Exceptional geochemical preservation of vertebrate remains from the Eocene Messel Pit, Germany – Paleoenvironmental and paleoecological implications of the stable isotope signatures

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The 47-Myr-old middle Eocene oil shale deposits of the UNESCO World Heritage Site Messel (Mertz and Renne, 2005) are famous for their exceptionally well-preserved articulated vertebrate fossils that often still display soft tissue preservation. The cause is the special taphonomic situation – anoxic bottom-water conditions – of the Lagerstätte, which prevailed during the more than 600 ka existence of the Messel maar lake.

The isotopic compositions of oxygen, carbon and strontium were analyzed from the fossil skeletal remains of some of Messel's terrestrial (propalaeothere) and aquatic vertebrates (fish, turtle and crocodile) to determine the condition of geochemical preservation. Phosphatic coprolites, authigenic phosphate (messelite, montgomeryite), and carbonate (siderite) minerals, as well as the embedding oil shale, were also analyzed to characterize the isotope compositions of diagenetic mineral phases.

The oil shale and siderite have values of $\delta^{18}O_{CO3}$ (0.3 to 1.5‰) and $\delta^{13}C_{CO3}$ (14.8 to 17.8‰); these are much higher than those of all vertebrate remains (Fig. 1). Such positive values are typical for siderite from Messel and other Eocene anoxic lake settings (Felder and Gaupp, 2006). The strong ^{13}C enrichment is likely due to methanogenesis in the anoxic bottom water of Lake Messel. The enamel of *Propalaeotherium,* a European genus of early hippomorph perissodactyls, has preserved, low $\delta^{13}C$ values of around −8.8±0.7‰ (n=6), typical for C_3 plant feeders (Fig. 1). This is in accordance with its presumed leaf-dominated diet in a C_3-plant ecosystem. In contrast, the dentin of the same teeth has about 17‰ higher $\delta^{13}C$ values, which indicates a significant diagenetic alteration of the dentin. Bone and dentin of the aquatic vertebrates also have positive $\delta^{13}C$

