

Iron isotope geochemistry with a synchrotron light beam

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Previous studies have suggested that iron isotopes could be good tracers of redox conditions during melting [e.g., 1]. However, we lack a reliable database of equilibrium fractionation factors between melts and igneous minerals such as olivine to interpret the rock record [2]. Iron equilibrium fractionation factors (or more specifically reduced partition function ratios, β) can be derived from Nuclear Resonant Inelastic X-ray Scattering (NRIXS) experiments at a synchrotron facility [3,4]. We have developed a new method (i.e., the *general moment* approach), based on a Bernoulli expansion of the reduced partition function ratio, to calculate β -factors from the moments of raw NRIXS spectra [4]. The first term in this expansion corresponds to the mean force constant of the iron bonds [5], a quantity that is readily measured and often reported in NRIXS studies [6]. We have used this technique to determine the β -factors of olivine and geologically relevant silicate glasses.

At a given $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio, the force constants of basaltic, andesitic, and dacitic glasses are almost identical. However, the force constant of rhyolitic glass is higher. For all samples, the force constant increases with the Fe^{3+} content. Thus, for mafic melts, there is little structural control on iron isotopic fractionation; redox effects seem to dominate. The relationship between force constant and $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ for basalt, andesite, and dacite is approximately linear. We can estimate the force constants of Fe^{2+} and Fe^{3+} in basalt by interpolating the data to $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}=0$ and $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}=1$. At 1,100 °C, we calculate an equilibrium $\delta^{56}\text{Fe}$ fractionation of +0.25 ‰ between the two oxidation states of iron in magmas. The olivine-melt and melt Fe^{2+} - Fe^{3+} iron isotopic fractionations derived from NRIXS data may explain the heavy iron isotopic compositions measured in MORBs.

This study provides a solid reference for interpreting Fe isotopic variations in igneous rocks. Specifically, it reveals the potential of using Fe isotopes to trace redox variations and magmatic differentiation processes in planets.

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Cyclic growth layers in calcareous biominerals

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Mollusc shells are among the best known calcareous biominerals. The calcitic prisms of *Pinna* and *Atrina* are often used because of their large size and simple geometry. As other biominerals, they are organo-mineral composites [1,2]. Thin sections observed in polarized light show they behave as monocrystals [3]. However, polished and etched sections show they are composed of growth zonations. Thickness of a growth line is about 1-3 μm . Moreover, the distribution of chemical elements is not uniform. Outer organic walls have low Mg and high S contents. Within the prisms, more or less intense zonations are visible. In both structural and chemical images, zonations are synchronous across adjacent prisms, showing the strict physiological control of the biomineralization processes. The comparison of chemical maps show that the rhythm and intensity differ according to the element.

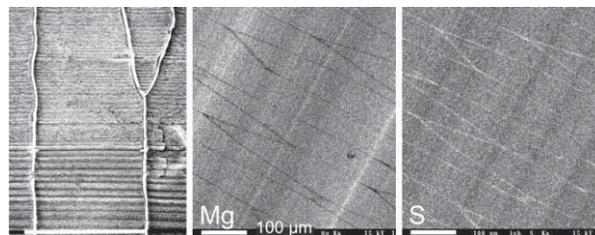


Figure: structural growth lines and chemical zonations in the calcitic prisms of *Pinna*

AFM images show that prisms are made of granules surrounded by a cortex. TEM data show that in distinct regions of a prism, granules are amorphous, while others are crystallized as subunits of a large single crystal. At the boundary of the two regions, granules display a crystallized core and an amorphous rim [4]. Such a limit probably marks out an arrested crystallization front having propagated through a previously biocontrolled architecture of the piling of amorphous micro-domains.

Such a crystallization process, developed within the organic matrix, differs from the usual model occurring within a fluid, the composition of which is assumed to be close to sea water. Such a model, used in the palaeo-climate/ geochemical areas, cannot account for any species-specific property of the calcification process. A matrix-driven crystallization within the spheroids of the growth layers provides us a reasonable way to explain the black-box of the "vital effect".

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