

Isotopic signatures of organic carbon in Cretaceous black shales

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We determined isotopic ratios of total organic carbon for samples collected throughout the Cretaceous black shale (Livello Bonarelli) enriched in organic carbon (up to 25%). About 500 samples were measured in a 1 m sequence of Bonarelli to reconstruct high resolution isotopic record in the black shales. The carbon isotopic ratios of total organic carbon show an upward increasing trend throughout the horizon with the maximum values of -22 permil in the upper part of the horizon. The trend probably reflects a widely recognized positive excursion of carbon isotopic ratio around Cenomanian/Turonian boundary due to the enhanced burial rate of organic matter associated with Oceanic Anoxic Event 2 (OAE2). We also found localized sharp negative spikes of carbon isotopic ratios where isotopic ratios are down to -36 permil. The value is substantially lighter than those previously reported both from the Livello Bonarelli and other Cretaceous black shales. The sharp and rapid negative spikes of carbon isotopic ratios could not simply be ascribed to variability of isotopic fractionations by source organisms of the black shales. Instead, it would reflect either partial contribution of organic matter derived from organisms metabolizing isotopically light carbon sources (such as methanotrophic bacteria or archaea) to the organic matter of these intervals, or negative excursion in isotopic ratios of metabolizable inorganic carbon dissolved in sea surface (probably due to rapid release of methane from gas hydrate like Eocene/Palaeocene Event). In order to examine these possibilities, we determined carbon isotopic ratios of lipid compounds extracted from several intervals including the ^{13}C -depleted intervals. Importantly, the carbon isotopic ratios of extractable lipid compounds mostly range from -30 to -25 permil even in the ^{13}C -depleted intervals. Therefore, the carbon isotopic ratios of solvent-extractable lipid compounds may not be related to those of total organic carbon. This suggests that the ^{13}C -depleted organic matter should occur as non-extractable kerogen in the black shale horizon. If the carbon isotopic ratios of in surface water becomes lighter due to rapid release of methane from gas hydrate, most organic matter (both marine and terrestrial) would be influenced by the isotopically light carbon reservoir (Hesseblo et al., 2000). Our results therefore eliminate the latter possibility by showing that the carbon isotopic ratios of lipid compounds are independent from the isotopically light carbon reservoir reflected by the deposition of ^{13}C -depleted intervals. Although further confirmation is required, the partial contribution of organic matter derived from methanotrophic organisms seems most likely. In the presentation we will report some additional information about the carbon isotopic compositions of lipid biomarkers in the ^{13}C -depleted intervals to further understand the short-term events we found.