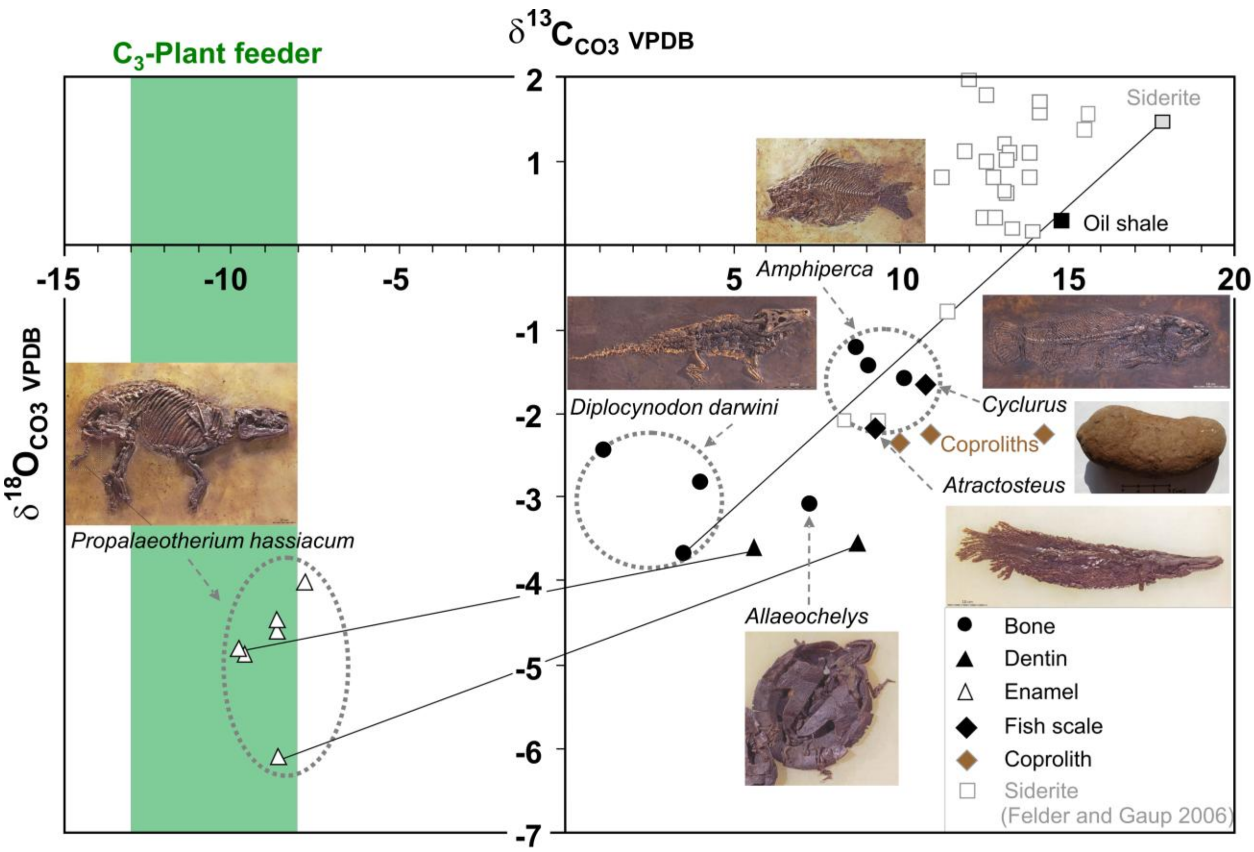

Figure 1. $\delta^{13}C$ and $\delta^{18}O$ values of the structural carbonate in the bioapatite of fossil skeletal remains of different terrestrial and aquatic vertebrates as well as some coproliths from Messel. For comparison isotopic values of siderite from Messel after Felder and Gaupp (2006) are given. These likely represent the isotopic values of the diagenetic endmember because siderite forms during early diagenesis under anoxic bottom-water conditions. The lines connect enamel and dentin samples from the same tooth and in the other case bone, siderite crust, and embedding oil shale of the crocodile specimen. In green the range of bioapatite $\delta^{13}C$ values typical for mammals feeding on C_3 plants is highlighted.

values from 1.1 up to 10.8‰ (Fig. 1). These are among the highest $\delta^{13}C$ values reported for skeletal apatite so far, and likely result from diagenetic alteration and/or indicate high $\delta^{13}C$ values of dissolved inorganic carbon in the lake water.

However, the enamel still contains *in vivo* values and seems geochemically well preserved. This is further supported by a high enamel $^{87}Sr/^{86}Sr$ value of 0.7114, reflecting the feeding habits of *Propalaeotherium* on Permian sedimentary and granitoid bedrocks in the area surrounding Messel Lake. Furthermore, the dentin of the same tooth has a much lower $^{87}Sr/^{86}Sr$ value of 0.7057, clearly indicating diagenetic Sr uptake from the volcanically influenced lake/pore water of the Messel maar lake. This is further supported by the low bone $^{87}Sr/^{86}Sr$ value of 0.7047 of the aquatic crocodile *Diplocynodon darwini.*

Enamel $\delta^{18}O_{PO4}$ values of the *Propalaeotherium* teeth are systematically lower than those of the dentin from the same teeth as well as the bones and scales of most aquatic vertebrates. This further corroborates the preservation of biogenic values in enamel. Hence, enamel $\delta^{18}O_{PO4}$ values (18.1±0.6‰, n=6) can be used to infer the $\delta^{18}O$ value of water ingested by *Propalaeotherium* by using a transfer function for modern mammals (Amiot *et al.*, 2004). The calculated drinking water $\delta^{18}O_{H2O}$ value is –6.4±0.7‰, which is about 2‰ higher than that of the modern precipitation number in the Messel area, reflecting significantly warmer climate conditions during the middle Eocene. Using a global modern-day $\delta^{18}O_{H2O}$-air-temperature relation (Amiot *et al.*, 2004) a mean annual temperature (MAT) of around 18±2°C can be determined. This value is similar to but somewhat lower than the MAT of approximately 22°C inferred for Messel from paleobotanical proxies (Grein *et al.*, 2011). Using the $\delta^{18}O_{PO4}$ value of a single turtle bone, the $\delta^{18}O_{H2O}$ of Lake Messel can be tentatively estimated to be –0.5‰, hence the lake water was ^{18}O-enriched compared to meteoric water, which is not uncommon for longterm lakes (Tütken *et al.*, 2006). Using this $\delta^{18}O_{H2O}$ and the fish scale $\delta^{18}O_{PO4}$ values, the phosphate–water fractionation equation of Longinelli and Nuti (1973) yields a water temperature of around 22°±3°C, which is in good agreement with the MAT inferred from paleobotanical data by Grein *et al.* (2011).

In conclusion, not only are the vertebrate carcasses of Messel exceptionally well preserved but also the geochemical composition of their tooth enamel. Enamel of *Propalaeotherium* still contains original C, O, and Sr isotope compositions, while bone and dentin samples appear clearly diagenetically altered. Isotope analysis of enamel from Messel vertebrates can thus be used to recontruct their diet, habitat use and mobility, yielding new insights into the paleoenvironment and the paleoecology of the Messel ecosystem.

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