

## What regulated organic carbon preservation in coastal oceans through the Paleocene-Eocene thermal maximum?

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Climatic recovery from the Paleocene-Eocene boundary thermal maximum (PETM) involved a rapid burial of thousands of petagrams of carbon, a significant fraction of which may have been sequestered in marginal marine sediments. This burial flux may have been modulated by changes in climate, biology, sea level, and sediment flux, but the primary pathways and controls on excess carbon burial have remained speculative to this point. We use the global carbon isotope excursion at the PETM as a tracer of organic carbon input to three coastal ocean sites (Tawanui, New Zealand; IODP leg 302, Arctic Ocean; and Wilson Lake, NJ, USA). We show that sedimentary OC can be partitioned into two distinct pools: biologically- and chemically-resilient particulate material (POC), and relatively nitrogen-rich compounds stabilized through association with mineral surfaces (MBC). In addition, we observed that elevated PETM OC burial was dominated by POC, in contrast to the suggestion by Kennedy *et al.* [1] that mineral stabilization OC has primary role in coastal OC burial. Approximately 80% of OC buried at sites with high sediment accumulation rates was recently photosynthesized POC, constituting a direct sink for atmospheric CO<sub>2</sub>. Carbon burial as MBC supported a more uniform, less dynamic flux across the study sites. Data from Arctic Ocean sediments suggest that regional bottom-water anoxia during the PETM reduced the selectivity of OC preservation via these mechanisms, promoting higher, more ubiquitous OC burial. Our results demonstrate that coastal OC burial during the PETM was regulated by decoupled and heterogeneous responses of the POC and MBC pathways, but that burial modes and dynamics were closely linked to sediment accumulation rate and bottom water oxygenation.

[1] Kennedy, Pevear & Hill (2002) *Sci.* **295**, 657-660.

## A new method integrating ID-TIMS U-Pb geochronology with zircon trace element analysis

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U-Pb zircon geochronology by high-precision isotope dilution thermal ionization mass spectrometry (ID-TIMS) has revealed that it is common for zircons within magmatic rocks to crystallize over  $>10^5$  years. Interpreting such data in terms of emplacement or eruption processes is aided by analyzing zircon chemistry. Combining trace element zircon data directly with U-Pb dating, however, has so far been restricted to low-precision *in situ* dating techniques.

We developed a method in which the chemical constituents of dissolved zircon used for ID-TIMS U-Pb dating are analyzed on the same volume of zircon using solution nebulization ICP-SFMS with matrix-matched external liquid calibration. U and Pb are routinely separated from the other elements in zircon by ion exchange chromatography prior to TIMS isotope measurement. Here, we retain separated elements including Hf, Y, Sc, Nb, Ta, and the REE in  $< 1$  ml solution, resulting in concentrations between 1 and  $>10^4$  ppt. Careful preparation and analysis of standard solutions and procedural blanks enables accurate measurement of these elements to  $\geq 10$  ppt in the solutions. However, fractionation of these elements (except the REE) during chromatography requires correction. We show that REE patterns are accurately reproduced by this method.

Application of this method to a suite of samples from the ca. 40-30 Ma Adamello batholith, northern Italy, reveals significant differences in REE patterns between zircons from different pulses of magma and also within single samples. We can use Ce/Ce\* and Eu/Eu\* in these zircons to 1) track the oxidation state of different parts of the magmatic system as a function of time, and 2) identify the changing role of plagioclase fractionation in an evolving magmatic system. This improves our understanding of magmatic systems as a function of time and also aids in identifying xenocrystic, antecrystic and autocrystic zircons and thus interpreting high-precision datasets accurately. This method has wide-spread application in ID-TIMS geochronology of magmatic and metamorphic rocks on numerous accessory minerals.