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Comment

Discussion of the paper by Galuskin and Galuskina (2003), "Evidence of the anthropogenic origin of the 'Carmel sapphire' with enigmatic super-reduced minerals"

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We thank the Galuskins for their detailed study of the explosion breccias and the nitrides included in corundum aggregates from Mt Carmel; space considerations have limited our previous publication of such detailed data on this interesting aspect of these important samples. Their images of other samples of the 'Carmel Sapphire' are a useful supplement to those we have published elsewhere.

However, we deem it necessary to correct some unfortunate mistakes in the presentation. These do not affect the descriptions of the images but can improve the usefulness of the article. Material in quotation marks are from the manuscript in *Mineralogical Magazine*, vol. **87**, https://doi.org/10.1180/mgm.2023.25 by Galuskin and Galuskina (2023).

1. The authors do not identify the location of their sample (there is no "Carmel locality at the Kishon River"), the methods by which it was obtained, nor the other minerals found in the heavy concentrate. This is unfortunate because it would have improved the scientific usefulness of the paper.

2. "Typically the Carmel Sapphire is in small fragments of breccia with white cement". This is incorrect; the vast bulk of Carmel sapphire grains investigated by us have no coating and are not associated with the breccias.

3. "skeletal osbornite occurring as inclusions in corundum". The illustrated nitrides are not 'skeletal crystals' – they may appear to be so because they are controlled by crystallographically controlled void spaces in skeletal corundum (Griffin *et al.*, 2016; 2021a, 2022; Oliveira *et al.*, 2021). These spectacular structures are only one form of TiN in the Carmel sapphire; it also occurs in large inclusions coexisting with Fe–Ti silicides and TiB_2, and as regular crystals that appear to have crystallised directly from Fe–Ti silicide melts (Griffin *et al.*, 2020a, 2021a, 2022).

4. "as a result of CH_4+H_2 fluid flowing through the magmatic melt". This is not quite correct; we have proposed that such fluids interacted with melts, and may have flowed through melt-escape channels together with melts, to produce the skeletal crystals of the Carmel sapphire (Oliveira *et al.*, 2021).

5. "On only one occasion the amorphous carbon is recorded in the cement of the 'white breccia'." The authors confuse the white material that coats some grains with the explosion breccias illustrated by us (Xiong *et al.*, 2017; Griffin *et al.*, 2018b). The matrix of the explosion breccias, which may include the one large grain described by the authors, are dominated by amorphous carbon, as identified by petrographic, EBSD and TEM studies. We have noted micro-inclusions of corundum, but not bauxite, in the matrix of the explosion breccias. The authors provide no evidence that bauxite, or any other Al-hydroxide, is present in the matrices. The EDS spectra given for "böhmite-like material" are equally consistent with corundum. We suggest that the report of böhmite /bauxite represents analyses of spots consisting of amorphous carbon plus micro-inclusions of corundum; this would be consistent with the apparently higher C content of the EDS spectrum. If böhmite actually is present, it may equally reflect partial alteration of corundum fragments. Whether this fine-grained material could be considered as an ash component is a semantic question.

6. "Osbornite from Carmel sapphire grains…as a rule are confined to glass inclusions". This is not correct. The osbornite 'skeletal crystals' typically extend well outside the melt pockets, and occur as isolated inclusions in the corundum (as seen in 3D-µCT as well as 2-D slices; Griffin *et al.*, 2021a, 2022). See also point (3) above.

7. "Griffin *et al.* (2021b) underline the non-stable composition of osbornite". This is simply not correct; we have done no such thing. The cited reference presents analytical data and shows that they are consistent with experimental studies on the Ti–O–N system. There is nothing "non-stable" there.

8. "Bigger corundum aggregates contain silica glass"; "usually squeezed out between corundum grains". This is misleading; the glasses in the melt pockets are calcium–aluminium–silicate (CAS) glasses (typically with 40–45 wt.% SiO_2) with moderate levels of Mg, Ti and S, as well as high levels of REE and Zr. In some parageneses with cumulate-like structures the melts are indeed concentrated along grain boundaries, whereas in the more skeletal corundum aggregates the melts occur both along grain boundaries and as isolated inclusions. 3µCT images (Griffin *et al.*, 2021a) illustrate this very clearly.

9. ".. 'white breccia' … as a source of Carmel sapphire". This is misleading; nearly all investigated grains of Carmel sapphire have

no traces of the white coating, and there is no evidence that they have been brecciated.

10. Zr-bearing glass as debris from "special laboratory glassware". As noted above, the internal melts in the Carmel sapphire are high in Zr and the Carmel sapphire contains many Zr-bearing phases. Some corundum-aggregate xenoliths have thick rims of a Ba-rich or K-rich glass full of tiny crystals of zircon or baddeleyite. The high Zr contents reflect the fact that most of the melts left in the corundum aggregates by the time of eruption were highly differentiated. The spectrum in fig. 7d in the author's manuscript is very similar to those of the glasses in melt pockets in one type of Carmel Sapphire. It is unfortunate that these spectra were not accompanied by quantitative chemical analyses, which would have aided comparison with published data.

11. ".. terrestrial examples [of krotite and grossite] are questionable and require verification." The authors might read our papers (Griffin *et al.* 2019a, 2020a) on the coarse-grained xenoliths of hibonite+ grossite+V^0, which require a very H_2-rich atmosphere and show the crystallisation sequence:

corundum + Liq → (low-REE) hibonite → grossite + spinel ± krotite → $Ca_4Al_6F_2O_{12}$ + fluorite. The occurrence of grossite in meteorites cannot invalidate the existence of these samples; their disaggregation during eruption is responsible for inclusions of krotite, hibonite and grossite in the breccias. These clearly did not result from the hydration of hypothetical precursor minerals.

