



## 20th century acidification of the Caribbean Sea reflected in sclerosponge proxy records

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Atmospheric CO<sub>2</sub> increased during the 19th and 20th century by 90 ppm. This increase is mainly due to the anthropogenic CO<sub>2</sub> production from fossil fuel combustion and deforestation. As the source of this CO<sub>2</sub> is organic carbon, the atmospheric increase in pCO<sub>2</sub> is paralleled by a decline of the δ<sup>13</sup>C of CO<sub>2</sub> (Suess effect). About one third of the released CO<sub>2</sub> is taken up by the oceans (IPCC 2001). In the oceans CO<sub>2</sub> reacts with water to form carbonic acid, leading to a decline in the surface ocean pH (Raven et al. 2005). It is expected that this pH change will lead in the long term to a CaCO<sub>3</sub> undersaturation of parts of the surface oceans, with major consequences for benthic (tropical and cold water reefs) as well as pelagic carbonate producers (Orr et al. 2005).

Most of these predictions are based on models and on observations made since the 1970s. Only few pH reconstructions based on proxy records are available that go back to preindustrial times: Böhm et al. (2000) measured δ<sup>11</sup>B in a Caribbean sclerosponge and found indications for an industrial pH decline. Pelejero et al. (2005) found significant interdecadal pH variations but not the expected acidification trend in a δ<sup>11</sup>B coral record from the tropical Pacific. So far, no proxy records of the carbonate ion concentration in surface ocean waters exist. Reaction of CO<sub>2</sub> with CO<sub>3</sub><sup>-</sup> is the cause of the expected decline in ocean CaCO<sub>3</sub> saturation. Therefore, CO<sub>3</sub><sup>-</sup> concentration may be more relevant for calcifying marine organisms than pH. Recent investigations of Lemarchand et al. (2004) showed that calcium isotopes may be a good proxy for marine CO<sub>3</sub><sup>-</sup> concentrations. Therefore, combined boron (δ<sup>11</sup>B) and calcium (δ<sup>44</sup>/40Ca) isotope records may allow to reconstruct both the pH and saturation history of a marine site.

We therefore measured  $\delta^{11}\text{B}$  and  $\delta^{44}/^{40}\text{Ca}$  in aragonitic skeletons of the tropical sclerosponge *Ceratoporella nicholsoni* from the Caribbean Sea (Pedro Bank, Jamaica). Carbon isotope and Sr/Ca records are available from the same specimens (Böhm et al. 2002; Haase-Schramm et al. 2003). The  $\delta^{11}\text{B}$  values show significant scatter (ca. 2 permill), compatible with the observations of Pelejero et al. (2005), but also display a clear decline (-1.3 permill) from the early 19th to the late 20th century. The  $\delta^{11}\text{B}$  decline is equivalent to a pH decrease of about 0.1 units. This value is in the range of pH decline expected for the  $\text{pCO}_2$  increase of 50 ppm during the same period (Etheridge et al. 1996). Moreover, the  $\delta^{11}\text{B}$  trend correlates well with the  $\delta^{13}\text{C}$  decline measured in the same sponges (Suess effect).

The corresponding decrease of the carbonate ion concentration should be reflected in a 0.1 permill decrease of  $\delta^{44}/^{40}\text{Ca}$ . However, the measured data show no significant trend and limit the possible change to less than +0.11/-0.07 permill (95% confidence level). Taking into consideration that Sr/Ca records from the same sponges show a temperature rise of 3 K over the same time period, this discrepancy can be explained: The increasing temperature slightly amplifies the pH decline, but at the same time reduces the  $\text{CO}_3^-$  decline. Additionally the temperature effect on  $\delta^{44}/^{40}\text{Ca}$  leads to an increase of the isotope values. Together these effects would result in a calcium isotope increase of 0.03 permill, which is too small to be resolved with the available data.

We conclude that the anthropogenic surface water pH decline resulting from the rising atmospheric  $\text{pCO}_2$  can be reconstructed with boron isotope records from sclerosponges. On the other hand, the corresponding decline of the carbonate ion concentration in Caribbean surface waters is probably offset by rising temperatures and is still too small to be measured with calcium isotopes.

References: Böhm et al. (2000) EOS Trans. AGU, 81, Fall Meet. Suppl.; Böhm et al. (2002) *Geochem. Geophys. Geosys.*, 3(3), 10.1029/2001GC000264; Etheridge et al. (1996) *J. Geophys. Res.*, 101, 4115-4128; Haase-Schramm et al. (2003) *Paleoceanography*, 18(3), 1073, doi:10.1029/2002PA000830; IPCC (2001) *Climate Change 2001*, Cambridge University Press, Cambridge; Lemarchand et al. (2004) *Geochim. Cosmochim. Acta* 68, 4665-4678; Orr et al. (2005) *Nature* 437, 681-686; Pelejero et al. (2005) *Science* 309, 2204-2207; Raven et al. (2005) *Ocean acidification due to increasing atmospheric carbon dioxide*. Royal Society Policy Document 12/05