

Grain-boundary and intra-crystal dissolution-reprecipitation reactions in alkali feldspars

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Most alkali feldspars exhibit exsolution or replacement microtextures (perthite). Regular, μm -scale 'strain-controlled' perthites form by continuous processes involving only volume diffusion of Na^+ and K^+ (plus Ca^{2+} and coupled Al^{3+} in ternary feldspars) through an Al-Si-O framework which remains continuous (coherent). The different ionic radii of Na^+ and K^+ lead to elastic strain and exsolution lamellae adopt crystallographic orientations which minimize strain energy. Irregular, much coarser, discontinuous (incoherent) 'deuteric perthites' form by dissolution-reprecipitation 'unzipping' reactions driven by release of coherency strain. These affect entire >1 cm crystals without modification of crystal shapes.

In the Klokken intrusion layers of impermeable fine-grained syenite (feldspar bulk composition $\sim\text{Ab}_{60}\text{Or}_{40}$) are interleaved with layers of compositionally similar, permeable coarse grained syenite. Sub- μm cryptoperthites in the former have a 'braid' configuration which is modified by forces acting between adjacent crystals, so that the textures form a 'strain-map'. The textures coarsen to $\sim 20\mu\text{m}$ near crystal boundaries leading to 'pleated rims' in which Na- and K-rich volumes alternate on opposing crystal surfaces. The local change in bulk composition leads to change in the lamellar texture to parallel films with edge dislocations (semi-coherent). The dislocations allow ingress of water into crystals and local development of patch perthites.

Patch perthites (up to $250\mu\text{m}$) dominate in the coarse syenites although relics of braid microtexture persist. TEM shows that individual patches are mosaics of incoherent subgrains which CL shows have well developed, 1-10s of μm oscillatory zoning at blue-UV wavelengths. Adjacent albite or microcline subgrains may display the same zoning pattern, with individual zones traceable over 100s of μm , implying dissolution in laterally extensive fluid films. Laser ICPMS shows that Ga, Rb, Sr, Ba, La, Eu, Pb and Cs partitioned isochemically in bulk from braid into Ab- and Or-rich patches, whereas Fe, Ti, Ni, La, Ce, Pr and Nd were lost from crystals during unzipping. After unzipping, Or-rich patches underwent a further phase of strain-controlled exsolution leading to straight lamellar cryptoperthites with dislocations. Solvus relationships show that this occurred at $\leq 350^\circ\text{C}$, implying that the deuteric fluids had ceased to play a role below this T .

Importance of Ar, He transport and partitioning in grain boundaries

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Analysis of noble gases, most notably Ar and He, in rocks and minerals are used in a variety of geological applications including geo- and thermochronology, tracing crustal recycling, and reconstructing Earth's degassing history. Interpretations of such data are effected by the manner in which the gases are partitioned between system phases (or reservoirs) and therefore reflect the noble gas content of the environment from which the samples were derived. Partitioning also effects the net rate by which the gases are transported in a given system. Mineral-mineral grain boundaries represent one reservoir common to all "dry" rocks into which noble gases may be partitioned and stored, and through which noble gases may be efficiently transported.

An experimental method has been developed for the measurement of grain boundary partition coefficients for noble gases. ^{37}Ar and ^4He are introduced into solid diopside composition glass samples via neutron irradiation. Samples are crystallized in sub-solidus conditions in a piston cylinder at 1350-1550 C and 2-3 GPa. Noble gases simultaneously equilibrate between the evolving crystal and grain boundary reservoirs. After equilibration, G.B. Ar and He is differentiated from that within the crystals by means of bulk step heating analysis. Results suggest an expected trend of decreasing bulk G.B. noble gas content with increasing grain size and yield a value of effective grain boundary surface partitioning, K_{surf} , in units of $(\text{mol Ar}/\text{m}^3 \text{ of solid})/(\text{mol Ar}/\text{m}^2 \text{ of GB})$ of $6.8 \times 10^3 - 2.4 \times 10^4 \text{ m}^{-1}$. Values for He are less well constrained but lie in a similar range.

These data suggest that grain boundaries constitute a significant, but not infinite, reservoir, and therefore bulk transport pathway, for noble gases in nominally dry systems (i.e. free of a fully wetting fluid phase). For example, this parameter may be used in a physical model of the local development of excess Ar (or He) (Baxter 2003) to help predict the amount of excess Ar (or He) that would be sequestered in the phases of a nominally dry system such as many ultra-high-pressure crustal settings or portions of the mantle. Also, partitioning and transport of noble gases into melts will be influenced initially by mineral-mineral grain boundaries where up to 30% of the bulk rock noble gas could potentially be stored before incipient melting.

Reference

Baxter E.F., (2003) *EPSL* 216, 619-634.