Nucleation and growth of acicular rutile in garnet: a case of open system precipitation

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Crystallographically oriented precipitates of rutile grew within garnet in metapelites from the Greek Rhodope during exhumation and cooling from eclogite and granulite facies conditions. Homgeneous nucleation produced a three-dimensional array of mostly acicular rutile precipitates with aspect rations between 10 and 100. Rutile c-axes are inclined at an average angle of 27° to the needle long axes (oblique extinction), and EBSD analysis reveals a clear but complex crystallographic orientation relationship with the garnet host. TEM-imaging shows semi-coherent to incoherent phase boundaries and a small but significant lattice mismatch even along those phase boundaries with the best relative match. The “idiomorphic” rutile needles are terminated by low-index planes of garnet, the most common ones being (110), (100) and (112).

Another set of micrometer-sized rutile inclusions in the same garnets is more isometric and granular and is interpreted as resulting from heterogeneous nucleation at dislocations; TEM-data show very poor lattice match (complete incoherence along all interfaces). Garnet from another metapelite sample shows arrays of oriented rutile needles embedded in a very fine grained (nanometer-sized) “dust” – most likely a later generation of rutile precipitates – with clear zones free of “dust” around the needles and larger precipitate-free zones (also free of needles) along the garnet rims.

The mechanism of rutile precipitation from garnet is not trivial and in fact impossible stoichiometrically unless one assumes significant amounts of Ti^{4+} on the tetrahedral site in garnet [1, 2]; Yang et al, 2005). Hence, a mechanism called open system precipitation (OSP; Proyer et al. 2008, 2011) is invoked, defined as precipitation made possible by exchange of chemical components with external reservoirs such as the rock matrix and/or fluid inclusions). Several open system reaction equations can be devised, the most effective one being a redox reaction by which Fe^{2+} from the dodecahedral site is oxidized to Fe^{3+} and moves onto the octahedral site in order to replace exsolving Ti^{4+}, accompanied by diffusion of electrons and divalent cations. Part of Ti^{4+} may also be reduced to Ti^{3+} because many of the large primary rutile inclusions found in the same garnets display a colour change from brown to grayish-purple, which is typical for reduced rutile. In that case, Ti^{3+}-bearing overgrowths on primary rutile inclusions would be another type of heterogeneously nucleated precipitate.

Garnets with oriented acicular rutile precipitates are not uncommon from high-grade amphibolite, granulite and also eclogite facies rocks, but the typical garnets from such rocks are precipitate-free, and the actual geological significance – particularly the T-t information recorded by the various precipitate types, their size, spatial distribution and morphology – is yet unclear.

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Stable Vanadium Isotope Fractionation During Differentiation

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Understanding and quantifying fractionation processes is key to the application and interpretation of both traditional and non-traditional stable isotopes. In this study we examine the effects of magmatic fractionation on the nascent stable vanadium (V) isotope system [1, 2]. Vanadium exists in multiple valence states and $\delta^{51}V$ should be strongly influenced by changing oxidation state. We present $\delta^{51}V$ of lavas from Hekla, Iceland [3]. Hekla is a fissure volcano with eruptive products ranging from basalt to rhyolite with remarkably coherent liquid lines of descent. The evolution from basalt to basaltic andesite can be clearly related to crystal fractionation [e.g., 4]. In addition to Sr, Nd, Pb, U-series, and O isotopes, Hekla lavas also boast studies of stable Si [3] Li and Fe [5] isotopes, making them arguably the best-characterized differentiation suite in terms of non-traditional stable isotopes. Hekla is therefore ideal to examine $\delta^{51}V$ against a wide backdrop of geochemical data.

We concentrate on basalt to basaltic andesite lavas where V concentrations decrease sharply from ~300 ppm to ~10 ppm. We find a large range in $\delta^{51}V$ of ~2 ‰, which co-varies with major and trace elements. The crystallising mineral phases are olivine, plagioclase, clinopyroxene and magnetite; with magnetite as the dominant V host.

Co-variation of $\delta^{51}V$ with indices of differentiation could implicate Rayleigh fractionation similar to that proposed for $\delta^{56}Fe$ variations at Hekla [5]. No mineral-melt isotope fractionation factors are available, and a bulk *f* must be assumed. However, unlike Fe, V is dominantly controlled by one phase. If Rayleigh fractionation is occurring, then magnetite must be extremely light in order to drive the lava to the observed heavy $\delta^{51}V$ compositions.

The incorporation of V into magnetite will depend partly on the oxygen fugacity of the system. Determining mineral-melt fractionation factors by measurement of $\delta^{51}V$ in both natural and experimental materials could pave the way for the use of magnetite as a unique single mineral tracer of oxygen fugacity.

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