Greenhouse gas driven hyperthermals of the Paleogene: How much carbon, how fast?

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Terrestrial and marine deposits from the early Cenozoic record a 55 million year old transient warming of the Earth's surface, dubbed the 'Paleocene/Eocene Thermal Maximum' (PETM). The occurrence of a prominent carbon isotopic excursion indicates massive release to the ocean and atmosphere of CO_2 and/or CH_4, thought to be similar in magnitude to current fossil fuel reserves. The PETM thus represents a potentially compelling analogue candidate for future greenhouse gas driven global change. In particular, understanding this event could provide us with invaluable insights into key mechanisms of feedback between climate and global carbon cycling as well as what the long-term impacts on calcifying plankton and animals of surface ocean 'acidification' might be. However, the parallels that can be drawn with anthropogenic climate change hinge critically on the magnitude and time-scale of the greenhouse gas forcing of this hyperthermal event.

Here we apply an Earth system model (GENIE-1) to the interpretation of the marine geologic record of the PETM and tackle the question of what the rate and total input of carbon to the ocean and atmosphere might have been.

Surface structural modeling at the solid-solution interface of nanocrystalline anatase

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To begin to assess the effects of particle size on the surface reactivity and charging of metal-oxide nanoparticles in aqueous solutions comprehensive experimental and characterization studies were completed. Commercially available crystalline anatase (TiO_2) particles were used in the study. Particle size ranged from 200 to 3 nm diameter, with corresponding BET surface areas of 10 to 350 m^2/g, respectively. Potentiometric and electrophotetic mobility titrations of the anatase samples were performed in NaCl media at ionic strengths from 0.005 to 0.3 molality, at 25°C. All samples were characterized extensively; using electron microscopy and aberration corrected electron microscopy (ACEM), neutron and X-ray small-angle scattering, and laser diffraction techniques.

A principle parameter obtained from the surface titration studies was the pH_{znpc} value. The pH_{znpc} of 40 nm diameter anatase particles ($pH_{znpc} = 6.22$) corresponded closely to previously published values; whereas, the pH_{znpc} value of 3 nm particles was higher ($pH_{znpc} = 6.90$). Furthermore, the development of positive surface charge was enhanced for larger anatase nanoparticles (>20 nm) over 3 nm diameter particles; in spite of this, the overall development of negative surface charge, relative to the respective pH_{znpc} values, was approximately the same for all particles sizes studied. At high ionic strengths the apparent pH_{znpc} value of the 3 nm particles was offset slightly toward lower pH values, which suggests some specific adsorption of the Na^+ electrolyte ions.

Surface complexation modeling (SCM) was completed to rationalize the bulk surface titration data. The SCM's incorporate all available molecular information (e.g., Ti-O bond lengths), with crystallographic information acquired from the ACEM. ACEM imaging revealed that the [100] face predominates on the 20 nm particles, and edges/facets include [010], [001], and [0-11]. A MUSIC model description of surface protonation permitted rationalization of the decrease in pH_{znpc} values with increasing particle size. Additionally, a Stern-layer representation of the EDL, and inner-sphere adsorption geometry of the electrolyte cation were also accounted for.