

## Iron isotopes constrain the roles of biologic and abiologic processes in formation of banded iron formations

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Iron isotope compositions of 2.5 Ga banded iron formations (BIFs) from the Hamersley Basin and Transvaal Craton identify the iron sources and formation pathways during BIF genesis. <sup>56</sup>Fe/<sup>54</sup>Fe ratios for magnetite reflect a strong inheritance from Fe(III) hydroxide precursors, with a peak about  $\delta^{56}\text{Fe}=0$ . Near-zero  $\delta^{56}\text{Fe}$  values for the Fe(III) hydroxide precursors may be produced by complete or near-complete oxidation of Fe(II)<sub>aq</sub> derived from marine hydrothermal fluids, suggesting the existence of a significant oxidant in the upper water column at 2.5 Ga. Transformation of the Fe(III) hydroxide precursors to magnetite occurred through several diagenetic processes that produced a range of  $\delta^{56}\text{Fe}$  values: 1) addition of marine hydrothermal Fe(II)<sub>aq</sub>, 2) reduction by bacterial dissimilatory Fe(III) reduction (DIR), and 3) interaction with excess low- $\delta^{56}\text{Fe}$  Fe(II)<sub>aq</sub> that was produced by DIR.

The range in  $\delta^{56}\text{Fe}$  values for siderite reflects a mixture of iron sources including seawater Fe(II)<sub>aq</sub> and Fe(II)<sub>aq</sub> produced by DIR. The inferred Fe sources and pathways for magnetite and siderite from adjacent bands, however, are distinct, and these minerals did not generally form in Fe isotope equilibrium. Instead, the Fe isotope variability of magnetite and siderite document fine-scale isotopic heterogeneity that reflects a strong component of diagenesis. Support for an important role of DIR in siderite formation in BIFs comes from previously published C isotope data on organic carbon and siderite, which may be explained as a mixture of C produced by bacterial and seawater sources.

Several factors likely contributed to the important role that DIR played in formation of the 2.5 Ga BIFs from the Hamersley Basin and Transvaal Craton, including high rates of ferric hydroxide formation in the upper water column, delivery of organic carbon related to photosynthesis, and low clastic input. We infer that DIR-driven Fe cycling was much more important during deposition of these BIFs than in modern marine systems. Low pyrite contents in oxide-facies BIFs suggests that bacterial sulfate reduction (BSR) was minor, and the absence of sulfide allowed preservation of magnetite and siderite; low BSR also provided a competitive advantage for DIR. When compared to BIFs that formed prior to 3.0 Ga, the Fe isotope signature for DIR is absent in the older sequences, suggesting that this metabolism may have been absent in the Early Archean. Moreover, the generally positive  $\delta^{56}\text{Fe}$  values for the older BIFs suggests that oxidants were more limited, which in turn would limit DIR activity.

## Slab dehydration beneath central Mexico inferred from melt inclusions and geodynamic modeling

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To investigate volatiles (H<sub>2</sub>O, CO<sub>2</sub>, S, Cl) and magma formation in subduction zones, we have analyzed olivine-hosted melt inclusions from 10 basaltic centers at varying distances from the trench in the Michoacan-Guanajuato Volcanic Field in central Mexico. Our data from these primitive basaltic cones (most contain Fo87-90 olivine) reveal the surprising result that H<sub>2</sub>O contents are high (3.0-5.2 wt%) from the volcanic front to ~140 km behind the front. The high H<sub>2</sub>O across the arc, combined with high S and Cl, suggest that flux of volatiles from the subducted plate has affected a broad region of the underlying mantle.

To understand the depths over which subducted slab components dehydrate beneath the arc, we have modeled the thermal structure of the mantle wedge and slab using a 2D numerical model (Manea *et al.*, 2005). We then use phase equilibria to evaluate dehydration of subducted sediment, altered oceanic crust, and hydrated lithospheric mantle in the slab (Rupke *et al.*, 2004). An important constraint is that volcanism has migrated towards the trench over the last 3 Ma, suggesting an increase in slab dip angle. Thus our studied cones farthest from the trench are older than those closer to the trench, and their volatile contents likely reflect mantle hydration resulting from a different slab geometry than the present-day configuration.

For the present-day slab model (13 Ma oceanic crust at trench), maximum mantle wedge temperatures beneath the volcanic front (1200-1300°C) agree with petrological calculations. The model results predict dehydration of subducted sediment and altered oceanic crust beneath the forearc, the volcanic front, and extending ~50 km behind the front. Subducted lithospheric mantle, if hydrated, would undergo dehydration beneath the arc ~50 km behind the volcanic front. In addition, chlorite formed by hydration of the overlying mantle wedge would no longer be stable ~100 km behind the volcanic front. Thus the width and high magmatic H<sub>2</sub>O in the Quaternary arc may be due partly to dehydration of subducted serpentized mantle and the stability of chlorite in the overlying mantle wedge. For the 3 Ma slab model, subducted sediment and oceanic crust dehydrate largely beneath the wide forearc during near-horizontal subduction. The main source of H<sub>2</sub>O to flux the wedge beneath the volcanic front at 2-3 Ma comes from dehydration of serpentized lithospheric mantle in the slab. Thus our results for both the present-day and 3 Ma slab configurations suggest a role for deserpentinization of the downgoing slab in magma generation beneath Mexico.