



## Fire-driven mineral and geochemical differentiation at the Earth's surface

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Fires potentially exert a significant influence on the mineralogy and geochemistry at the soil to air interface, driving high temperature differentiation reactions in an environment that is otherwise dominated by low temperature processes. Although wildfires have been a recurrent, geographically wide-spread feature of the Earth System since the proliferation of vascular plants in Late Devonian, a lack of suitable sampling media means that the geochemical impact of high intensity fires has proven difficult to test. Here we show that magnetic iron pisoliths, present in fire affected soils globally, are a promising new sampling medium to assess the impact of fire.

We use detailed petrographic and mineralogical analyses of the nodules to demonstrate that maghemite occurs as part of a high temperature mineral assemblage including hematite and  $\chi$ -alumina<sup>1</sup>. The nodule mineral assemblage and microfabric is indicative of fire-induced dehydroxylation and sintering of non-magnetic precursors at temperatures greater than 600 °C (ref 1). Therefore, comparison to non-magnetic precursors offers insights into the geochemical impact of fire.

Our results show that magnetic nodules are depleted in Si, Y, Zr and HREE but enriched in Fe and Cr relative to co-located, precursor non-magnetic nodules. Magnetic nodules also show variable but distinctly low Y/Ho ( $21.4 \pm 0.4$ ) and Zr/Hf ( $29.3 \pm 0.8$ ). In situ laser ablation analyses show that this is largely due to  $\chi$ -alumina with no involvement from zircon (ref 1). We further identify depletions of up to 85% in the concentration of alkali and alkaline earth metals (Li, Rb, Sr, Cs) in fire affected materials relative to their precursors.

We propose a multi-stage process of formation where fire transforms non-magnetic nodule precursors into proto-magnetic nodules, with destruction or alteration of thermally labile clay, Fe and Al oxihydroxide phases. Preferential loss of the weathering-sensitive alteration products then results in geochemical differentiation of magnetic nodules relative to their non-magnetic precursors. We suggest that the elevated Zr/Hf and Y/Ho ratios previously reported for Australian fluvial sediments reflect, at least in part, the long history of palaeo-fires in the catchments of these rivers. The marked loss of alkali and alkaline earth metals following thermal alteration of common soil components such as clays, Fe and Al oxihydroxide suggests that fires play an important role in the mobilisation of these elements in the Earth surface weathering environment, and may complicate the use of Li as a weathering proxy. In addition, since magnetic Fe nodules are demonstrably related to fire, they may represent a promising, directly dateable record of severe fires, which can complement the sedimentary charcoal record.

1 - Löhner et al (2017). *Geochimica Et Cosmochimica Acta*, 200, 25–41.