Nitrogen recycling in subduction zones: A strong geothermal control

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Although several studies already dealt with N recycling in subduction zones, controversy still persists about the amount of N actually recycled to the deep mantle. From the study of fumaroles and hot springs in the Central America, Fischer et al. (2002) showed that subducted N can be efficiently transferred to the surface via arc volcanism and concluded that N is not recycled to the deep mantle. In contrast, occurrence of high amount of N in metamorphic microdiamonds from Kokchetav massif (Kazakhstan) indicates that it can be subducted to ultrahigh-pressures (Cartigny et al., 2001). The comparison between three sequences of subducted metasediments also demonstrates different behaviours of nitrogen during subduction. In the Catalina Schists (California) and the Erzgebirge Schists (Germany), N content decrease and $\delta^{15}N$ increase with increasing metamorphic conditions indicate that N was strongly affected by devolatilization processes during subduction (Bebout and Fogel, 1992; Mingram and Bräuer, 2001). On the contrary, a study of the Schistes Lustrés metasediments (western Italian Alps) showed that N (together with other fluid-mobile elements, K, Rb, Cs, H) was entirely preserved during subduction down to 90 km depths (Busigny et al., 2003). All of these results can be reconciled if the thermal structure of the subduction zone is considered. While N is dramatically devolatilized in "warm" subduction zones, it can be deeply recycled in "cold" slab environment, which is the case of most current subduction zones.

An important implication of this work concerns the evolution of N recycling through geological times. Because the thermal regime of the early Earth was hotter than today, the N recycling was certainly less efficient during this time. N was likely devolatilized and fractionated, producing an increase of the $\delta^{15}N$ value of the remaining recycled nitrogen.

References

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Fe isotope fractionation during Fe (II) monosulfide precipitation from aqueous solutions at pH 8 and ambient temperatures.

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FeS (mackinawite) was formed at 2 - 40°C and pH 8 by addition of aqueous sulfide to excess Fe solution. The precipitate was collected by filtration on 0.02 and 0.45µm membrane filters, washed and taken up in 30% HCl. The residual dissolved Fe was collected for analysis by precipitation as FeS using excess sulfide. For analysis, Fe solutions were pretreated using ion-exchange chromatography and analysed on a Micromass Isoprobe MC-ICP-MS relative to both the IRMM Fe isotopic standard and the Fe reactant. Data are presented as $\varepsilon^{56}Fe$ where $\varepsilon^{56}Fe=(R_{smpl}/R_{stnd} - 1)x10^4$.

Results

FeS precipitated from aqueous Fe(II) is ^{56}Fe depleted relative to its aqueous Fe source reservoir by up to 9 ± 0.5 $\varepsilon^{56}Fe$. Ageing of the precipitated FeS in contact with the residual Fe(II) solution results in progressive ^{56}Fe enrichment of the precipitated FeS product from -9 ± 0.5 (t=0) to -3 ± 0.5 (t =168h.) $\varepsilon^{56}Fe$, relative to the initial Fe source reservoir. A constant fractionation of -9 ± 0.5 (t=0) $\varepsilon^{56}Fe$ was observed over the temperature range 2-40°C.

Discussion

FeS precipitation from these solutions is rapid with characteristic times of ms. (Rickard 1995). Even so, this instant precipitation results in a significant $\varepsilon^{56}Fe$ fractionation. The FeS precipitate develops from aqueous FeS clusters, containing structural moieties similar to those in bulk mackinawite. This precipitate includes 2nm nanoparticles which grow with time to larger particles. The observed fractionation trends on ageing are consistent with equilibration of the FeS-Fe with the solution-Fe as the particles develop. The results suggest that natural mackinawite in sedimentary environments will display $\varepsilon^{56}Fe$ depletion of ca. -3 ± 0.5 relative to the Fe source, although the initial precipitate, which may be involved in further reactions, will be more heavily ^{56}Fe depleted.

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