

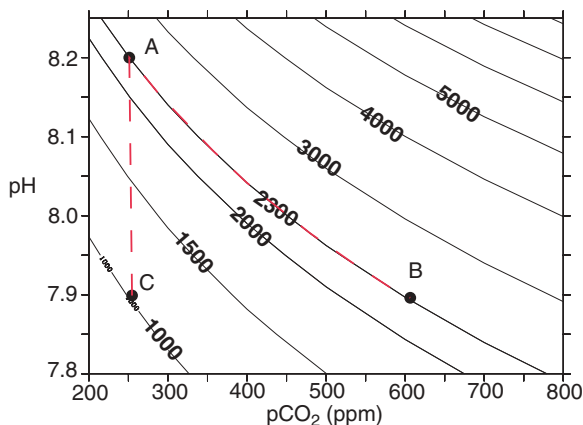
# Comment on “Preindustrial to Modern Interdecadal Variability in Coral Reef pH”

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Based on the boron isotopic composition of coral from the southwestern Pacific, Pelejero *et al.* (Reports, 30 September 2005, p. 2204) suggested that natural variations in pH can modulate the impact of ocean acidification on coral reef ecosystems. We show that this claim cannot be reconciled with other marine carbon chemistry constraints and highlight problems with the authors’ interpretation of the paleontologic data.

Pelejero *et al.* (1) analyzed the boron isotope composition of *Porites* coral from the southwestern Pacific and reported large interdecadal variations in pH (between 7.9 and 8.2) with a strong periodicity of about 50 years. This implies that natural pH variability in the ocean is greater than pH variation attributed to anthropogenic factors (a decrease of 0.1 pH units since 1880). (2). Pelejero *et al.* argue that the implied natural pH variability cannot be associated with variations in either sea surface temperature (SST) or sea surface salinity (SSS). Instead, they attribute the pH variation to “coral reef calcification combined with limited flushing of reef water exerting an important local control over the buildup of partial pressure of CO<sub>2</sub> (P<sub>CO2</sub>) within the reef.” However, they do not calculate the implied P<sub>CO2</sub> magnitude associated with such a large pH change. If we use the observed water properties (SST = 25°C, SSS = 35.3) and the authors’ assumption of constant alkalinity (2300 μmol/kg), the range in pH implied from their boron isotope measurements must be associated with interdecadal P<sub>CO2</sub> variations between 250 and 600 parts per million (ppm) (Fig. 1, points A and B). Because preindustrial atmospheric P<sub>CO2</sub> values were about 280 ppm, the inferred estimate of pH range implies that P<sub>CO2</sub> within the seawater of the coral reef was maintained at levels up to double that of the atmosphere for a decade. However, this interpretation is unrealistic for two reasons. First, the

equilibration rate of CO<sub>2</sub> for the ocean is less than 1 year, and even shorter for very shallow reef environments where the observations in (1) were



**Fig. 1.** Contour plot of alkalinity (μmol/kg) as a function of pH and P<sub>CO2</sub>. Points A to B denote the trajectory for reproducing the observed pH change but maintaining a constant alkalinity of 2300 μmol/kg as assumed in (1). Points A to C denote the trajectory for reproducing the observed pH change but maintaining constant P<sub>CO2</sub> as required to satisfy the physical constraint that the seawater would equilibrate with the atmosphere in less than 1 year. The figure demonstrates that an alkalinity change from 2300 μmol/kg to 1000 μmol/kg is required to reproduce the observed pH change but maintain a P<sub>CO2</sub> value close to the initial value at point A.

collected. The implication that P<sub>CO2</sub> can build up over 300 ppm beyond the atmospheric concentration on a decadal time scale is not possible because exchanges of CO<sub>2</sub> with the atmosphere would bring the P<sub>CO2</sub> of the water back to a value that is in equilibrium with the atmosphere. Second, if P<sub>CO2</sub> were to experience such large variations as suggested by the pH changes, this would drive large changes in air-sea flux of CO<sub>2</sub>. Such changes would in turn alter the isotopic composition of dissolved inorganic carbon (δ<sup>13</sup>C-DIC) because the air-sea flux process fractionates <sup>12</sup>CO<sub>2</sub> preferentially relative to <sup>13</sup>CO<sub>2</sub> (3). Therefore, we would expect to find

clear correspondence between the interdecadal variability in the calculated pH and the observed δ<sup>13</sup>C-DIC, which is not the case.

Alkalinity changes could potentially account for the large pH variations reported by Pelejero *et al.* However, to satisfy the implied pH variations would require an interdecadal change in alkalinity from 2300 μmol/kg to 1000 μmol/kg (Fig. 1, points A and C). These alkalinity changes are unreasonably large given that the typical variations within the studied section of the Great Barrier Reef are only about 40 μmol/kg (4, 5). Other studies on coral reefs in the Indo-Pacific show maximum alkalinity variability of 100 μmol/kg (6, 7), far less than the 1300 μmol/kg that is required over decadal periods in the Pelejero *et al.* study. Calcification is the main process that reduces alkalinity of seawater around the reef, but the calcification rates of the corals used to estimate the pH in (1) do not show any correlation with the pH variations. Further, empirical studies of coral reef calcification show declines in calcification as the pH declines (8), which is counter to the trend required to produce the inferred pH variability. Therefore, explaining the large pH variability in terms of changes in alkalinity also appears unrealistic.

Ocean acidification is clearly a threat to coral reef ecosystems, and the implication of the Pelejero *et al.* study is that these ecosystems are subject to large natural variations in pH. This interpretation has important implications for assessing the response of coral reefs to future ocean acidification. Although boron isotopes have been shown to be a useful pH proxy, our carbon chemistry calculations show that the Pelejero *et al.* interpretation of the paleontologic data suggesting large decadal changes in pH is not consistent with acceptable changes in either P<sub>CO2</sub> or alkalinity. This ultimately casts doubt on the notion that corals have already undergone such large natural variations in pH and are capable of adapting to the pH changes projected to occur over this century.

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