Reduced iron and molybdenum in the end-Permian sulphidic sedimentary rocks

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The presence of reduced iron (Fe) and significant increases in molybdenum (Mo) concentration in sedimentary rocks have been taken as evidence of reducing and highly reduced sulphidic depositional conditions, respectively. We performed extended X-ray absorption fine structure (EXAFS) analyses of Fe and X-ray absorption near edge structure (XANES) and Mo in lithified silicic sedimentary rocks from the pelagic deep-sea Permian–Triassic boundary section to determine their oxidation states and the bonding environments of the host phase of each element. The most dominant Fe-bearing minerals were pyrite and illite. Ferric minerals such as hematite were absent, which suggested reducing depositional and/or post-depositional conditions throughout the Permian–Triassic transition. On the other hand, tetravalent and hexavalent Mo (Mo(IV) and Mo(VI), respectively) were observed in the studied section by the XANES analysis. It is impossible to rule out the oxidative weathering in the outcrop and/or following experimental procedures for the presence of Mo(VI)-O species. However, Mo(IV)-S species dominates in the end-Permian horizons, which suggests that any post-depositional oxidative effect did not occur significantly at least for these samples and originated from sulphidic depositional environment with following diagenetic effects. Considering features of matured rock samples, preservation of Mo(IV) species would be helped by molybdenite formation during thermal late diagenesis and dense cementation by silicic materials forming matured sedimentary rocks. The absolute concentrations of Fe hosted in pyrite (Fe-pyrite) and S-bonding Mo(IV) (Mo(IV)-S) increased in the siliceous claystone beds just below the mass extinction boundary. However, the Fe-pyrite concentrations decreased while those of Mo(IV)-S species increased across the mass extinction boundary. This trend reflects decreased reactive Fe in bottom waters, likely caused by massive pyrite formation and increased reduced Mo(IV) under the prolonged stagnation of sulphidic deep water and ambient continental margin regions at the end-Permian.

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