

Interactive comment on “Methane release from gas hydrate systems during the Paleocene-Eocene thermal maximum and other past hyperthermal events: setting appropriate parameters for discussion” by G. R. Dickens

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Dear Lee,

Thank you for the comments (as always).

I absolutely agree with the first set of generic comments. I think the community at large has generally neglected to frame the PETM and other short-term negative carbon isotope anomalies of the early Paleogene within the context of the long-term carbon (and sulfur) isotope variations. I tried to note this (Dickens, EPSL, 2003); you independently

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nailed the topic much better (Kurtz et al., *Paleoceanography*, 2003). For reasons unknown, very few people have picked up and pursued this idea in the last 8+ years. (The same is true with other time intervals marked by prominent negative carbon isotope anomalies).

It seems to me highly unlikely that enormous amounts of ^{13}C -depleted carbon were stored somewhere on Earth's surface for 3 Myr (as indicated by the $\sim+1$ per mil late Paleocene rise in $\delta^{13}\text{C}$), that following this a slow release of ^{13}C -depleted carbon occurred (as indicated by the ~-2 per mil late Paleocene drop in $\delta^{13}\text{C}$), that superimposed on this template was a series of rapid releases and sequestrations of ^{13}C -depleted carbon (as indicated by the CIEs and recoveries of the early Eocene hyperthermals), and that the three phenomena were not related. Equally important, as you all first emphasized, it would seem highly serendipitous to suggest that major changes in carbon and sulfur isotopes are completely disconnected. In other words, I think your idea (Kurtz et al., 2003) of storing massive amounts of organic carbon without sulfur somewhere during the late Paleocene and releasing portions of this organic carbon during the early Eocene, sometimes sporadically, all the while during the early Eocene generating Fe sulfides, is beautiful and probably correct.

I would argue, however, that coal deposition is indeed a red herring, at least in terms of carbon cycling. Consider the mass balance. The world's proven coal reserves (from strata throughout the Phanerozoic) are on the order of 2000 Gt C. Your modeling to explain the pronounced positive $\delta^{13}\text{C}$ excursion of the late Paleocene suggests burial of 60,000 Gt C in terrestrial systems during this time interval. (With my crude modeling, I can get this down to about 20,000 Gt C as a minimum, if I play around with carbon masses and fluxes). So, do you really want to suggest that something like 90-99% of late Paleocene coal, which would be indicative of this massive terrestrial carbon burial, has been removed, but that the small remainder is somehow meaningful to understanding past global biogeochemical cycling? I am open to the idea ... but it does push the bounds of creativity. And then, of course, there is the backside of this

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issue: the argument for massive terrestrial organic burial during the late Paleocene hinges on the decoupling of the C and S cycles – so why did Fe-sulfides precipitate without excess organic carbon burial in the early Eocene?

I will add an interesting aside here (one that I am positive that you already know). I find it really difficult (in my admittedly crude models) to drive a +1 per mil positive $\delta^{13}\text{C}$ excursion in the exogenic carbon cycle over 3 Myr through excess organic carbon burial alone without invoking large increases in carbon inputs from weathering or volcanism. By this I mean that, yes, excess burial of ^{13}C -depleted organic carbon over 3 Myr (somewhere between 20,000 Gt and 60,000 Gt, depending on the tempo of the input, and the mass and composition of the exogenic carbon cycle) can cause a +1 per mil positive $\delta^{13}\text{C}$ excursion during the late Paleocene. But this would have to be counter-balanced by a somewhat similar excess carbon input with a composition similar to that of the ocean, otherwise the mass of the exogenic carbon cycle becomes very small (a drop by at least 40%). Importantly, for the late Paleocene, the necessary excess weathering/volcanism would have to have happened as the world cooled. Maybe my models are incorrect, maybe this is how the world works or ...

... maybe the simple and most straightforward way to couple the long-term changes in $\delta^{13}\text{C}$ and $\delta^{34}\text{S}$ is through seafloor methane systems, with methane storage (gas hydrates), methanogenesis and anaerobic oxidation of methane (AOM). Incorporation of a seafloor methane capacitor shrinks the mass balance problem behind the late Paleocene positive carbon isotope excursion immensely, because, during storage of ^{13}C -depleted methane (very depleted in ^{13}C), the other bi-product of methanogenesis (substantially ^{13}C -enriched bicarbonate) returns to the ocean. This means the 1 per mil positive carbon isotope excursion of the late Paleocene can be driven by something like an addition of 5,000 Gt C (as methane) to marine sediment over 3 Myr (independent of any increase in organic carbon burial or external carbon fluxes) rather than 20,000 - 60,000 Gt C (as organic carbon) to terrestrial systems. The slow return of this methane also drives the sulfur isotope excursion during the early Eocene.

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With this view, the primary and admittedly “cop-out” reason that the $d_{34}S$ record has been relatively constant since ~ 50 Ma is that there have been no major (Myr-scale) fluctuations in methane storage and release since this time. (Here, three things should be noted. First, the postulated relationship is not straightforward because the carbon and sulfur cycles have very different residence times. Second, I find this difficult to model because a lack of constraints – see forthcoming response to Bowen’s comment. Third, the carbon isotope high in the middle Miocene presents an intriguing problem).

I am aware of implications of my ideas, at least some of them, if perchance they are correct. A major one is that long-term changes in the $d_{13}C$ of the exogenic carbon cycle (e.g., the $d_{13}C$ high in the late Paleocene) may have nothing to do with changes in the organic carbon burial flux. Such changes can be alternatively viewed as times of differential storage and release of the products of methanogenesis (i.e., ^{13}C -depleted methane; ^{13}C -enriched bicarbonate) along continental slopes. I am also fully aware that I’ll probably be regarded as some crazy heretic for suggesting this idea . . . but we shall see.

Jerry

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