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Comment on the Kaiho et al., paper "A forest fire and soil erosion event during the Late Devonian mass extinction" [Palaeogeography, Palaeoclimatology, Palaeoecology 392 (2013): 272–280]

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ABSTRACT

Kaiho et al. (2013, Palaeogeography, Palaeoclimatology, Palaeoecology 392 (2013): 272–280) interpreted the occurrence of elevated concentrations of high molecular weight polycyclic aromatic hydrocarbons and dibenzofuran as indicators of wildfires and enhanced run-off near the Frasnian–Famennian (F–F) boundary. We argue that other processes, including weathering or hydrothermal oxidation (not discussed by Kaiho et al.) led to the observed increase in the concentration of these compounds and also changed their distribution. Kaiho et al.'s evidence for soil erosion and eutrophication-induced euxinia is also weak in the case of the investigated Belgian sections. Finally, Kaiho et al. rather unfortunately omitted a great wealth of important data published elsewhere, choosing instead to include only those which support their ideas and interpretations.

1. Introduction

Kaiho et al. (2013) claim that widespread forest fires and massive soil erosion took place during the Frasnian–Famennian event, leading to eutrophication, the development of anoxic/euxinic conditions in the water column, and in consequence mass extinction (more correctly, biodiversity crisis; Stigall, 2012) of marine biota. Although this scenario is novel and intriguing, it does, in our opinion lack sufficient evidence.

Firstly, we have to stress that biostratigraphic control of the only Belgian succession studied (Sinsin) is poor, and therefore chemostratigraphic correlation with the auxiliary (Hony) section is provided (Fig. 3), "in order to fix the base of the *linguiformis* Zone" (Kaiho et al., 2013; p. 274). The authors used $\delta^{13}C$ curves, derived from whole-rock analysis, but this correlation is largely unreasonable because: (1) low-resolution of the data; (2) the base of the *linguiformis* Zone is not marked by any isotopic event; and (3) negative $\delta^{13}C_{carb}$ values (up to −4‰) are almost certainly controlled by carbonate diagenesis, as shown by the supra-regional C-isotope curves (e.g., Buggisch and Joachimski, 2006). In fact, this is a surprisingly risky analytical approach in the brachiopod-rich successions: $\delta^{13}C_{carb}$ value variations in the coeval basin successions in Poland (Fig. 5 in Racki et al., 2002) indicate that only limestone lithologies (below 5% clay content) are useful. Thus, C-isotope composition of organic matter would be very helpful (Joachimski et al., 2001; Chen et al., 2005), especially since Azmy et al. (2012) discovered in nearby Belgian localities an enigmatic "global F–F pre-event".

2. Wildfire evidences

In our judgment, the interpretation of the distribution of polycyclic aromatic hydrocarbons (PAHs) provided by Kaiho et al. (2013) is an over-simplification. Those authors used benzo[*e*]pyrene (B*e*P), benzo [*ghi*]perylene (B[*ghi*]Pe) and the coronene (Cor) to phenanthrene (Ph) ratio as indicators of combustion processes. First of all, we do not understand why Ph was used in the above formula as a non-combustion compound. This PAH is typically generated during different kinds of burning processes, and was detected as one of the major compounds in both recent and ancient wildfire records (e.g. Venkatesan and Dahl, 1989; Alves et al., 2011) as well as wood combustion tests (Fine et al., 2001). Certainly, the source of Ph is usually more complex in sediments, but rocks with confirmed evidence of wildfires (e.g. co-occurrence of charcoal) are characterised by significant concentration of Ph (e.g. Killops and Massoud, 1992; Marynowski and Simoneit, 2009; Marynowski et al., 2011a; Denis et al., 2012). The only exception to this is where sediments have been influenced by early diagenetic or secondary weathering/water washing processes. However, Kaiho et al. (2013) completely ignore the possible impact of weathering (and other secondary processes) on organic matter (OM), even though oxidative

