Interpreting the Ca isotopic signal of ocean acidification in the rock record

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The Ca isotope proxy (δ^{44}Ca) has been applied recently to the interpretation of changes in the global Ca cycle associated with significant events in the geologic past, such as mass extinctions and widespread ocean anoxia. Ocean acidification, in particular, has been cited as the primary driver of changes in sedimentary δ^{44}Ca. Such an interpretation, however, appears to be ambiguous, complicated, and/or poorly understood, as it has been used to explain both transiently increasing and decreasing values of sedimentary δ^{44}Ca.

We propose a complementary approach to the identification of ocean acidification events in the rock record, and suggest that such events should be accompanied by the formation of authigenic carbonate in the sedimentary column. This signal has the potential to be both large and ubiquitous in the global ocean. This proposed approach is predicated on: (1) the fact that Ca isotopic fractionation associated with diagenetic $CaCO_3$ formation is ~0‰ (i.e., producing $CaCO_3$ that is ~2‰, distinct from the typical 0.6‰ $CaCO_3$ derived from the surface ocean), and (2) field and model-based observations that ocean acidification events on an Earth with a silicate weathering feedback induce a prolonged deepening of the CCD during the recovery phase. This hypothesis is supported by recent measurements of bulk sediment δ^{44}Ca over the Paleocene-Eocene Thermal Maximum (PETM), which indicate sizeable (>0.5‰) shifts in the δ^{44}Ca of bulk carbonate sediments at two ODP sites over the PETM [1]. Such shifts in δ^{44}Ca are large compared to the Ca isotope signals currently being interpreted (<0.3‰).

An Earth system model of intermediate complexity (GENIE; http://www.seao2.info/mycgenie.html) is used to evaluate the possibility of a significant authigenic component associated with ocean acidification events. The output from simulations is used to: place the previously reported PETM data in context, evaluate the spatial extent of the signal, and suggest length scales over which the signal may be present in the rock record. Such constraints are critical both to understanding the utility of the proxy tool and to proposing sampling schemes for finding such signals in the rock record.

[1] Griffith, Fantle, Eisenhauer, Paytan, and Bullen, (2015). *Earth Planet Sci Lett* **419**, 81-92