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Fe isotope composition of Fe-Mn crusts in Pacific and its significance for Paleoceanography

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Ferromanganese (Fe-Mn) hydrogenetic crusts have very slow growth rates (1-3mm/Ma) and may be considered to be condensed stratigraphic sections. The record of Nd, Pb and Hf isotopes of successive growth layers in Fe-Mn crusts from all the major ocean basins have been used as paleoceanographic proxies for changes in continental weathering, ocean floor hydrothermal activity, and ocean circulation and their relation to tectonic and climatic events. In Fe-Mn crust, dissolved Fe in seawater is mainly precipitated as Fe-rich δ-MnO_2mineral (ferruginous vernadite). Providing that no significant Fe isotope fractionation occurs during formation of Fe-Mn crusts, Fe isotopes may provide promising new proxies for paleoceanography.

In this study, we report temporal variations in new Fe isotope time series from crust MP2D06 (recovered from the Central North Pacific) and crust MED69 (recovered from western Pacific) and provide new insights into possible variations of Fe sources in seawater over time and their significance for paleoceanography. Fe, Pb isotopic composition was measured by MC-ICP-MS *Neptune* at WHOI. External precision for the δ^{56}Fe measurements is typically better than $\pm$ 0.1‰ (2σ) and values are reported relative to IRMM-14 standard.

Both crusts were dated using Co-flux dating and by comparison of Pb isotopic ratios with those of other dated crusts in the central Pacific and yield time series for the past 78.35Ma and 73.49Ma in crusts MP2D06 and MED59 respectively. Those ages are close to the ages of the nearby seamounts which suggest that the crusts formed shortly

after formation of the seamount. Because of the uncertainty in the approach for age calculation, ages are given with uncertainty of about 3Ma.

The Fe isotope composition in crust MP2D06 ranges from -0.52 to -0.43‰ between 0 to 14Ma, and from -0.25 to -0.34‰ between 31 to 47Ma. There is marked and continuous increase of δ^{56}Fe values from –0.46 to -0.08‰ between 64 to 78Ma. For crust MED59, δ^{56}Fe values ranges from -0.24 to -0.38‰ between 0 to 10Ma, from -0.19 to -0.07‰ between 12 to 27Ma and there is also marked and continuous increase from –0.49 to -0.13‰ between 64-73Ma which is similar to Fe isotope variations of crust MP2D06.

The analyses of δ^{56}Fe values in both crusts reveal significant similar variations over time. Secondary phosphatization occurred in both crusts older than 62Ma and the positive correlation between δ^{56}Fe values and P concentration suggests that such post-depositional effects remove lighter Fe isotopes and yield isotopically heavier crust relative to unphosphated section. Low δ^{56}Fe values down to –0.5‰ are recorded in both crusts at $\sim$65Ma and may reflect widespread hydrothermal input or volcanic seamount weathering. Fe isotope variation show similar pattern and essentially the same amplitude in section younger than 64Ma and indicate that dissolved Fe in pacific seawater, as recorded in Fe-Mn crusts, was homogenous with δ^{56}Fe values $\sim$ -0.3‰. After 12Ma, the western Pacific crust has isotopically heavier δ^{56}Fe values compared to central Pacific crust, which may suggest higher contribution of terrestrial material or dust (δ^{56}Fe $\sim$ 0‰) delivered to the western Pacific water mass relative to the central Pacific.

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