Chemical species of iron and molybdenum in deep-sea sedimentary rocks across the Permian-Triassic boundary

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We report chemical species of iron (Fe) and molybdenum (Mo) in a pelagic deep-sea Permian–Triassic boundary section, that records redox variations across the end-Permian mass extinction event. We applied X-ray diffraction (XRD) and extended X-ray absorption fine structure (EXAFS) at the Fe K-edge and X-ray absorption near-edge structure (XANES) at the Mo K-edge to silicic sedimentary rock samples for analysis of the study section. According to the EXAFS and XRD analyses, pyrite was the dominant Fe-bearing mineral in most samples, whereas ferric minerals such as hematite were absent throughout the Permian–Triassic transition. The Fe in pyrite mineral quantified by EXAFS spectra displayed synchronous variation with sulphur but with total organic carbon content, which revealed the Fe-limited conditions for pyrite formation in the pelagic region. The XANES analysis indicated the presence of tetrahedral and octahedral configurations of Mo bonded to oxygen and sulphur, which were referred to as MoO_4^{2-}, MoO_3 (as a possible alternative reference material of Mo in organic ligands), MoO_2 and MoS_2. The MoS_2 species dominated in the end-Permian horizons, coinciding with high abundances of total Mo, which suggests a sulphidic depositional environment. The MoS_2 and MoO_3 species were the main contributors to these high Mo abundances in the end-Permian strata. The presence of the molybdenite (MoS_2) species in the studied section indicates that the samples were subjected to alteration under high temperatures, with sufficiently sulphidic and limited reactive Fe availability conditions for MoS_2 formation during late diagenesis. The Fe in pyrite decreased across the mass extinction boundary, which coincided with the highest total Mo amount with the MoS_2 and MoO_3 species. These trends reflected a decrease in reactive Fe in the sediments and contemporaneous seawaters under sulphidic conditions.