope Ratios in Groundwater. Procedia Earth and Planetary Science, 2015, 13, pp.296 - 300. 10.1016/j.proeps.2015.07.069 . hal-03699932

HAL Id: hal-03699932

https://brgm.hal.science/hal-03699932v1

Submitted on 20 Jun 2022

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Procedia Earth and Planetary Science 13 (2015) 296 – 300

Procedia
Earth and Planetary Science

11th Applied Isotope Geochemistry Conference, AIG-11 BRGM

Extreme boron isotope ratios in groundwater

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Abstract

Examples of "extreme" boron isotope ratios in groundwaters are presented, both in the positive $\delta^{11}B$ range (up to +75‰) and negative range (down to -30‰) relative to the "typical" $\delta^{11}B$ groundwater values of -10‰ to +40‰. A conceptual model of ^{11}B-enrichment in aquifers affected by salinization is provided. Rayleigh distillation by preferential sorption of ^{10}B-enriched borate on clays under open system conditions during progressing salinization explains the observed ^{11}B enrichment in modified salinized groundwater. The relative rarity and spatial limitation of extreme positive values >+50‰ is explained by a conjunction of factors necessary for such shifts from the seawater composition ($\delta^{11}B$=39‰). In contrast, ^{11}B-depleted groundwater must have interacted with a solid phase itself depleted in ^{11}B (e.g. amphiboles, tourmalines, continental borates, coals…) as there is no known natural effect preferentially removing ^{11}B from the solution and the mobilization of boron from the solid phase is not associated with isotopic fractionation.

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Peer-review under responsibility of the scientific committee of AIG-11

Keywords: B isotopes, Rayleigh distillation, adsorption, groundwater salinization, water-rock interaction

1. Introduction

As Thode *et al.*[1] stated in 1946 in their pioneer work on the isotopic variations of boron in natural materials, *"it would not be surprising to find some variations in the isotopic content of boron"* and indeed, their first analytical results on secondary B minerals seemed to confirm this statement, even if, at this early stage of mass spectrometry, the significance of the observed differences might be questioned[2]. In the following 70 years, considerable and reliable knowledge has been acquired on the stable isotope ratios of B in a large diversity of geological matrices, minerals, rocks, organic matter, low- and high-saline surface- and subsurface fluids. Barth[3] , in 1993, reported an overall range for natural B $\delta^{11}B$ of 90‰; twenty years later this range has been extended to 145‰[4], from -70‰ vs. NBS951 measured in coals[5] and +75‰ encountered in a contaminated coastal aquifer[6].

This isotopic variability is due to (1) the high relative mass contrast between ^{11}B and ^{10}B leading to significant mass-depending fractionation; (2) the pH-dependent predominance of two dissolved B species, the trigonal undissociated boric acid $B(OH)_4^-$ and the tetrahedral borate ion $B(OH)_3^0$; and (3) a strong equilibrium isotope

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doi:10.1016/j.proeps.2015.07.069

fractionation between both species and a very different geochemical behavior leading to chemical and, consequently, isotopic fractionation accompanying the transformation processes of the global B cycle.

Here we present, together with examples from literature, some "extreme" $\delta^{11}B$ values in groundwaters measured over the years in the TIMS laboratory of the French Geological Survey (BRGM), as starting point for an evaluation of the mechanisms that have led to these exceptional ^{11}B enrichments or depletions in subsurface waters and the frequency of their occurrence relative to the more "traditional" isotopic range of -10‰ to +40‰.

