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The origin of needle-like rutile inclusions in natural gem corundum: A combined EPMA, LA-ICP-MS, and nano-SIMS investigation—Discussion

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INTRODUCTION

Palke and Breeding (2017) claim that rutile needles with shape-preferred orientation included in gem corundum result from epitaxy of rutile on the corundum surface during growth of corundum in a magmatic environment. This is in contrast to the presently accepted view of oriented rutile needles in corundum being products of exsolution during cooling.

EXSOLUTION VS. EPITAXY

While confirming that Ti dissolves into gem corundum and precipitates as rutile needles to obtain star sapphire, and that both processes are common practice in the heat treatment of ruby and sapphire at high temperatures (1800–1100 °C; e.g., Schmetzer et al. 2015), Palke and Breeding (2017) doubt that rutile exsolution occurs in nature during metamorphism, without substantiating their case.

However, subsolidus rutile nucleation is not a significant energetic barrier because the structural mismatch between rutile and corundum is minimal (Moon and Phillips 1991). Hence the determining factor of rutile precipitation is diffusion. Ti^{4+} substitutes in corundum by at least two mechanisms: by (Mg^{2+}, Fe^{2+})$TiAl_{-2}$ and by $Ti_3\square Al_{-4}$ (e.g., Langensiepen et al. 1983). In the case of Al-substitution in olivine, either by $Al_2Mg_{-1}Si_{-1}$ or by $Al_4Si_{-3}\square_{-1}$, the vacancy mechanism was shown to be the faster one (Zhukova et al. 2017), and the same might be expected for Ti in corundum. Even though reliable Ti-diffusion data for corundum are lacking (Doremus 2006), a reasonable estimate for Ti diffusivity would lie between that of Ti^{4+} in quartz (Cherniak et al. 2007) and Cr^{3+} in corundum. A simple calculation can be made, using a relationship between diffusion length (L) and time (t) like: $L = \sqrt{4Dt}$, with diffusivity D containing the temperature dependence: $D = D_0 \exp(E_a/RT)$, where E_a is the activation energy.

While the gemological literature (e.g., Nassau 1981; Emmet and Douthit 1993) lacks relevant heat treatment parameters (temperature, time, and redox control), some materials science papers are useful. For example, Moon and Phillips (1991) treated disks of both transparent and turbid (exsolution-bearing) natural sapphire for 20 h at 1700 °C in O_2 atmosphere and then annealed the crystals in air at 1150 °C for 50 h. TEM examination revealed both acicular and smaller isometric ("embryonic") rutile grains of <1 μm size and with very narrow (<1 μm) precipitate spacing. These parameters are best reproduced by the data for Ti-diffusion in natural quartz of Cherniak et al. (2007), which would in turn predict rutile precipitates of larger size and wider (10–100 μm) spacing as in natural samples in 2000 to 200 000 yr at 800 °C and in 2.55–255 Ma at 600 °C, provided that we can extrapolate these experimental results to lower T and much lower f_{O_2}. This corroborates the possibility of precipitate formation during metamorphic cooling.

MELT INCLUSION EVIDENCE

Palke and Breeding (2017) interpret melt inclusions found in three alluvial corundum grains from Montana and Australia as being primary. The melt inclusions are said to be still glassy, which is why rutile needles observed in the same region as the melt inclusions are considered to be encapsulated primary inclusions rather than precipitates. This is because precipitates would require prolonged annealing to form, during which glass inclusions would recrystallize. Unfortunately the evidence presented in support of primary melt inclusions is minimal: only two of the four photomicrographs in Figure 1 show rutile needles near the melt inclusions—most solid inclusions are actually nano- to micrometric, unidentifiable "dust"—and no evidence (microthermometric or analytical) is presented to show that the "melt inclusions" are actually not fluid inclusions.

Moreoever, in another paper (Palke et al. 2017), EPMA data are provided for the melt inclusions from the two Montana alluvial sources, with the result that inclusions deemed primary are compositionally indistinguishable from those considered secondary. The only difference between the melt in which the corundum grains allegedly formed and the magma that transported them to the surface was considered to be the amount of volatiles, deduced from the difference between analytical totals and 100 wt%. Such a difference, however, can easily be explained by minor differences in gas bubble volume, i.e., outgassing kinetics from the same original (rhyolitic to dacitic) magma.

