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# Look between the grains

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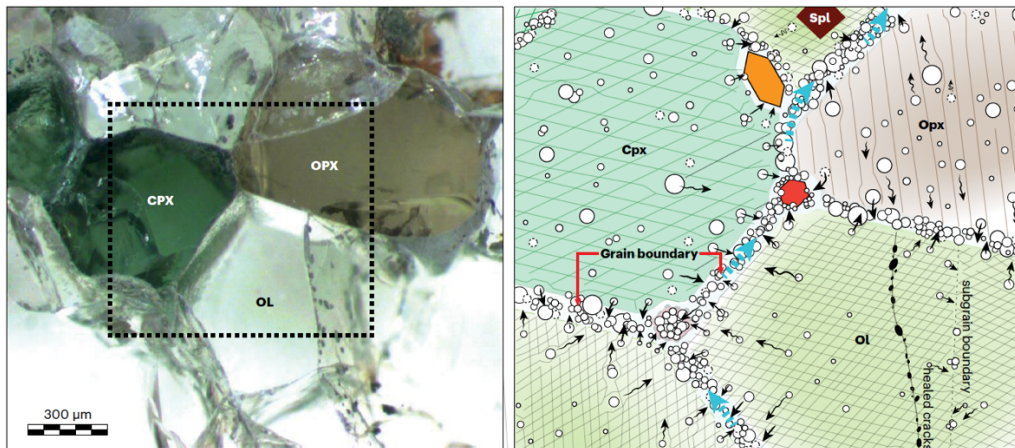
Rocks are seen as aggregates of minerals, with specific compositions, crystallographic characteristics and capacities for the substitution and storage of trace elements, such as volatiles. But rocks are not mere aggregates of crystals; the grains have imperfect interfaces and nano- to micro-interstitial phases are commonly found within this interstitial media. We argue that this interstitial component could represent an underappreciated repository for water-derived species and other volatile elements. Grain boundaries have specific geochemical properties, distinct atomic structures and less strain and order than crystalline lattices of individual minerals<sup>1</sup>, resulting in a higher density of vacancies along these interfaces. Thus, grain boundaries in rocks influence processes controlling mass transfer in the Earth's lithosphere and asthenosphere, such as ionic diffusion, ductile deformation, and grain growth. Furthermore, the high vacancy density of grain boundaries offers the possibility to store larger ions, such as incompatible elements, that typically do not fit into the tight crystal lattice of mantle minerals such as olivine for example<sup>2</sup>. Grain boundaries could therefore act as a sink for all of the misfit elements that were initially incorporated into the grain lattice or that pass through during the percolation of and the reaction with small volume-melts.

When accounting for the trace element inventories in the crystal lattices of rock-forming mineral grains only, the bulk concentrations of incompatible trace elements such as light rare earth elements (LREE: La, Ce, Sm, Pr, Nd), large ion lithophile elements (for example, U, Th, Rb, Sr, Ba, Cs) and high field strength elements (for example, Nb, Ta, Zr, Hf) are never fully accounted for<sup>3–5</sup>. The large ionic radius and/or charges of incompatible elements imply that they have difficulty to fit in the relatively tight crystal structures. In the absence of metasomatic phases showing high affinity for such elements, the more accommodating structure of the grain boundary offers an energy efficient alternative. Indeed, incompatible elements are known to be hosted at the grain boundaries of mantle peridotites in large quantities<sup>3–5</sup>.

Geochemistry techniques cannot yet assess if an interstitial component is related to grain boundary or to micro/nano-phases as imaged by some studies<sup>4</sup>. However, one can envision a continuum between these two repositories where grain boundaries complex transition<sup>1,6</sup>, which involve changes in structure composition and properties of these grain boundaries, will lead through segregation of impurities (that is, the misfit elements) to local chemical saturation triggering the formation of interstitial micro/nano-phases (Fig. 1). Therefore, to be as inclusive as possible, we refer to a grain boundary and intergranular component (GBIC) that combines both.

Hydrogen incorporation into nominally anhydrous minerals is strongly dependent on vacancy concentration<sup>7</sup>. From a geochemistry point of view this 'water' component is clearly an incompatible element, as investigation of mantle melts suggest that 'water' and the incompatible element Ce behave geochemically in similar ways<sup>8</sup> and experimental partition coefficients for water are similar to those obtained for incompatible elements for example<sup>9</sup>. Thus, as it has been proposed for the very incompatible and volatile noble gases<sup>10,11</sup> the GBIC could represent a key repository phase for water-derived species and other volatile elements.

If ‘water’ and other volatiles are hosted in the GBIC in substantial amounts then there are implications for the petrophysics and geophysical properties of the mantle — for example, the electrical conductivity and seismic attenuation — that must be considered. Similarly, our understanding of the abundance and behaviour of volatiles in the deep Earth will require revision if substantial water and volatiles are held in the GBIC with implications for geodynamic mantle processes, ductile deformation and chemical transfer between the deep Earth and exospheres. Despite the potential for grain boundaries and their (related) interstitial components to store vast amounts of water, this geochemical reservoir remains poorly explored. We therefore encourage researchers studying mantle rocks to examine not only the minerals, but also the properties of the grain boundaries, for between the grains could lie a greater understanding of the volatile cycle and all that it affects.



**Fig. 1 | A peridotite xenolith from Patagonia showing a typical upper-mantle mineral assemblage.** A section of microphotograph (a) is depicted in the schematic view (b), highlighting incompatible atomic impurities such as volatiles and trace elements (represented by white circles of various sizes, not to scale) in lattice vacancies, their distribution and mobility (arrows) from crystal lattice toward grain boundary and interstitial media. Ol, olivine; Opx, orthopyroxene; of Cpx, clinopyroxene; Spl, spinel; red and orange minerals denote micro/nano metasomatic phases (for example, amphibole, mica, apatite etc.). Black ellipses along grain boundaries represent typical supercritical CO<sub>2</sub> inclusions observed in peridotite olivines. Mobility of compatible elements easily incorporated in silicates are not shown.

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