2. Conditions for ^{11}B enrichment in groundwater

Hypersaline solutions have been the first milieus where $\delta^{11}B$ values largely exceeding the seawater value of 39.5‰ were measured by A. Vengosh and coworkers in Australian salt lakes[7] and Dead Sea brines[8]. In both cases, direct or indirect marine origin was postulated for the brines, and in both cases, $\delta^{11}B$>seawater and B/Cl<seawater were explained by preferential loss of ^{10}B from solution through sorption on clays. Seawater evaporation well beyond the halite stage can also enrich the residual brines in ^{11}B, as $\delta^{11}B$ values in evaporated seawater reaching +55‰ have been reported [9]. At the extreme opposite of the salinity range, we find "man-made" freshwater with $\delta^{11}B$ values up to +60‰[10]. Chemical selectivity of high-pH reverse osmosis, now a standard procedure for seawater desalination, would lead to this strong ^{11}B-enrichment in the produced permeate. Penetration of such artificial freshwater or evolved marine brines into aquifers may cause extreme B isotope ratios in groundwater but examples are still rare in literature. A more frequently encountered mechanism of ^{11}B enrichment beyond the seawater ratio seems to be saline intrusion into coastal aquifers. The most spectacular example is the landfill leachate- and seawater-contaminated coastal aquifer on Staten Island[6]. In this case study highly saline groundwater was affected by seawater intrusion near the shoreline exhibited marine $\delta^{11}B$, whereas a spatially limited zone of diluted seawater has been identified in the aquifer where $\delta^{11}B$ reach the current world record value of +75‰. We postulate that such extreme ^{11}B enrichment cannot be explained simply by a closed system equilibrium fractionation between seawater and clays but rather by a dynamic, Rayleigh distillation-like open system process where seawater is intruding into a clay-rich aquifer losing ^{10}B to the clay minerals and progressively becoming enriched in ^{11}B. The enrichment factor ε between seawater and clays at seawater pH lies around -26‰[11-13] so that the clay-adsorbed B-fraction will fall around +15‰. Indeed, Spivack *et al.* (1987)[12] found a narrow $\delta^{11}B$-range of +13.9 to +15.8 for the desorbable B-fraction of marine sediments.

In a strongly urbanized, coastal aquifer system at Recife, Brazil, our previous study showed $\delta^{11}B$ values ranging from +63.7 to +68.5 ‰[14] in three wells. Those wells lie in a very limited zone of the fluvio-lacustrine siliclastic Beberibe aquifer, geographically close to the Capibaribe River, which is under tide influence. The large majority of groundwater in this aquifer showed marine $\delta^{11}B$ values (36.8-42.5 ‰), indicating (paleo-)seawater intrusion and dilution by local freshwater recharge with equally marine $\delta^{11}B$. The ^{11}B-rich waters are strongly diluted with respect to seawater (190 to 220 mg/L Cl, 74 to 126 µg/L B). Given the widespread occurrence of seawater intrusion in coastal surface- and groundwater bodies and of clay minerals in coastal basins, we could ask why highly ^{11}B-enriched B is not reported more frequently and only in very limited parts of the aquifers. The conditions that would favor groundwater $\delta^{11}B$ shifting above the seawater value are:

- A high $\delta^{11}B$ "starting point" in the initial fluids, prior to adsorption, i.e. seawater $\delta^{11}B$,
- The presence of clay minerals, hydroxides or organic matter capable to adsorb B,
- A low water/rock ratio (i.e., a low dissolved B/sorbent ratio). The effect will thus be stronger for diluted solutions, low porosity and a high content of sorbents in the aquifer material, so that sorption, as B sink, has significant influence on the total aquatic B mass balance in the residual water.
- Exchange sites available for significant B sorption. This is a complex condition as the different B species will be sorbed on different sites and are competing with different other ions. The negatively charged borate ion is predominant at pH>~8,5. With its affinity for positively charged surface sites it will be stronger sorbed than $B(OH)_3^0$ so that pH increase will lead to stronger sorption. The pH effect is modulated by the fact that anion exchange will be favored only for a pH below the point of zero charge (PZC) for a given mineral. In other words, at higher pH (>9 for kaolinite[15]) there will be competition with OH- ions so that there is an optimum pH "window" around 8.5 (~ seawater value)[15]. Also, a strong effect of ionic strength is observed[16]: Maximum adsorption capacity of soil for B is increased by 75% for an increase of salt concentrations from 0.01 to 0.5M[16]. Here, again, B

