

# Response to Comment on "Preindustrial to Modern Interdecadal Variability in Coral Reef pH"

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Coral reefs are exceptional environments where changes in calcification, photosynthesis, and respiration induce large temporal variations of pH. We argue that boron isotopic variations in corals provide a robust proxy for paleo-pH which, together with the likely concomitant changes in the reconstructed partial pressure of CO<sub>2</sub> (*P*CO<sub>2</sub>) calculated by Matear and McNeil, fall within ranges that are typical of modern coral reef ecosystems.

Matear and McNeil (1) recognize the usefulness of boron isotopes in corals to record changes in seawater pH but question our pH reconstruction (2) for three reasons. First, they suggest that the reconstructed pH variability (7.9 to 8.2 units) is unreasonably large, because it would imply variations in *P*CO<sub>2</sub> and alkalinity that are unrealistic. Second, they question whether such large changes in *P*CO<sub>2</sub> could have been maintained for decades. Third, they argue that had these *P*CO<sub>2</sub> changes persisted, that large variability in the air-sea flux of CO<sub>2</sub> would have altered the δ<sup>13</sup>C-DIC (dissolved inorganic carbon) values and that this should be reflected in the coral skeleton δ<sup>13</sup>C.

As stated in (2), the pH variability of our reconstruction represents Flinders Reef seawater, not the open ocean. Local pH values can change considerably, especially within coral reefs where changes in calcification, photosynthesis, and respiration have been shown to induce large variations of pH over diurnal and seasonal time scales. Yates and Halley (3) reported diurnal pH changes from 7.82 to 8.42 units in a Molokai reef flat, with associated ambient seawater *P*CO<sub>2</sub> values of 170 to 935 μatm. Ohde and van Woesik (4) found diurnal changes of up to 0.7 pH units in a coral reef atoll close to Okinawa, with concomitant changes in *P*CO<sub>2</sub> of 100 to 900 μatm. Suzuki *et al.* (5) reported diurnal variations of up to 1 pH for a stagnant

coastal reef, and Schmalz and Swanson (6) reported diurnal changes of about 0.15 pH units for the Enewetak atoll, an open-ocean reef similar to Flinders Reef. This latter variation is similar to the seasonally resolved change observed in Flinders Reef, based on our high-resolution coral δ<sup>11</sup>B data [figure 2C in (2)].

Matear and McNeil (1) estimated associated *P*CO<sub>2</sub> changes in Flinders Reef water using the assumption of constant alkalinity and obtained variations between 250 and 590 parts per million, which they considered unrealistic. However, if the buildup of reef-water CO<sub>2</sub> due to calcification is a main mechanism for pH variation, alkalinity will decrease to some extent during the low reef-water pH periods, rendering the assumption of constant alkalinity invalid. Nevertheless, even this wide range of *P*CO<sub>2</sub> values falls within the range commonly encountered in reef systems (3–7). In addition to calcification, the buildup of CO<sub>2</sub> from respiration will play a key role in decreasing pH during periods of poor flushing of reef waters. These factors, combined with possible oceanographic changes in the open-ocean water masses bathing the reef, hinder the calculation of the whole set of seawater carbonate system parameters based on boron isotope-inferred pH data alone.

Matear and McNeil also claim that the high levels of *P*CO<sub>2</sub> in Flinders Reef could not be maintained for decades assuming an air-sea equilibration rate of less than 1 year for CO<sub>2</sub>. We agree that reef-water pH at Flinders is likely to vary on shorter time scales, but the 5-year resolution of the coral paleo-pH record averages any diurnal to seasonal variability. Even during high-*P*CO<sub>2</sub> (low pH) multidecadal periods, *P*CO<sub>2</sub> in Flinders reef water may have periodically reached lower values closer to global atmospheric levels. On the other hand, coral reef systems that are not dominated by algae, like Flinders Reef, are known to be sources of atmospheric CO<sub>2</sub> because the release of CO<sub>2</sub> from coral calcification is greater than that fixed by photosynthesis (8, 9). Therefore, we maintain

that the effects of progressive acidification of the oceans are likely to differ between coral reefs because reef-water *P*CO<sub>2</sub> and consequent changes in seawater pH will rarely be in equilibrium with the atmosphere.

Finally, Matear and McNeil note that large changes in the air-sea flux of CO<sub>2</sub> would alter the 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>. However, the air-sea equilibration time for carbon isotopes is about 10 years (10), which is 10 times as long as for CO<sub>2</sub> itself. Furthermore, coral skeletal δ<sup>13</sup>C has proven to be a complex nonunique environmental tracer because of complicated interactions that involve strong isotopic fractionation including photosynthesis, respiration, skeletal calcification, and the changing balance between heterotrophy and autotrophy (e.g., 11–15). The sum of these influences on coral δ<sup>13</sup>C could easily mask the effect of any change in δ<sup>13</sup>C of DIC brought about by air-sea fluxes of CO<sub>2</sub>.

In summary, the arguments proposed by Matear and McNeil are based exclusively on open-seawater behavior of carbon system parameters. By contrast, our reconstruction focuses on seawater properties of a coral reef, where local processes can induce large variations in pH. Our study (2) clearly demonstrated the potential of boron isotopes in massive coral skeletons to contribute to our understanding of how the world's coral reefs will respond to future ocean acidification. Given that instrumental records of seawater pH exceeding a single decade are not yet available, the boron isotopic composition of long-lived corals currently offers the only practical means to determine such changes back through time.

## References

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