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Redox control on the chromium distribution of tropical red soils revealed by Cr isotopes

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Red soils in China support a large part of rice production but the concentrations of potentially toxic metals (e.g. chromium (Cr)) can be high (600 μg/g for Cr), posing a public health risk. In tropical red soils with strong weathering, authigenic ferromanganese nodules (FMNs) are commonly found and may serve as potential sinks for these heavy metals. In this study, we investigated the Cr distribution and fate in a paddy red soil profile used for rice production in Guangxi province, southern China. Geochemical, mineralogical and Cr isotope data (reported as $\delta^{53}Cr$) were obtained in FMNs and the surrounding soils of each horizon as well as from fertilizers and from the water drainage system.

In soils, the $\delta^{53}Cr$ of the surrounding soils varies among horizons and the maximum occurs in the waterlogged horizon, which is linearly related to the inverse of chromium concentrations. The $\delta^{53}Cr$ of FMNs is systematically higher than in the surrounding soils ($\Delta^{53}Cr_{FMNs\text{-}soil}$ = 0.614 ± 0.144‰, n=15). Given that FMNs are formed by the nucleation of iron hydroxides from the soil solution and that Cr is co-precipitated during this step, we suggest that the heavy $\delta^{53}Cr$ of FMNs may be due to the capture of a dissolved and heavy Cr-isotope pool rich in Cr (VI) oxyanions. Additional CBD (citrate-bicarbonate-dithionite) extractions were carried out to isolate Fe-oxide bound Cr (FeO) and clay mineral bound Cr (Clay) in FMNs and surrounding soils. In the clay fraction, the distinct $\delta^{53}Cr$ signatures recorded in FMNs (0.51 ± 0.04‰, n=5) and in the surrounding soils (-0.02 ± 0.05‰, n=5), indicate that FMNs are probably preserved objects which reflect past weathering conditions and thus which are not contemporary of the current surrounding soils. The $\delta^{53}Cr$ of FeO fractions in FMNs and soils is always heavier than the clay fractions, supporting the sequestration of heavy Cr isotopes during Fe oxide precipitation. Interestingly, the FeO extraction shows that the variability of $\delta^{53}Cr$ recorded in the bulk surrounding soils is only driven by the extent of the iron oxide precipitation process, which is likely explained by the changing redox state with depth and with hydrological conditions.