Boron in groundwater of the Atlantic Coastal Plain, USA: A mechanism for elevated B and ^{11}B enrichment

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During seawater (SW) intrusion, B is typically adsorbed to clays and groundwater acquires B/Cl ratio < B/Cl_{SW}. The ^{11}B-depleted $B(OH)_4^-$ species is preferentially adsorbed relative to $B(OH)_3$ [1], so B adsorption leaves groundwater ^{11}B-enriched [2]. Conversely, B desorption during freshening typically results in $B/Cl > B/Cl_{SW}$ and $\delta^{11}B < \delta^{11}B_{SW}$.

Previously we reported $\delta^{11}B$ in groundwater from the Pliocene Yorktown (YT) aquifer in coastal North Carolina (0.6-280 mM Cl^- and 0.01-0.24 mM B) [3]. Here we present $\delta^{11}B$ results in groundwater from the Cretaceous Cape Fear (CF) aquifer (0.1-132 mM Cl^- and 0.03-0.61 mM B). In both aquifers, $B/Cl > B/Cl_{SW}$ (0.004-0.26 vs. B/Cl_{SW} of 0.0008). In YT, $\delta^{11}B < \delta^{11}B_{SW}$ (20.9-34.7‰$_{NBS951}$ vs. $\delta^{11}B_{SW}$ of 39‰) and $\delta^{11}B$ is negatively correlated with B/Cl, expected for desorption of SW-derived boron from marine clays [3].

$\delta^{11}B$ in CF was 8.5-51.8‰. Although $\delta^{11}B$ is negatively correlated with B/Cl in CF, many samples imply B release ($B/Cl > B/Cl_{SW}$) *and* ^{11}B enrichment ($\delta^{11}B > \delta^{11}B_{SW}$). This is inconsistent with desorption of SW-derived B during freshening and implies a B source with $\delta^{11}B \geq$ ~50‰. SW paleo-reconstructions [4,5] suggest that $\delta^{11}B_{SW}$ has not varied as much since the Cretaceous to explain the CF values.

Explanations for $B/Cl > B/Cl_{SW}$ and $\delta^{11}B > \delta^{11}B_{SW}$ may include: (a) The B could be derived from marine brine, which is inconsistent with the formation history and the composition of the water; or more likely (b) Desorption could have occurred at slightly lower pH than adsorption. Over repeated sea level fluctuations coupled with pH modification during water-rock interaction, adsorbed B would become ^{11}B-enriched because fractionation between adsorbed and dissolved B is larger at lower pH and K_d is smaller at lower pH [1]. $\delta^{11}B$ may improve our understanding of the evolution of Na-rich, fresh to brackish coastal plain groundwater and may distinguish recent from ancient seawater intrusion.

[1] Palmer et al. (1987) *Geochim. Cosmochim. Acta* **51**, 2319-2323. [2] Vengosh et al. (1994) *Environ. Sci. Technol.* **28**, 1968-1974. [3] Vinson et al. (2011) *Hydrogeol. J.* **19**, 981-994. [4] Lemarchand et al. (2002) *Chem. Geol.* **190**, 123-140. [5] Simon et al. (2006) *Chem. Geol.* **225**, 61-76.