The fact that all melt inclusions, primary and secondary, in Figure 2 of Palke et al. (2017) show planar features around them that could stem from decrepitation or the annealing of a former melt-filled fracture, illustrates the difficulty of properly classifying inclusions as primary or secondary.

MICROCHEMICAL EVIDENCE

Three different corundum crystals from alluvial deposits in Madagascar, Sri Lanka, and Tanzania, of skarn or high-grade metamorphic origin, were chosen for microchemical analysis by Palke and Breeding (2017). These crystals had no melt inclusions but rutile needles were identified in two of the samples as part of very fine-grained "dusty" or "cloudy" core regions surrounded by inclusion-free rims. Palke and Breeding (2017) found no correlation in LA-ICP-MS traverses between Ti and the divalent cations and concluded that substantial amounts of Ti were incorporated not just by the (Mg^{2+},Fe^{2+})$TiAl_{-2}$ substitution

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but by syngenetic inclusion of epitactic rutile needles.

The above observations, however, can be easily explained by several factors: Fe occurs both in the ferrous and ferric state (hence no clear correlation of Fe + Mg = Ti); Ti can also substitute by a vacancy mechanism (and perhaps other mechanisms); and divalent cations can be lost to the matrix during open-system precipitation of rutile (cf. Proyer et al. 2013).

Another argument is based on the detection of Ta-rich rutile in one sample from Tanzania (TUN) for which three different analyses show consistently high levels of Ta_2O_5 (20.35–22.40 wt% corresponding to 0.084–0.094 apfu). As Palke and Breeding (2017) point out, corundum is unlikely to dissolve sufficient Ta to generate such Ta-rich rutile precipitates. This observation would be a strong argument if each of these particular grains had been demonstrated to be of acicular shape, with shape-preferred orientation, and not rather isometric like the common primary inclusions of rutile or (Nb-Ta enriched) ilmenorutile in many sapphires worldwide (e.g., Guo et al. 1996). Such primary Nb-Ta-enriched inclusions can be confused with exsolved acicular rutile in BSE imaging if they are of similarly small grain size, and they might be more inviting to place an analysis point due to their more isometric shape. Primary inclusions of Ti-, Nb/Ta-, or W-rich minerals are considered possible and even likely parts of the cloudy inclusion zones—they would explain some of the high Ti- and W-values in ICP-MS analyses, and the Ta-rich rutiles discussed above, but they would be equant rather than acicular in shape, even though they could serve as nucleation points for later rutile exsolution.

The nano-SIMS image shown for one of these grains does not reliably confirm the EPMA analysis because Ta is not quantified—any rutile will always contain more Ta than surrounding corundum and hence appear as in Figure 5b of Palke and Breeding (2017). The scale marker bar in Figure 5b for Ta says zero counts across the entire color scale, but it should range to higher values given that one out of 10 cations is Ta.

Several additional arguments speak against syngenetic epitaxy. (1) Primary rutile from metamorphic and perhaps also most magmatic environments does not have such high aspect ratios of 10–100 (it is prismatic rather than acicular), whereas needles are typical for precipitates. A typical example is rutile precipitates in metamorphic garnets (Proyer et al. 2013 and other studies quoted therein), where stubby and usually much larger primary rutile is almost always present in addition to the fine acicular later precipitates. (2) If acicular rutile were present in a magmatic growth environment of sapphire, it would also be included in arbitrary orientation, not just in strict crystallographic orientation to the host mineral structure, and a systematic coarsening of such rutiles from corundum core to rim can be expected. The ratio of crystallographically vs. arbitrarily oriented rutile needles is, however, usually high, which again is typical for a precipitate origin. (3) While primary inclusions tend to attach on all growth faces of corundum, including prismatic and pyramidal faces, with the inclusion long axes often (near) parallel to corundum [0001] (Baldwin et al. 2017), rutile precipitates mostly form in the (0001) plane (Phillips et al. 1980; Moon and Phillips 1991). (4) Epitactic rutile, like other surface irregularities would be preferred entrapment sites of coexisting melt—Palke and Breeding (2017) have not reported observations of rutile needles trapped in contact with or within melt inclusions. Considering the above, I do not find the evidence presented by Palke and Breeding (2017) convincing enough to advocate syngenetic epitactic growth of rutile in corundum, but do acknowledge that there is increasing evidence for melt-present growth of corundum in some cases other than quartz-absent muscovite breakdown (Sutherland et al. 1998; Kullerud et al. 2012; Palke et al. 2016; Karmakar et al. 2017; Baldwin et al. 2017).

