

Experimental evidence for shallow recycling of ocean crust in the Archean Earth

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Discussion about the relevance of modern style subduction to Archean processes has tended to overlook the fact that the only high-pressure experiments investigating metamorphic reactions during subduction have considered modern mid ocean ridge basalts. Here, we present the results of experiments on metamorphic transitions in picrite-komatiite, representing MgO-rich parts of the oceanic crust (cumulates or possibly volcanics) during the Archean. Our results show that metamorphism of MgO-rich oceanic rocks during the Archean produced pyroxenites, some olivine-bearing, but which are plagioclase-free.

The composition of the early continental crust requires that it formed by melting of garnet amphibolite, and not eclogite or pyroxenite¹. This is consistent with a scenario in which melting of garnet amphibolite and eclogite was volumetrically unimportant in the early Archean. Melting of garnet amphibolite first became prevalent during subduction in the late Archean, consistent with a large increase in continental crust mass between 3.2 and 2.5 Ga.

The rarity of melting of garnet amphibolite in the early Archean was due to the thickness of ocean crust exceeding 24km which could not be subducted as a unit². Lower parts of the crust were returned to the mantle and melted as pyroxenite. Melting of large volumes of amphibolite required subduction of the hydrothermally altered uppermost 4km of crust, which first occurred towards the end of the Archean when the crust became thinner.

Eclogite xenoliths in kimberlites from Siberia represent the best samples we have of ocean crust from the ocean basins during the late Archean. These have exceptionally depleted trace element characteristics³ relative to modern upper mantle, and may indicate that strong depletion of a thin layer of the uppermost mantle occurred during the early Archean. This would imply shallow subduction and recycling of oceanic crust in the early Archean. The current controversy about the misfit between geochemical depletion models and geophysical models for mantle convection including deep subduction may be explained by continuous deepening of the depleted layer through geological time.

1 Foley, S.F., Tiepolo, M. & Vannucci, R. This volume.

2 Abbott, D.H. (1996). *Lithos* 37, 113-127.

3 Jacob, D.E. & Foley, S.F. (1999) *Lithos* 48, 317-336.

Iron isotope fractionation: does equilibrium or disequilibrium rule?

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A central question confronting workers in the emerging field of heavy element stable isotope geochemistry is the extent to which isotope fractionation results from either equilibrium or disequilibrium processes. This issue is particularly relevant to our understanding of abiotic Fe isotope variations observed thus far in experimental and natural systems. A critical finding, based on both theoretical and experimental approaches, is that at equilibrium aqueous Fe(III) is 3-5 per mil heavier than coexisting aqueous Fe(II) in terms of the ⁵⁶Fe/⁵⁴Fe ratio. This amount of fractionation is greater than that yet observed in natural systems, which suggests that abiotic Fe isotope fractionation in nature may bear the overprint of disequilibrium, or "kinetic isotope effects" on the equilibrium fractionation. In fact, several features of abiotic Fe isotope fractionation suggest control by kinetic isotope effects. For example, although the Fe in ferrihydrite produced during Fe oxidation at circum-neutral pH is heavy relative to the coexisting aqueous Fe(II), the amount of fractionation observed is less than 3 per mil perhaps due to a kinetic isotope effect imposed by the nearly irreversible oxidation reaction. Similarly, ferric oxides and oxyhydroxides precipitated from Fe(III)-rich solutions at low pH contain Fe that is lighter than the coexisting aqueous Fe(III), suggesting control by a kinetic isotope effect during precipitation. However, in the case of Fe(II) oxidation the amount of fractionation increases with increasing oxidation and solid precipitation rates, while in the case of Fe(III) precipitation the amount of fractionation decreases with increasing precipitation rate. The trend toward progressively heavier Fe in the solids with increasing reaction rate is opposite to that expected to result from abiotic kinetic isotope effects. Although a minor role for kinetic isotope effects cannot be ruled out, we suggest that equilibrium exchange between coexisting Fe(II) or Fe(III) aqueous metal ions and complexes provides a more consistent explanation and mechanistic framework with which to explain Fe isotope variations observed in natural and experimental systems.