Argon Isotopic Composition of Marine Biogenic Carbonates and Implications for Tracking the Secular Variation of the Atmosphere through the Phanerozoic

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Degassing of the solid Earth has had a profound effect on Earth’s atmosphere. Ar comprises nearly 1% of the modern atmosphere and is dominated by radiogenic 40Ar produced by K decay, with an isotopic abundance of 99.6% (40Ar/36Ar ~ 300). The monotonic increase in atmospheric 40Ar/36Ar resulting from degassing means that Ar measurements from geological reservoirs can be used for dating old ice in Antarctica and for better constraining Earth’s degassing history. Highly precise isotopic measurements from ice cores documented a 0.006%/Myr rate of increase over the last 800 ka [1]. This rate is consistent with results from the Devonian Rhynie Chert [2] and from ~3 Ga hydrothermal quartz [3]. Additional reservoirs are needed to refine the record between the Quaternary and the early Paleozoic, but many potential reservoirs are compromised by mixing with the modern atmosphere and by in situ production of 40Ar. We test the applicability of independently-dated marine biogenic carbonates as paleo-atmospheric Ar archives.

We measured modern corals and fossil corals and brachiopods that were previously screened for alteration using an Isotopx NGX-600. We obtained 40Ar/36Ar isotope ratios for modern corals that are consistent with the modern atmosphere. Measurements have a precision of 0.05% (1σ) for 40Ar/38Ar and 0.08% (1σ) for 40Ar/36Ar on 6e-13 to 2e-11 moles of Ar. The Ar concentration of fossil and modern marine biogenic carbonates is 2e-11 to 4e-11 moles/gram. In order to obtain the paleo-atmospheric Ar composition from fossil biogenic carbonates, measurements require a correction for the in-situ production of 40Ar. High-precision K measurements are pending, but the Ar data suggest small 40Ar production corrections that are consistent with a range of 14-200 ppm K, as reported in modern biogenic carbonates [4]. These measurements suggest a great deal of potential for using fossil marine carbonates to constrain Earth’s degassing and atmospheric Ar isotope evolution history.

[4] Li et al. (2021), GCA 304, 364-380.