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References cited

Baldwin, L.C., Tomaschek, F., Ballhaus, C., Gerdes, A., Fonseca, R.O.C., Wirth, R., Geisler, T., and Nagel, T. (2017) Petrogenesis of alkaline basalt-hosted sapphire megacrysts. Petrological and geochemical investigations of in situ sapphire occurences from Siebengebirge Volcanic Field, Germany. Contributions to Mineralogy and Petrology, 172, 43.

Cherniak, D.J., Watson, E.B., and Wark, D.A. (2007) Ti diffusion in quartz. Chemical Geology, 236, 65–74.

Doremus, R.H. (2006) Diffusion in alumina. Journal of Applied Physics, 100, 101301.

Emmet, J.L., and Douthit, T.R. (1993) Heat treating the sapphires of Rock Creek, Montana. Gems & Gemology, 29/4, 250–272.

Guo, J., O'Reilly, S.Y., and Griffin, W.L. (1996) Corundum from basaltic terrains: a mineral inclusion approach to the enigma. Contributions to Mineralogy and Petrology, 122, 368–386.

Karmakar, S., Mukherjee, S., Sanyal, S., and Sengupta, P. (2017) Origin of peraluminous minerals (corundum, spinel and sapphirine) in a highly calcic anorthosite from the Sittampundi Layered Complex, Tamil Nadu, India. Contributions to Mineralogy and Petrology, 172, 67.

Kullerud, K., Nasipuri, P., Ravna, E.J.K., and Selbekk, R.S. (2012) Formation of corundum megacrysts during H_2O-saturated incongruent melting of feldspar: *P-T* pseudosection-based modelling from the Skattøra migmatite complex, North Norwegian Caledonides. Contributions to Mineralogy and Petrology, 164, 627–641.

Langensiepen, R.A., Tressler, R.E., and Howell, P.R. (1983) A preliminary study of precipitation in Ti^{4+}-doped polycrystalline alumina. Journal of Materials Science, 18, 2771–2776.

Moon, A.R., and Phillips, M.R. (1991) Titania precipitation in sapphire containing iron and titanium. Physics and Chemistry of Minerals, 18, 251–258.

Nassau, K. (1981) Heat treating ruby and sapphire: technical aspects. Gems & Gemology, 17/3, 121–131.

Palke, A.C., and Breeding, C.M. (2017) The origin of needle-like rutile inclusions in natural gem corundum: A combined EPMA, LA-ICP-MS, and nano-SIMS investigation. American Mineralogist, 102, 1451–1461.

Palke, A.C., Renfro, N.D., and Berg, R.B. (2016) Origin of sapphires from a lamprophyre dike at Yogo Gulch, Montana, USA: Clues from their melt inclusions. Lithos, 260, 339–344.

——— (2017) Melt inclusions in alluvial sapphires from, Montana, USA: Formation of sapphires as a restitic component of lower crustal melting? Lithos, 278-281, 43–53.

Phillips, D.S., Heuer, A.H., and Mitchell, T.E. (1980) Precipitation in star sapphire I. Identification of the precipitate. Philosophical Magazine A, 42/3, 385–404.

Proyer, A., Habler, G., Abart, R., Wirth, R., Krenn., K., and Hoinkes, G. (2013) TiO_2 exsolution from garnet by open system precipitation: evidence from crystallographic and shape preferred orientation of rutile inclusions. Contributions to Mineralogy and Petrology, 166, 211–234.

Schmetzer, K., Steinbach, M.P., Gilg, A., and Blake, A.R. (2015) Dual-color double stars in ruby, sapphire and quartz: cause and historical account. Gems & Gemology, 51/2, 112–143.

Sutherland, F.L., Hoskin, P.W.O., Fanning, C.M., and Coenraads, R.R. (1998) Models of corundum origin from alkali basaltic terrains: a reappraisal. Contributions to Mineralogy and Petrology, 133, 356–372.

Zhukova, I., O'Neill, H., and Campbell, I.H. (2017) A subsidiary fast-diffusing substitution mechanism of Al in forsterite investigated using diffusion experiments under controlled thermodynamic conditions. Contributions to Mineralogy and Petrology, 172, 53.

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