1   **REVISION 1**

2   **The origin of needle-like rutile inclusions in natural gem corundum: A combined EMPA,**

3   **LA-ICP-MS, and nano-SIMS investigation – Reply**

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6   **Introduction:** Proyer (2017) disagrees with our recent findings indicating that, in some gem

7   corundum, oriented rutile needles grew by epitactic coprecipitation rather than the usual

8   assumption of exsolution. Proyer's concerns are, in part, related to a misunderstanding of our

9   model and, in places, his arguments are based upon claims that are not supported by the cited

10   literature. We welcome the opportunity to clarify the matter. However, before starting, it was

11   pointed out to us that the correct term is "epitactic" and not "epitaxial" (Bailey et al. 1978). The

12   term "epitactic" is meant to describe the intergrowth of two minerals having 2-dimensional

13   coherence at their interface.

14   **Microchemical Evidence:** It bears mentioning at the outset that in Palke and Breeding 2017 we

15   were careful not to overreach. We felt there was a strong argument for epitacticl coprecipitation

16   in our samples but never concluded that exsolution never occurs in natural gem corundum. Our

17   argument was dominantly supported by the observation of high-field strength elements (HFSE)

18   such as Nb^{5+} and Ta^{5+} by LA-ICP-MS and the identification of the HFSE host as oriented

19   needle-like rutile by EPMA. Given that HFSE are likely to be highly incompatible in corundum,

20   the exsolution hypothesis seems untenable. Even compatible ions like Ga^{3+} are typically

21   incorporated at less than 100 ppm atomic levels, so the presence of comparable amounts of Nb^{5+}

22   and Ta^{5+} can only be rationalized through coprecipitation of Nb- and Ta-bearing inclusions.

23   Proyer acknowledges that this is a strong argument in favor of the coprecipitation

24   hypothesis, yet doubts that the HFSE-enriched rutile inclusions we analyzed were oriented and

25   needle-shaped [although it is unclear why as it was clearly mentioned in Palke and Breeding

26   (2017) in the EPMA results section and the **Table 2** title that we analyzed needle-shaped

27   oriented rutile]. **Figure 1** shows a BSE image of sample TUN. Rutile in this region is needle-like

28   and oriented. These are the types of rutile grains analyzed by Palke and Breeding (2017).

29   Proyer's concerns about the morphology of our rutile inclusions are unwarranted, which

30   strengthens our conclusion of coprecipitation according to Proyer's own admission.

31   The concern about low Ta counts in nanoSIMS is understandable, but low Ta counts are

32   expected. NanoSIMS was used to identify the Be host. While nanoSIMS is capable of measuring

33   light and heavy elements at the same time, it is not capable of being simultaneously *good* at both

34   tasks. To improve sensitivity of Be we had to sacrifice Ta counts. While Ta in rutile couldn't be

35   quantified by nanoSIMS, this was accurately done with EPMA. The high Ta/Nb ratio is not an

36   artifact as suggested by Proyer as it was confirmed by both LA-ICP-MS and EPMA.

37   Proyer incorrectly states that we showed no correlation between divalent cations and Ti.

38   In fact, **Figure 4** of Palke and Breeding (2017) clearly shows a 1:1 correlation between atomic

39   Mg and Ti at low concentrations. While Ti^{4+} can also be charge-balanced by Fe^{2+}, at these low

40   concentrations this is clearly not happening to any significant extent. Ti seems to be fixed by Mg

41   in this low range despite the fact that there is sufficient Fe to allow for additional Ti

42   incorporation. These low-Ti areas were also largely non-included areas. The data only moves

43   away from the 1:1 line to higher Ti concentration in heavily included areas. This strongly

44   suggests that in the corundum lattice, Mg^{2+} is charge balancing the bulk of the Ti^{4+}, and it further

45   suggests that excess Ti is likely related to a simple mechanical mixture of rutile and corundum.

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46 **Melt Inclusion Evidence:** Proyer questions whether the melt inclusions we studied are primary.

