What controls metamorphic de-coupling of Lu-Hf from Sm-Nd?

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The effect of metamorphism on Nd and Hf isotope systematics was evaluated for granulite, eclogite and upper amphibolite facies conditions. Rocks of known protolith ages and metamorphic overprint ages were investigated in order to assess crustal de-coupling of these two isotope systems.

For *granulite facies* rocks whole rock (WR) Nd isotope data reflect protolith ages: Nd depleted mantle model ages (T_{Nd}) as well as Sm-Nd WR isochrons correspond well with inherited zircon core ages. Hf model ages (T_{Hf}) of granulite facies rocks sometimes reflect protolith ages while Lu-Hf WR errorchron age for granulites corresponds well to the granulite event. For *upper amphibolite facies* rocks Sm-Nd does not give geologically reasonable WR isochron ages but mostly reasonable T_{Nd}'s reflecting protolith ages. T_{Hf}'s of upper amphibolite facies rocks also sometimes point to protolith ages but the Lu-Hf WR isochron ages scatter and yield a poorly defined slope between protolith and metamorphic overprint ages. *Eclogite facies* rocks do not yield realistic WR ages for both Sm-Nd and Lu-Hf, nor T_{Hf} and T_{Nd}. However, *garnet* data yield Lu-Hf WR-grt isochrons pointing towards the eclogite event (Faryad et al., 2002, Mineral. Petrol. 74, 49-73) whereas the WR-grt pairs are disturbed in Sm-Nd showing a de-coupling of both isotope systems.

We observe a complete resetting of the Hf isotope system during granulite facies metamorphism, but an incomplete one in amphibolite facies. This is antithetic to the Sm-Nd, which preserves protolith ages in granulites but not in amphibolites. The Hf and Nd isotope systems were variably de-coupled in granulite and upper amphibolite facies. The most obvious difference between both systems is that one is a REE-REE pair and the other a REE-HFSE pair. The phase showing strongest REE fractionation is garnet, which is present in all of our rocks. Garnet formation alone does not shift the WR point, which only can be perturbed in chemically open systems. Where mass transfer took place, garnet selectively modifies Lu/Hf relative to Sm/Nd.

Conclusions: (i) the Lu-Hf isotope system is clearly de-coupled from Sm-Nd during high-grade metamorphism, (ii) the Lu-Hf isotope system is, unlike the Sm-Nd system, completely reset during granulite metamorphism, i.e. a useful geochronometer, (iii) Lu-Hf WR-grt isochrons are more useful than WR isochrons in eclogites.

The isotopic signature of Fe-mineralisation during early diagenesis

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Iron in the sedimentary environment occurs in a wide range of ferric and ferrous minerals with varying reactivity. During early diagenesis these undergo a series of dissolution and re-mineralisation processes, which are facilitated by inorganic or microbially mediated reactions. In this study we are examining the Fe and S reduction kinetics and isotopic signatures of marine and fresh-water sediments. The principal difference between marine and fresh-water sedimentary environments in terms of organic matter re-mineralisation is the presence of sulphate. Consequently, whilst mircobial sulphate reduction is often the dominant pathway for carbon oxidation in marine systems, metal-reduction and methanogenesis typically take on this role in fresh-water environments. Porewaters from this study persistently show enrichment in the lighter isotopes with δ^{56}Fe exceeding 5‰, higher than any previously reported data for natural systems. The bulk reductive dissolution kinetics of iron oxides and associated isotopic effects have been simulated in the laboratory with time-series extraction experiments. The rate of abiotic Fe reduction is largely controlled by the crystal structure of the iron oxide, with the observed ranges in reaction rates covering three orders of magnitude. Available evidence from microbial reduction experiments, in contrast, suggests that the effect of iron oxide mineralogy on enzymatic reduction rates is of lesser importance and that the gross surface area becomes the primary controlling factor. Moreover, enzymatic reduction rates vary within only one order of magnitude. The change in fractionation factors between initial and final dissolved Fe during the bulk reductive dissolution experiment are of similar magnitude as published data for kinetic isotope fractionation between Fe(II) and Fe(III) (Matthews et al., 2001). Because of the considerable abiotic isotope effects that have been observed in laboratory studies and natural systems, a detailed understanding of the kinetics of Fe-oxide reduction is instrumental in understanding the relative contributions of biotic versus abiotic Fe isotopic fractionations.

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