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A multiproxy geochemical record of the early Aptian Selli event (OAE1a) from the platform carbonates of southern Italy

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In the geological record, several events of rapid global warming have been recognized, triggered by huge injections of CO_2 into the atmosphere. These events are associated with perturbations in overarching biogeochemical cycles and severe palaeoenvironmental disturbances. Especially short-term events ($<$1Ma), like Oceanic Anoxic Events (OAEs), are marked by widespread deposition of organic-rich facies in epicontinental and oceanic basins under oxygen-depleted conditions. In many deep-marine organic-rich and carbonate-free facies, geochemical proxies that are preserved only in carbonate minerals cannot be recorded: examples include lithium isotopes and carbonate-associated sulphur isotopes. Hence, shallow-water carbonates offer an ideal archive for investigations of certain proxies during major climatic perturbations, including those affecting shallow-water environments.

This study has focused on OAE1a or Selli Event ($\sim$120Ma, early Aptian), one of the most important Mesozoic OAEs. In order to determine the relative extent of oxygen-depleted water masses in the oceans and the role of weathering as both an OAE initiator (via nutrient supply) and terminator (via CO_2 sequestration), sulphur isotopes, redox-sensitive elements (Ce/Ca, Ce/Ce* and Mn/Ca) and lithium isotopes have been analysed in Lower Aptian shallow-marine carbonate sections from the Tethyan realm.

Lithium isotopes in seawater are mainly controlled by continental silicate weathering and high- and low-temperature alteration of oceanic crust. With increasing weathering rates of silicates at the onset of OAEs, a shift to lighter isotopic values is expected. In fact, the studied sections record decreasing lithium isotopes to a minimum value coincident with the negative spike in carbon isotopes pinpointing the onset of OAE1a. This geochemical relationship is consistent with the hypothesis that an increase in silicate weathering, in conjunction with organic-carbon burial, ultimately led to the drawdown of atmospheric CO_2.

The sulphur-isotope composition of the oceans is largely dependent on the input via hydrothermal fluxes and weathering of sulphur-bearing minerals and the output of gypsum and pyrite burial. The precipitation of gypsum affects mainly the sulphur concentration in seawater and has only a minor isotopic effect. Conversely, the formation of sulphide from microbial sulphate reduction produces isotopically light pyrite. An overall positive correlation of carbon and sulphur isotopes during the early Toarcian and the Cenomanian–Turonian OAEs suggests enhanced pyrite burial under euxinic conditions. A similar pattern can be recognised during OAE1a in the platform carbonates of southern Italy.

The concentration of cerium in seawater increases with decreasing oxic sinks in the oceans. Therefore, a higher Ce/Ca ratios and a more positive Ce anomaly is expected during OAEs. Manganese enrichments are usually formed in pore-waters rich in Mn^{2+} with appropriate levels of carbonate alkalinity. However, it has been observed that during OAEs manganese is depleted in many deep-marine organic-rich and carbonate-poor facies, whereas shallow-water platform carbonates are enriched. As expected, in the studied sections, cerium and manganese analyses show a positive shift during OAE1a, indicating the expansion of oxygen-depleted water-masses into shallow-water regions.

These data highlight the significant geochemical changes during the OAE, which suggest that climate change of a complex system has severe impacts possibly leading to a cascade of perturbations including deep-water anoxia/euxinia.