47 Melt inclusions were identified as primary by microscopy as they were sufficiently removed

48 from other inclusions, fractures, or crystal surfaces. These are criteria commonly used in fluid

49 and melt inclusions studies (Roedder 1984). It is unlikely the size of the bubble is related to the

50 volatile content of the glasses as no fluid phases were detected by Raman spectroscopy,

51 suggesting they are very low density contraction bubbles. The separation into primary and

52 secondary melt inclusions by Palke et al. (2017) based on microscopy and dissolved volatile

53 content of the glasses seems to be valid. Melt inclusions were identified by their similar

54 appearance in the microscope relative to those analyzed chemically by Palke et al. (2017)

55 (relative relief of corundum, melt inclusion, and its bubble) and by their lack of any fluid/vapor

56 Raman signal. In all cases, needle-like rutile inclusions were identified in close proximity to the

57 melt inclusions also by Raman spectroscopy (as stated in Palke and Breeding 2017). Our

58 argument that the coexistence of melt inclusions and rutile needles suggests an epitaxial

59 coprecipitation mechanism still holds. It is unclear why Proyer seems hesitant to accept that

60 corundum could have primary silicate melt inclusions as many petrological studies and

61 thermodynamic models suggest that it is relatively common for corundum to grow in the

62 presence of a silicate melt (e.g. Altherr et al. 1982; Raith et al. 2010).

63 **Exsolution versus epitaxy:** In the first section of the discussion Proyer presents an argument

64 that rutile exsolution should be possible in gem corundum at metamorphic conditions and

65 timescales. While it was never our intention to claim that this is impossible, Proyer's arguments

66 should be critically assessed. Many of Proyer's literature references are not applicable to the

67 question of rutile exsolution in natural corundum. For instance, the study of Langensiepen et al.

68 (1983), which is used to suggest that Ti can be incorporated without charge compensating

69   cations, was performed on synthetic sapphire grown at highly reducing conditions in order to

70   stabilize Ti^{3+}. This is common for synthetic star sapphires and rubies, in these cases annealing in

71   an oxidizing environment converts Ti^{3+} to Ti^{4+} leading to rutile exsolution. This process is

72   unrelated to natural corundum and, in fact, it has been shown that the solubility of Ti in

73   corundum in the absence of other elements is extremely low at more geologically realistic

74   oxygen fugacity (Roy and Coble 1968). Similarly, the study of Moon and Phillips (1991) showed

75   that rutile could be precipitated in natural corundum heated to 1150 °C for 50 hours. However,

76   Moon and Phillips (1991) first had to heat their natural corundum to an unnaturally high

77   temperature of 1700 °C in order to dissolve preexisting rutile needle inclusions. In this

78   experiment, it may be that rutile could be exsolved at 1150 °C only because artificial heating at

79   1700 °C created a supersaturation of Ti by dissolving rutile that may never have been dissolved

80   in corundum in the first place (e.g. epitactic coprecipitation). This artificial heating experiment is

81   not proof of rutile exsolution in natural corundum.

82   Proyer makes the bold assumption that the diffusivity of Ti^{4+} in corundum ought to be

83   between that of Ti in quartz and Cr in corundum. It is unclear why this is presumed to be a valid

84   assumption and no explanation is given. In the absence of hard data on Ti^{4+} diffusivity, any

85   calculations on timeframes for rutile exsolution in natural corundum are mere guesswork.

86   At the end of the discussion Proyer argues epitactic coprecipitation is unlikely as needle-

87   like rutile is not often found on its own in nature and that any needle-like rutile would be

88   randomly incorporated rather than oriented. This argument is based on a misunderstanding of our

89   model. We do not argue that needle-like rutile grows independently and then corundum

90   randomly grows around it. Instead we argue that rutile could be epitactically precipitated at the

91   crystal faces of a growing corundum crystal and grow along the energetically favored direction,

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92   thereby leading to the formation of the oriented, needle-like rutile inclusions in corundum, as we

93   observed.

94   Proyer suggests in the final paragraph that only exsolved rutile grows as needles in the

95   (0001) corundum plane whereas primary (coprecipitated) rutile "tends" to form parallel to the

96   [0001] direction. However, this "tendency" for coprecipitated rutile to form along the [0001]

97   direction is based on only one study by Baldwin et al. (2017) which looked at corundum from

98   only one minor occurrence. Such an isolated incident can hardly be taken as proof of a

99   "tendency" of primary rutile to be included in corundum in only one specific orientation. Further,

100   the suggestion that only exsolved rutile grows in the (0001) plane could be based on a lack of

101   realization that epitactic coprecipiation occurs in natural corundum. If more cases of

102   coprecipitation of oriented rutile and corundum were recognized, this assumption would not be

103   considered to be valid. We stress that the exsolution hypothesis is so deeply entrenched not

104   because there is unassailable evidence supporting it, but rather because it has largely remained

105   unchallenged. We are confident our observations in Palke and Breeding (2017) indicate that, at

106   least in some cases, oriented rutile needles in corundum are the product of epitaxial

107   coprecipitation.

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135   aluminum oxide. Journal of the American Chemical Society, 51, 1-6.

136   **Figure Captions:**
137   **Figure 1:** Backscattered electron image of oriented rutile needles in sample TUN from Palke and
138   Breeding (2017).

50 μm