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weathering and hydrothermal oxidation influence on PAHs have been widely discussed in previous studies (e.g. Sun and Püttmann, 2001; Marynowski et al., 2011b). For example, Marynowski and Simoneit (2009) show variations in PAH distribution from Lower Jurassic samples, where huge differences were noted between early diagenetically affected paleosol and charcoal-rich sandstone (Fig. 6 therein). In the case of such low concentrations of total organic carbon (TOC) in both Hony and Sinsin sections (below 0.3%!), the occurrence of secondary processes seems to be more than probable. In Fig. 1 we show how (BeP + B[*ghi*]Pe + Cor)/Ph ratio values change due to oxidative palaeoweathering of black shale (for more details see Marynowski et al., 2011b). To demonstrate how changes of (BeP + B[*ghi*]Pe + Cor)/Ph ratio are caused by palaeoweathering, their values are plotted against TOC data (Fig. 1).

What is more, to support the proper use of the (BeP + B[*ghi*]Pe + Cor)/Ph ratio as a combustion indicator, Kaiho et al. (2013) should provide analyses of charcoal or fusinite as independent proxies of wildfires. Instead, Kaiho et al. (2013) cite Scott and Glasspool (2006), stating that: "The increase in charcoal occurrence from Frasnian (small amounts of microscopic charcoal fragments) towards the end of the Famennian could be explained by an increase in O_2 levels to ~17% PAL". However, Scott and Glasspool (2006) in their crucial paper pointed out that in Frasnian–Famennian rocks "… charcoal occurrences are rare with only isolated fragments of charred (…) wood reported from this interval (Rowe and Jones, 2000) and small amounts of inertodetrinite… p. 10863". The same authors mentioned also that: "…Famennian charcoal assemblages become more common…p. 10863" as has been confirmed by numerous papers before and since (Rowe and Jones, 2000; Cressler, 2001; Marynowski and Filipiak, 2007; Marynowski et al., 2010, 2012; Prestianni et al., 2010; McGhee, 2013, p. 120–124).

3. Depositional conditions

Kaiho et al. (2013) reconstruct marine redox conditions based on such groups of organic compounds and biomarkers identified in the investigated material including: isoprenoids (pristane to phytane ratio — Pr/Ph), 2,3,6-trimethylarylisoprenoids (AI) and aromatic sulphur compounds (dibenzothiophene — DBT). All of them are non-indicative and should be used in caution in palaeoenvironmental reconstruction. It is widely known from the early work of Didyk et al. (1978), that Pr/Ph ratio is of limited use for determining redox conditions due to the variable source input of both isoprenoids, variations of the Pr/Ph ratio at high maturity and some other problems (summary in Peters et al., 2005). In consequence this ratio is not recommended as a palaeoredox proxy without additional independent proxies. Unfortunately, aryl isoprenoids identified and used as indicators of photic zone euxinia (PZE), can also be diagenetic decomposition products of β-carotene and therefore are also not indicators of PZE without supporting data (Koopmans et al., 1996). Surprisingly, throughout their whole paper, Kaiho et al. (2013) fail to mention isorenieratane, the most excellent PZE biomarker. This biomarker, together with other organic and inorganic proxies was used by Joachimski et al. (2001) and later by Marynowski et al. (2011c) to decipher the environmental conditions across the F–F boundary and in the early Famennian from Kowala quarry, Poland (see also Racki et al., 2002). Kaiho et al. (2013) do not mention these data in support of their interpretations. Finally, using DBT as an indicator of anoxic/euxinic conditions is not reasonable without much more extended discussion. Aromatic sulphur compounds (ASC) like DBT can form within sediments, not necessarily with the presence of PZE in the water column. Moreover, ASC can form during diagenetic processes (Asif et al., 2009), for example by influence of hydrothermal fluids on OM with the occurrence of iron sulphides (e.g. Rospondek et al., 2007). In the case of the F–F boundary from Kowala, the concentration of ASC is very low, even if the occurrence of PZE was undoubtedly proven (e.g. Joachimski et al., 2001; see also Bond et al., 2004).

