

## Mass-independent and mass-dependent sulfur processing throughout the Archean

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Measurements of the ratios of the four stable isotopes of sulfur (<sup>32</sup>S, <sup>33</sup>S, <sup>34</sup>S, <sup>36</sup>S) using a combination of multi-collector and mono-collector methods on a Cameca ims 1270 ion microprobe have confirmed Farquhar et al.'s (2000) discovery that both sulfides (pyrites) and sulfates (barites) display large anomalous or "mass-independent" effects throughout the Archean (3.9-2.5 Ga ago). Pyrites that are intimately associated with stratiform and cross-cutting barites have the same negative  $\Delta^{33}\text{S}$  (and positive  $\Delta^{36}\text{S}$ ) as the barites but are lighter in  $\delta^{34}\text{S}$  by as much as 20‰ (six examples from three continents). This isotopic difference between co-existing sulfate and sulfide is attributed to equilibrium fractionation in low-temperature, hydrothermal environments. In this case, the pyrites retained the anomalous negative (positive)  $\Delta^{33}\text{S}$  ( $\Delta^{36}\text{S}$ ) which the sulfates apparently acquired from UV-induced photochemical oxidation of  $\text{SO}_2$  in the anoxic Archean atmosphere (Farquhar et al., 2001). Alternatively, pyrites in black cherts and shales and banded iron formations are anomalously enriched in <sup>33</sup>S by as much as 7‰ ( $\Delta^{33}\text{S} > 0$ ,  $\Delta^{36}\text{S} < 0$ ) and, typically, have  $\delta^{34}\text{S} > 0$ . In this case, the pyrite is thought to be derived from elemental sulfur that obtained its anomalous  $\Delta^{33}\text{S}$  and  $\Delta^{36}\text{S}$  signatures as a result of UV-induced reduction of  $\text{SO}_2$ , ultimately to  $\text{S}^0$  (Farquhar et al., 2001; Pavlov and Kasting, 2002). Subsequent mixing of these two sulfide reservoirs in various geological environments has created pyrites in which  $\Delta^{33}\text{S}$  and  $\Delta^{36}\text{S}$  are, respectively, approximately proportional and inversely proportional to  $\delta^{34}\text{S}$ .

### References

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## Does slab serpentization and deserpentinization create the primary HIMU mantle component?

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Hydration and dehydration of oceanic lithosphere play an important role in element recycling at convergent margins. Most studies agree that subduction related recycling is necessary to explain some aspects of the mantle's chemical evolution. However, these recycling processes are not yet well understood: OIB type lavas sometimes show a radiogenic <sup>206</sup>Pb/<sup>204</sup>Pb component commonly termed HIMU whose origin is yet to be exactly determined. The MORB source appears to be even more influenced by this mantle component, with these depleted basalts having relatively high <sup>206</sup>Pb/<sup>204</sup>Pb ratios (an expression of the so called lead paradox). This indicates that the mantle's U/Pb ratio has increased over time, although MORB/OIB related melting would preferentially remove U over Pb. Thus it seems that a non-melting subduction related fractionation process leads to the recycling of a high U/Pb component.

Earlier studies attribute this increase in U to the recycling of oceanic crust and sediments. However, here we show that serpentized mantle is maybe the more likely slab lithology to recycle a high U/Pb component. The transport mechanism is aqueous fluid flow; preferential U-pumping occurs because U is easily transported into serpentizing lithosphere by oxidized seawater, while Pb is more easily removed from deserpentinizing lithosphere during reduced high-T fluid escape. Plate bending induced normal faulting at the outer rise can potentially create the conduits for seawater to reach and react with cold lithospheric mantle to serpentize it, leading thus to seawater transported U enrichment. Subsequent partial high P-T dewatering further increases the host serpentinite's ratio of U/Pb. Recycled serpentized mantle therefore shows high U/Pb ratios along with depleted, low abundance, Nd and seawater Sr isotopic ratios with low Rb/Sr. Evolving this lithologic composition can produce the signature of the proposed HIMU mantle component.

We model fluid release beneath differing subduction zones, to further explore these recycling processes which we find to vary significantly among differing subduction zones. For example, varying the incoming plate age for a given slab petrology shows that for a 30my old plate 55% of the serpentinite-hosted water is released - for a 100my old plate only 10%. Differing subducting slabs therefore recycle differing amounts of water and U into the deeper mantle which helps to produce the chemical heterogeneity of the earth's mantle evident in both ocean island basalts and MORB.