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Controls on metal enrichment in ferromanganese crusts: temporal changes in oceanic metal flux or phosphatisation?

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Oceanic hydrogenetic ferromanganese (Fe-Mn) crusts are a major repository for many metals, such as Co, Ni, Cu, Pt, Te and REE, which are essential for decarbonisation of transport and energy systems. Secondary mineralisation processes, occurring during phosphatisation episodes, commonly impregnate the shallow deposits with carbonate fluorapatite (CFA). In absence of appropriate and accurately-dated unphosphatised Fe-Mn crusts to compare to, the suboxic to anoxic oceanic conditions during such events have been frequently invoked to explain the lower Co content and unusually high Ni, Cu, Zn and Pt content of older phosphatised crusts. Here, the hypothesis of suboxic diagenetic recrystallization induced by phosphatisation episodes as a driving mechanism for Ni, Cu, Zn and Pt enrichment and Co depletion is evaluated. Accurately dated geochemical profiles, spanning 75 Ma of depositional history, for a shallow (1100 mbsl) phosphatised sample and a deeper (3100 mbsl) unphosphatised sample from Tropic Seamount in the north-east Atlantic, are compared. An isocon analysis, which permits compensation for the dilution effect induced by the addition of CFA in the Fe-Mn crusts, demonstrates that no loss of Co has occurred in the phosphatised crust, whilst Pt, Te, Cu, Ni and Zn are enriched relative to younger, unphosphatised Fe-Mn crust. Both geochemical profiles show sympathetic trends and similar amplitudes of variation in concentration. This excludes phosphatisation as the driving mechanism for the metal enrichment and depletion. Systematic differences in metal content between the two samples, such as higher Cu and lower Co content in the deeper sample, are consistent with the depth profile of dissolved metal concentrations in the water column. The variability observed in the geochemical profiles is consistent with temporal changes in metal fluxes to the ocean, as a result of the evolving climate and oceanographic configuration of the north-east Atlantic Ocean through the Cenozoic. It is concluded that this, rather than secondary mineralisation process associated with phosphatisation, is the dominant control on the primary metal content in Fe-Mn crust deposits.