

Extreme variability in Hf isotopic components of aeolian dust and its implications for seawater Hf

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Isotopic compositions of Hf, Nd and Sr of aeolian dust recovered from pelagic sediments can be expected to vary as a function of changes in erosion and atmospheric transport processes. We have determined the Hf isotope compositions and Lu and Hf concentrations of the aeolian silicate fraction of Pacific pelagic sediments (a) from various localities downwind the central Asian dust source and (b) extending back to 11 Ma using the composite record of the ODP sites 885/886 (44.68°N/168.25°W), a time and place with essentially pure central Asian dust deposited from westerly winds.

The aeolian dust fraction was isolated from the bulk sediment by removing Fe-Mn oxi-hydroxides, zeolites and biogenic silica. Hf isotopic analyses were made using MC-ICPMS. For isotopic analyses, bulk dry dust fractions (for Hf ~ 100 mg) were surface cleaned in a 1 M ammonium acetate solution, in order to remove Hf, Nd and Sr from exchangeable sites of clays or adsorbed onto the sample surface. The ammonium acetate leachate fraction yielded an insignificant amount ($\leq 1\%$) of the total Hf present in the sample, despite the fact that this fraction is on the order of several percents for Nd and Sr.

Various dust dissolution techniques have been explored. Dry dust splits were dissolved in Savillex screw-top beakers (HF: HNO₃ ~9:1) but did not yield reproducible ϵ_{Hf} values in some cases ($\Delta\epsilon_{\text{Hf}} = 4$) indicating that these aliquots are inhomogeneous with respect to their Hf isotopic composition or that refractory minerals were only partially attacked during conventional beaker dissolution. In order to evaluate the importance of such refractory minerals for the Hf in dust, triplicate dry splits of two samples were dissolved in beakers and any residue centrifuged off. The beaker dissolution yielded almost identical Hf isotopic compositions and Lu and Hf concentrations. The residues of the beaker dissolutions were spiked and subsequently exposed to steel-jacketed bomb digestion at 180°C for 5 days. This procedure yields up to 0.4% and 2.5% of the total sample Lu and Hf abundances (i.e. $^{176}\text{Lu}/^{177}\text{Hf}$ ratios

around 0.003), consistent with zircon grains, implying transport of dense but fine grains by wind for distances of several thousand km, possibly as inclusions in clays or volcanic ash shards. Total sample bomb-dissolutions yielded equally or more radiogenic Hf compared to the least radiogenic beaker-dissolutions ($\Delta\epsilon_{\text{Hf}} = 5$). This suggests that (a) the amount of zircon in the sample is variable and (b) and that the grains originate from a relatively young source.

In order to assess the geochemical cycle of erosion and weathering of Hf and seawater Hf, we dissolved several samples in screw-top beakers only, minimizing the Hf fraction of the dust fixed in zircons. Our data therefore may help to constrain the geochemistry of the 'mobile' Hf fraction (i.e. the 'non-zircon component' as termed by White *et al.*, 1986). Hf and Nd isotopic compositions of these dissolutions, expressed as ϵ -values relative to CHUR $^{176}\text{Hf}/^{177}\text{Hf} = 0.282772$ (Blichert-Toft and Albarede, 1997; all cited ϵ_{Hf} values have been recalculated accordingly) and CHUR $^{143}\text{Nd}/^{144}\text{Nd} = 0.512638$, for modern aeolian sediment were found to vary between -4.5 and +16.2, and -10.9 and +3.8 (Nakai *et al.*, 1993; Jones *et al.*, 1994), respectively. The 'pure' modern dust source component from central Asia identified on the basis of constant $\epsilon_{\text{Nd}} \sim -10$ has a variable ϵ_{Hf} between -5 and -1. The strong correlation $\epsilon_{\text{Hf}} \sim \epsilon_{\text{Nd}} + 2$ documented for the modern earth mantle breaks down to a weak positive trend, if any, for modern dust with a much shallower slope and a more radiogenic ϵ_{Hf} for $\epsilon_{\text{Nd}} = 0$. Lu and Hf abundances of modern dust vary between 0.34 and 0.42, and 3.4 and 6.5 ppm, respectively; the corresponding $^{176}\text{Lu}/^{177}\text{Hf}$ ratios are between 0.011 and 0.016. This compares well with the mean values for shales ([Lu] = 0.59 ppm, [Hf] = 4 ppm, $^{176}\text{Lu}/^{177}\text{Hf} = 0.016$; Patchett *et al.*, 1984). ϵ_{Hf} values show a weak negative trend with [Hf] and a weak positive one with $^{176}\text{Lu}/^{177}\text{Hf}$ ratios as is expected if much of the variability is caused by binary mixing between central Asian dust and a

young volcanic arc component as was established on the basis of Nd isotopes (Nakai *et al.*, 1993).

Down-core samples from ODP-sites 885/886 are characterized by quite uniform ϵ_{Nd} (-9.0 to -10.2) but highly variable present-day ϵ_{Hf} values between -3.2 and $+11.0$. These observed Hf isotopic compositions are much more radiogenic than expected from their corresponding Nd isotopic signature. $^{176}\text{Lu}/^{177}\text{Hf}$ ratios span the restricted range between 0.008 and 0.011, and do not correlate with ϵ_{Hf} . Radiogenic ingrowth of ^{176}Hf since the dust source became a closed system for Lu-Hf cannot account for this extreme variability in ϵ_{Hf} . The results document a pronounced decoupling of the Lu-Hf from the Sm-Nd system, very much like that observed between Rb-Sr and Sm-Nd. As post-depositional modification of the Hf isotopic composition of the dust appears unlikely, the variability seems to represent a characteristic of the dust source terrain, very much like the variability in Sr isotopes ($0.711 < ^{87}\text{Sr}/^{86}\text{Sr} < 0.721$). No correlation between Hf and Sr isotopes is evident, however. Consequently, the Hf isotopic composition of unknown fluxes from continents to the oceans may not be estimated by using any linear $\epsilon_{\text{Hf}}-\epsilon_{\text{Nd}}$ relationship (White *et al.*, 1986), due to the fixation of an important, unradiogenic and variable fraction of Hf in zircons.

Modern hydrogenous ferromanganese crusts from the Pacific show ϵ_{Hf} values from $+7.0$ to $+9.3$ (Godfrey *et al.*, 1997), fairly close to MORB. Thus, it was proposed on the basis of literature values for the mean Hf isotopic composition of the continental crust that as much as 80% of seawater Hf (Godfrey *et al.*,

1997) may originate either through MOR hydrothermal venting or from the chemical weathering of young volcanic rocks, whereas such a contribution for both Nd and Sr is less important. Our dust data suggest that the more 'mobile' fraction of Hf in continental erosion may have highly variable and relatively radiogenic Hf isotopic compositions. This fraction may be released into solution and eventually reach the oceans (see also White *et al.*, 1986). The Hf isotopic composition of continental runoff may be extremely sensitive to changes in the intensity and/or style of continental weathering. In this respect the variations in the Hf isotopic composition of seawater through time may be difficult to interpret and the relative fluxes of Hf derived from continental erosion vs MOR hydrothermal venting may be hard to ascertain.

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