adsorption will be strongest in a salinity "window" allowing for sufficient dilution of B on the one hand and a sufficient remaining ionic strength on the other hand. A further factor is the presence of dissolved Ca^{2+}. The formation of positively charged ion pairs $CaB(OH)_4^+$ will increase B sorption in the alkaline pH range >8.5[15]. This monovalent cation (i.e., $CaB(OH)_4^+$) will successfully compete with Ca^{2+} for cation exchange sites whereas $B(OH)_4^-$ will occupy anion exchange sites.

- Replacement of the fluid in contact with the sorbent: Non-equilibrium fractionation of boron isotopes in an open system would favour a Rayleigh-like process of continuous preferential sorption of ^{10}B on fresh, B-undersaturated exchange/sorption sites, accompanied by increasing ^{11}B in the residual solution. This can, in theory, lead to considerable ^{11}B enrichment accompanied by B-loss from the solution and decrease of B/Cl ratios.

In sum, B sorption would be strongest during progressing salinization (Fig. 1), close to the salinization "front", where seawater is moderately diluted (i.e., pH close to seawater value, B relatively low but ion strength still high enough to enhance sorption). The presence of Ca^{2+} that may be liberated by cation exchange or carbonate dissolution is an additional trigger for boron adsorption. The narrow zone where these conditions are fulfilled will advance during saline intrusion, bringing intruding saline water, mixed with freshwater, constantly in contact with "fresh" and unsaturated clay minerals. In this open system, fractionation can lead to a Rayleigh-like accumulation of ^{11}B in groundwater as observed in some sites of the Recife aquifer.

Even if this could be a valid conceptual model for coastal aquifers, it is impossible, without stringent geochemical reactive transport modeling, to provide *a priori* ranges, e.g. pH or salinity, where extreme $\delta^{11}B$ values can be expected. The example of the Fessenheim island in the Rhine River where, over decades, brines from French potash mining were stored which partly infiltrated into the alluvial aquifer[17] shows that even for much higher salinities, in the range of 10 to 20 g/L Cl^-, $\delta^{11}B$ values of +57‰ can be reached[18]. In this case, the infiltrating brines were derived from halite/potash dissolution and B concentrations by two orders of magnitude lower than in seawater. These low B concentrations and the high clay contents the settling ponds and in the aquifer material led to the required low B/sorbent ratio mentioned above, regardless of the high salinity. Active cation exchange in this aquifer, accompanying brine dilution is evidenced by a strong relative depletion in monovalent cations (Na+K)/Cl ratios as low as 0.3 compared to 1 in the initial brines, giving rise to Ca-Cl type groundwater. Like for the Recife case, the extension of the zone of extreme ^{11}B enrichment is very limited (two wells).

