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3 **The origin of needle-like rutile inclusions in natural gem corundum: A combined EMPA,**
4 **LA-ICP-MS, and nano-SIMS investigation – Discussion**

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8 **INTRODUCTION**

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

13
14 **DISCUSSION**

15 **Exsolution versus epitaxy**

16 While confirming that both dissolving Ti into gem corundum and precipitating rutile needles
17 from it to obtain star sapphire are both common practice in the heat treatment of ruby and
18 sapphire at temperatures between 1800 and 1100 °C (e.g. Schmetzer et al. 2015) the authors
19 doubt that this process also prevails in nature during metamorphism, but do not substantiate their
20 case.

21 Rutile nucleation is not a significant energetic barrier because the structural mismatch is
22 minimal (Moon & Phillips 1991), hence the determining factor is diffusion. Ti⁴⁺ substitutes in
23 corundum by at least two mechanisms: by (Mg²⁺,Fe²⁺)TiAl₂ and by Ti₃□Al₄ (e.g. Langensiepen

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24 et al. 1983). In the similar case of Al-substitution in olivine, either by $\text{Al}_2\text{Mg}_{-1}\text{Si}_{-1}$ or by $\text{Al}_4\text{Si}_{-3}\square$.
25 \square , the vacancy mechanism was shown to be the faster one (Zhukova et al 2017). Even though
26 reliable Ti-diffusion data for corundum are lacking (Doremus 2006), a reasonable estimate for Ti
27 diffusivity would lie between that of Ti in quartz (Cherniak et al. 2007) and Cr in corundum
28 (Doremus 2006). A simple calculation can be made, using a relationship between diffusion length
29 (L) and time (t) like: $L = \sqrt{4Dt}$, with diffusivity D containing the temperature dependence: D
30 $= D_0 \exp(E_a/RT)$, where E_a is the activation energy in J/mol.

31 While even the more detailed gemological literature (e.g. Nassau 1981; Emmet and Douthit
32 1993) does not report the relevant heat treatment parameters (temperature, time and redox
33 control) in sufficient detail to derive or test diffusion equations, some material science papers are
34 more useful, in particular Moon and Phillips (1991). These authors treated discs of both
35 transparent and turbid (exsolution-bearing) natural sapphire for 20 hours at 1700°C in O_2
36 atmosphere and then annealed the crystals in air at 1150°C for 50 hours. TEM examination
37 revealed both acicular and smaller isometric (“embryonic”) rutile grains of $<1\mu\text{m}$ size and with
38 very narrow ($< 1\mu\text{m}$) precipitate-spacing. These parameters are best reproduced by the data for
39 Ti-diffusion in natural quartz of Cherniak et al. (2007), which would in turn predict rutile
40 precipitates of larger size and wider (10-100 μm) spacing in 2000 to 200,000 years at 800°C and
41 in 2.55 - 255 Ma at 600°C. This corroborates the possibility of precipitate formation during
42 metamorphic cooling.

43

44 **Melt inclusion evidence**

45 Palke and Breeding (2017) interpret melt inclusions found in three alluvial corundum grains
46 from Montana and Australia as primary, indicating corundum growth during presence of melt.
47 The melt inclusions are said to be still glassy, i.e. they did not devitrify, which is considered

48 incompatible with rutile needles in the same regions of the crystals that would have required a
49 rather protracted annealing period to form. Unfortunately the evidence presented in support of
50 primary melt inclusions is minimal: only two of the four photomicrographs in Figure 1 show
51 rutile needles near the melt inclusions – most solid inclusions are actually nano- to micrometric,
52 unidentifiable “dust” – and no evidence (microthermometric or analytical) is presented or quoted
53 to show that the “melt inclusions” are actually melt and not fluid inclusions.

54 For some reason, another paper by the first author (Palke et al. 2017) remains unmentioned, in
55 which melt inclusions from the two Montana alluvial sources were analysed by EPMA, with the
56 result that inclusions deemed primary are compositionally indistinguishable from those
57 considered secondary. The only difference between the melt in which the corundum grains
58 allegedly formed and the magma which transported them to the surface was considered to be the
59 amount of volatiles, deduced from the difference between analytical totals and 100 wt%. Such a
60 difference, however, can easily be explained by minor differences in gas bubble volume, i.e.
61 outgassing kinetics from the same original (rhyolitic to dacitic) magma.

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

65

66 **Microchemical evidence**

67 Three different corundum crystals from alluvial deposits in Madagascar, Sri Lanka and
68 Tanzania, of skarn or high-grade metamorphic origin were chosen for microchemical analysis.
69 They had no melt inclusions but rutile needles were identified in two of the samples as part of
70 very fine-grained “dusty” or “cloudy” core regions surrounded by inclusion-free rims. Palke and
71 Breeding (2017) found no correlation in LA-ICP-MS traverses between Ti and the divalent

72 cations, and concluded that substantial amounts of Ti were incorporated not just by the
73 $(\text{Mg}^{2+}, \text{Fe}^{2+})\text{TiAl}_2$ substitution but by syngenetic inclusion of epitactic rutile needles.

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

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

95 The nano-SIMS image shown of one of these grains does not reliably confirm the EMPA
96 analysis because Ta is not quantified – any rutile will always contain more Ta than surrounding
97 corundum and hence feature like in Fig 5b of Palke and Breeding (2017). The scale marker bar in
98 Fig. 5b for Ta says zero counts across the entire color scale while it should go to a higher range
99 given that per EPMA analysis ca. one out of ten cations is Ta and the ^{181}Ta isotope measured
100 covers 99.988% of natural Ta, while the ^{50}Ti measured only covers 5.4% of natural Ti and gives
101 nice counts, as does ^{56}Fe .

102 A number of additional arguments speak against syngenetic epitaxy: (1) Primary rutile from
103 metamorphic and perhaps also most magmatic environments does not have such high aspect
104 ratios of 10-100 – it is prismatic rather than acicular – whereas needles are typical for
105 precipitates. (2) If acicular rutile were present in a magmatic growth environment of sapphire, it
106 would also be included in arbitrary orientation, not just in strict crystallographic orientation to the
107 host mineral structure, and a systematic coarsening of such rutiles from corundum core to rim can
108 be expected. The ratio of crystallographically versus arbitrarily oriented rutile needles is,
109 however, usually high, which again is typical for a precipitate origin. (3) While primary
110 inclusions tend to attach on all growth faces of corundum, including prismatic and pyramidal
111 faces, with the inclusion long axes often (near) parallel to corundum [0001] (Baldwin et al.
112 2017), rutile precipitates mostly form in the (0001) plane (Phillips et al. 1980; Moon and Phillips
113 1991). 4) Epitactic rutile, like other surface irregularities would be preferred entrapment sites of
114 coexisting melt – Palke and Breeding (2017) have not reported observations of rutile needles
115 trapped in contact with or within melt inclusions. Considering the above, I do not find the
116 evidence presented by Palke and Breeding (2017) convincing enough to advocate syngenetic
117 epitactic growth of rutile in corundum, but do acknowledge that there is increasing evidence for
118 melt-present growth of corundum in some cases other than quartz-absent muscovite breakdown

119 (Sutherland et al. 1998; Kullerud et al. 2012; Palke et al. 2016; Karmakar et al. 2017; Baldwin et
120 al. 2017).

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