# Boron incorporation in synthetic calcite and aragonite revealed by B isotopes and $^{11}$B MAS NMR

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Boron isotopes measurements in marine carbonates are used as a proxy of the paleo-pH of the oceans. The reliability of these pH reconstructions lies in our understanding of the mechanisms of boron incorporation in carbonates. The paleo-pH calculations are based on the assumption that one of the two boron species in solution (borate $B(OH)_4^-$) is preferentially incorporated in calcium carbonates [1],[2]. Experiments show that there is a shift between expected and measured boron isotopic ratios ($\delta^{11}B$) at a given pH, which is attributed to the specifics of boron incorporation in biological organisms ("vital effect").

In order to better understand the mechanisms of boron incorporation in carbonates and by comparison, the modifications induced by vital effects, we carried out inorganic precipitation experiments of calcite and aragonite in NaCl solutions of wide-ranging pH values and at temperatures of 25°C and 5°C. Boron isotopic compositions of the carbonates were then measured by MC-ICP-MS and the proportions of trigonal and tetragonal B by $^{11}$B MAS NMR.

Our results confirm that the boron isotopic ratio of the carbonates is dependent upon the growth solution pH, but also upon crystal type and temperature. In calcite, both NMR and boron isotopic composition show that boron incorporation is not consistent with the single incorporation of the aqueous borate species $B(OH)_4^-$. Moreover, the NMR measurements show that the proportion of trigonal boron ($BO_3$) in calcite is higher than what is inferred from the isotopic signal by assuming that both boron aqueous species are incorporated in the carbonate. In aragonite, $BO_3$ is present in smaller proportions depending on pH and both NMR measurements and $\delta^{11}B$ are in good agreement with the hypothesis of the preferential incorporation of the borate species in calcium carbonates .

[1] Hemming and Hanson (1992) *Geochim et Cosmochim Acta* **56,** 537-543. [2] Vengosh et al. (1991) *Geochim et Cosmochim Acta* **55**, 2901-2910.

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# As, Sb, Mo, V, W, and Se oxyanions in Yellowstone's thermal waters

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Concentrations of As, Sb, Mo, V, W, and Se have been determined in hundreds of water samples from thermal features in Yellowstone National Park and from the Firehole and Gibbon River systems. Analytical methods include ICP-AES, ICP-MS, HGAAS, and GFAAS. Selenium is consistently less than 1 µg/L everywhere, V is often below detection up to 130 µg/L, Mo occurs up to 360 µg/L, Sb up to 370 µg/L, and As up to 14,600 µg/L. Concentrations of W are limited but generally similar to or a bit higher than those of Sb and Mo.

Arsenic concentrations are typically 0.5 to 3 mg/L but they are highest in Norris Geyser Basin waters, especially in the western part of the basin. This area seems to have accumulated arsenic through precipitation of considerable orpiment and realgar at low pH at or just below the ground surface. One pair of springs demonstrate remarkable mixing between two end-member compositions, a near neutral pH high-As and high-Cl water and a low-As, low-Cl acid water. This range of composition can explain the variable water compositions for many waters occurring in Norris Basin. Most waters exhibit a linear relation of As concentrations relative to Cl concentrations suggesting that arsenic is largely conservative and tends to stay with the aqueous fluid during boiling and dilution. More surprising, arsenic concentrations are not attenuated during 20-30 miles of river drainage. The Gibbon River maintains more than 100 µg/L dissolved As and the Firehole River increases to more than 400 µg/L in the lower reaches. The most likely hypothesis is that the high silica concentrations in the thermal waters precipitate in the river and coat the river bed sediments, decreasing its sorption capacity. There is also very little Fe in the overflows.

A complicating factor for speciation of As, Sb, Mo, and W is the formation of thio-complexes which have been explored for As and Sb but not for Mo and W. Such complexes may help to explain their mobility under reducing conditions.

Concentrations of Sb and Mo tend to track with As, with the highest concentrations occurring with the highest Cl concentrations but there is much more scatter in the data. For the Gibbon and Firehole Rivers, Sb and Mo concentration profiles are strikingly similar showing no attenuation. One anomaly occurs in the Gibbon River profile. A substantial inflow of Mo enters from Terrace Spring just before the convergence of the Gibbon with the Firehole. These trace elements are indicative of the deep geothermal reservoir composition and not greatly affected during transport to the surface.

Concentrations of V behave very differently from the other oxyanions; they are below 10 µg/L for nearly all Cl concentrations above 200 mg/L. Higher concentrations are only found in acid waters of low Cl concentration, regardless of temperature. These results suggest that V is dominantly derived from acid weathering of near surface rocks. Furthermore, V is the element in this group that forms a cation under reduced conditions which also helps to explain its higher concentration in acidic waters.

Both similar and dissimilar trends in these trace elements can be demonstrated. The biggest dissimilarity is the lack of any correlation for V with the other elements. The other elements generally behave similarly with the exception of some local anomalies. When thermal overflows enter river systems there is little to no attenuation likely because of continual silica precipitation and the lack of hydrated iron oxides.