We ask also one simple question of the Kaiho et al. (2013) data: if conditions were euxinic, as suggested by the authors, why are the TOC values so low (not exceeding 0.3%)? Even taking into account the discussion concerning productivity vs. preservation (e.g. Tyson, 2005), oceanic sedimentation during oxygen-deficient conditions always supports preservation of elevated OM amounts. The one exception is associated with secondary process influences on host rocks, like oxidative weathering and/or water washing (e.g. Marynowski et al., 2011b).

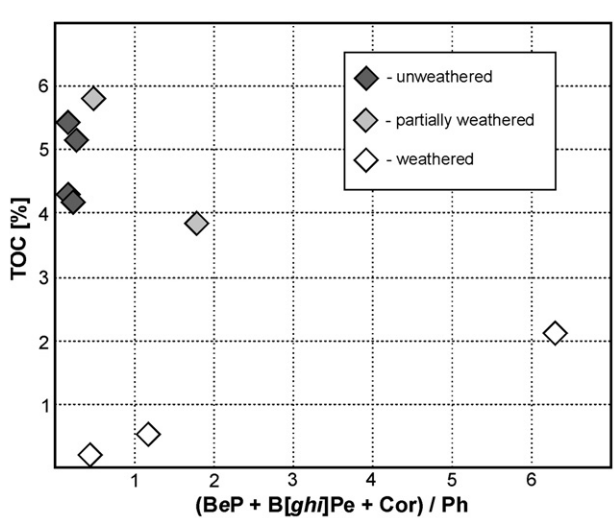

Fig. 1. Correlation plot of total organic carbon (TOC) vs. benzo[*e*]pyrene (BeP), benzo[*ghi*]perylene (B[*ghi*]Pe) and coronene (Cor) to phenanthrene (Ph) ratio for the Lower Carboniferous (Tournaisian) black shale palaeoweathering (see Marynowski et al., 2011b).

4. Comparison with the end-Permian soil crisis

The Permian–Triassic (P–T) boundary interval saw a significant influx of polysaccharide markers, taken as a proxy for soil-derived organic matter. Since the paper by Sephton et al. (2005), this unique signal is suggested to reflect high rates of soil erosion resulting from catastrophic deforestation (referred to as "soil crisis"). What is more, the massive soil redeposition approximately coincided with an onset of intensive wildfires recorded in frequent black organic particles and PAHs, and consistent with observed negative $\delta^{13}C$ shifts (e.g. Shen et al., 2011).

The consequences of terrestrial biosphere collapse (the Early Triassic "coal gap") attributable to extreme volcanogenic disturbance, with the contribution of mass wildfires, provides a direct link between terrestrial and marine ecological catastrophes, assumed also by Kaiho et al. (2013) for the F–F crisis. However, the P–T geochemical tracers are conclusively supplemented by much evidence for large-scale erosion processes promoted by the end-Permian vegetation loss. The most diagnostic signatures are summarised by Benton and Newell (2014) as: (1) the change of river systems from fine-grained meandering to conglomeratic braided styles; (2) transported soil clasts in claystone breccias, a signature of widespread debris flows and mudflows; and (3) accelerated accumulation rates in terrestrial and marine basins, linked with a substantial increase in the flux of clay-dominated terrigenous siliciclastics (also e.g., Retallack, 2005; Algeo et al., 2011). In particular, Retallack (2005, Table 5) reviewed probable soil-erosion crises during extraordinary circumstances of other global events, but the Late Devonian interval is not mentioned in this context (compare Retallack, 2011). The major differences between the implied (F–F) and proved (P–T) records of forest dieback due to mass wildfires were overlooked by Kaiho et al. (2013).

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