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Models of Secular Evolution of the Boron Isotopic Ratio in the Oceans: Implications for Oceanic Paleo-pH Reconstruction

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Changes of chemical composition of the oceans and long-term climate change are believed to be associated. In particular, the secular evolution of the oceanic pH is desirable as it may be related to the atmospheric pCO_2, and hence temperature (Goddéris and Francois, 1996; Berner, 1997; McCauley and DePaolo, 1997). The boron isotopes fractionation between seawater and carbonate being pH-dependent, their use has been proposed as a proxy for reconstructing the pH variations in the oceans (Vengosh et al., 1991; Hemming and Hanson, 1992). Nevertheless, deduce pH values from boron isotopic ratio in carbonates in only possible if the boron isotopic ratio of the oceans (noted $\delta^{11}B_{sw}$) is known when carbonate precipitated. To date, in the absence of independent data, paleo-pH is reconstructed taken as hypothesis that the isotopic composition of the oceans remained strictly constant through time. Although a number of previous works have led to the identification of the main processes affecting boron in the oceans, the boron oceanic cycle is still poorly constrained. The oceanic boron sinks are divided in three parts: uptake during low temperature weathering of the oceanic crust, adsorption on sediment and co-precipitation in carbonates. We have determined both the boron concentration and the boron isotopic ratio of 22 of the world's largest rivers, and deduced a total boron continental input of 38.10^{10} gB/yr with a mean isotopic composition of 10‰. This result shows that about 85% of the boron flux to the oceans is the continental input. Leading to a balanced boron oceanic budget, we then focused on the potential variations of $\delta^{11}B_{sw}$ through time. As the secular evolution of the riverine input is poorly constrained, three scenarios are presented and lead to a typical rate of boron isotopes change in the oceans of 0.1‰ (see Figure 1). The major consequence is that, with analytical errors of about 0.3‰, the hypothesis of $\delta^{11}B_{sw}$ remaining strictly constant through time is not tenable longer than 3 Myr. Calculation of seawater pH requires therefore reconstruction of $\delta^{11}B_{sw}$ for more ancient ages.

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