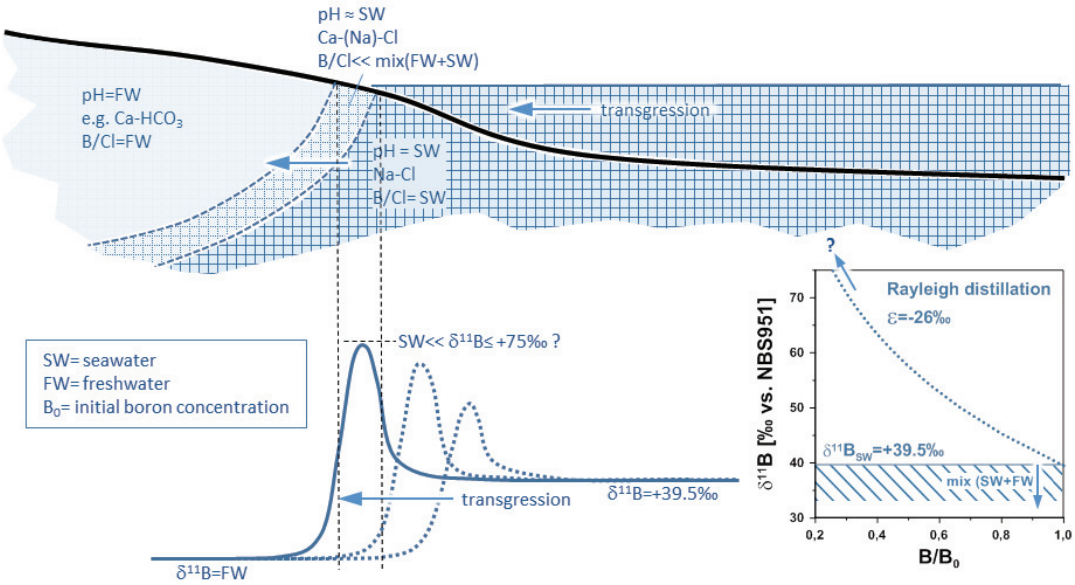

Fig. 1. Conceptual model of Rayleigh-distillation open system isotope fractionation by B-adsorption on clay during saline intrusion.

3. Cases of ^{11}B-depleted groundwaters

The other side of the coin is ^{11}B-depletion of "desorbable B" reversibly fixed on the clay surface exchangeable sites. This ^{11}B depleted B can be remobilized, for example, during freshening processes or marine regression and, in theory, would lead to low δ^{11}B values in the concerned aquifers. Given that equilibrium ε is around -26‰, clay desorbable marine B would have δ^{11}B values around +15‰[19], which is far from what can be qualified as "extremely low". As desorption is not fractionating, no Rayleigh distillation process could occur and desorbed B will simply mix with dissolved B from other sources in the groundwater. However, if the initial fluids from which the adsorbed boron originated was not seawater but B-rich fluid with lower δ^{11}B, the associated clay-fixed B could be much lower. This is demonstrated δ^{11}B values as low as -20‰ of leachates from coastal aquifer sediments affected by geothermal fluids[20, 21] due to equilibrium fractionation upon syn- or post-sedimentary contact with fluid outflow from the Larderello geothermal field (Tuscany, Italy)[20]. Still, the lowest values for groundwater leaching the clay-fixed boron this aquifer was -6.4‰ for boron concentrations up to 8 mg/L and such values are in the range observed in crystalline or volcanic freshwater aquifers[22-24], geothermal systems[25] , and also in municipal wastewater[23, 26]. Terrestrial boron derived from water-rock-interaction explains the much more negative value of -15.9‰ encountered in the Great Artesian Basin[7]. The new lowest δ^{11}B ever measured in the hydrosphere is -29.7‰ from groundwaters in a clastic Neogene graben filling in NW Macedonia, Greece, affected by natural CO_2-seepage, with heterogeneous lithology including carbonates, lignite, schists, gneiss as well as some ultramafic volcanic rocks[27]. Even if lignite (as well as other coals) can contain very ^{11}B-depleted boron (-21.3‰ measured for lignite kerogen)[5], water-rock interaction with the ultramafic minerals are the most likely explanation of both the extremely depleted B and Li isotope ratios[28, 29].

4. Conclusion

Extreme positive δ^{11}B in natural waters can be attributed to the selective affinity of clay minerals and other sorbents for the ^{11}B-depleted borate ion. Rayleigh-like fractionation processes in an open system, with constant renewal of the contact of marine B-bearing fluids with sorbents, e.g. during active saline intrusion, can lead to ^{11}B-enrichment beyond +60‰ but under very specific conditions in a limited range of dilution (i.e. dissolved B-sorbent ratio), pH, salinity so that extremely high δ^{11}B values have been observed only rarely and in limited zones. Negative δ^{11}B are exclusively due to (non-fractionating) dissolution of aquifer material itself strongly depleted in ^{11}B (magmatic or volcanic rocks, certain terrestrial borates, and coals).

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