12. "Glass fragments with inclusions of mullite". Mullite does appear in some melt inclusions in the corundum aggregates. This is expected because the compositions of some residual melts fall into the liquidus field of mullite in CAS space at low P, and the crystallisation of mullite might be expected to occur during eruption.

13. "There is no mechanism for the simultaneous removal of Fe and Si from natural melt systems". This is not correct. Reduction of an FeO-bearing silicate melt to f_{O_2} = IW-5 (as documented by the abundance of Ti^{3+}-bearing minerals in Carmel sapphire) will lead to immiscibility of Fe–Ti–Si silicides and supersaturation in Al_2O_3, leading to corundum crystallisation. Comparison of the analysed silicide-melt compositions with experimental data shows that this occurred at normal magmatic temperatures (1200–1400°C; Weitzer *et al.*, 2008; Griffin *et al.*, 2022). It is also worth noting that the presence of hydrogen can lower the melting points of metals and alloys by several hundred degrees (Fukai, 2005). Thus the 2000°C temperature of the industrial process is irrelevant to the natural case, although the observation that the silicide melts do sink to the bottom is a nice illustration of the process that we have proposed. We would appreciate a reference to the industrial process, which was not provided in the paper.

14. "formation from the melt requires extremely rapid quenching". We agree; this is consistent with the very rapid eruption rate of the host basalts (pyroclastics) of the Carmel sapphire, which carry mantle-derived peridotite xenoliths (O'Reilly *et al.*, 2010)

15. "Therefore all new minerals [from] Carmel sapphire should be discredited by the IMA–CNMNC". This is surely misguided (see below) and in any case is not appropriate to a journal article.

Finally, we must point out that a similarity between synthetic products (laboratory or industrial) and natural materials provides keys to the interpretation of natural processes (indeed, it is the *raison d'etre* of experimental petrology). However, such similarity cannot be taken as evidence for anthropogenic origin of the natural material. Duplication of mantle minerals in experiments does not imply that the minerals cannot exist in nature. This is the fundamental fallacy of the persistent criticisms by Litasov *et al.* (2019a,b,c) and Ballhaus *et al.* (2017, 2021) of the Mt Carmel work and many studies of similar mineral associations from numerous ophiolites by many researchers worldwide. Unfortunately, the experimental petrologists involved in this criticism have not followed scientific method; that would have included taking into account the overwhelming *geological* and *geochemical* evidence that makes an anthropogenic origin impossible, at least in the case of Mt Carmel (Griffin *et al.*, 2021b).

This evidence includes:

- The alluvial deposits in question are undisturbed Plio–Pleistocene palaeo-placers developed at the base of terraces that lie *ca* 10 metres above the current drainage of the Kishon River and are overlain by 4–10 metres of undisturbed finer-grained sediments (Griffin *et al.*, 2021b).
- Extensive sampling of known Cretaceous volcanic centres, which lie 50–350 metres *above* the Kishon River, shows that the vents collectively contain all of the minerals found in the alluvial deposits (Griffin *et al.*, 2021b), including moissanite and "Carmel Sapphire".
- Miocene sedimentary deposits in the Yizre'l valley include carbonate-cemented, quartz-rich beach placers containing corundum, coarse-grained moissanite and peridotite-derived garnet+cpx+spinel (Roup *et al.*, 2009). Anthropogenic industrial processes were not available at this time.
- The occurrence of the corundum-moissanite suite in the primary volcanic centres, in deeply buried Plio–Pleistocene placers, and in lithified Miocene beach placers demonstrates that the sample material was formed and deposited long before human occupation and makes arguments for industrial contamination unsustainable (Griffin *et al.*, 2021b).
- The detailed descriptions of parageneses (Griffin *et al.*, 2018b, 2019b, 2021a,b, 2022 and references therein) should lay to rest claims that such material was produced by lightning strikes (Ballhaus *et al.*, 2017).
- Cathodoluminescence imagery and Ti-zoning of corundum crystals ("Carmel Sapphire") record growth from a silicate melt in an evolving *open system* at very low oxygen fugacity (Oliveira *et al.*, 2021). This is not consistent with any industrial process known to us.
- In the Mt Carmel material, moissanite occurs in grains much larger than any common industrial abrasive (euhedral crystals up to > 4mm; Huang *et al.*, 2020). Aggregates of "Carmel Sapphire" and associated hibonite-grossite-vanadium assemblages are up to 2.5 cm across (Griffin *et al.*, 2019a, 2020a).

The Mt Carmel mineral assemblages show significant differences to the synthetic materials produced and/or described by those arguing for a contamination origin (Litasov *et al.*, 2019a,b,c).

- Tistarite, Ti_2O_3, in Carmel Sapphire does not have the high Al and Mg contents usually present in the synthetic material (Griffin *et al.*, 2016).
- Synthetic 'carmeltazite' (Litasov *et al.*, 2019a) shows a wide range in Zr content, requiring a high proportion of Ti^{4+} for charge balance. EELS analysis and single-crystal XRD analysis of the type carmeltazite from Mt Carmel show that all Ti is present as Ti^{3+} (Griffin *et al.*, 2018a).
- Synthetic TiB_2 in fused abrasives (Litasov *et al.*, 2019a) contains significant levels of Al and F, which are absent in the TiB_2 from Mt Carmel (Griffin *et al.*, 2020b).

- The only EMPA-detectable minor elements in Carmel Sapphire are Ti, Si and Mg, however it contains trace elements (Sc, V, Cr and Zr), most of which are correlated with Ti contents ranging up to 2.5 wt.%. (Oliveira *et al.*, 2021). In contrast, synthetic corundum produced from fused abrasives (Litasov *et al.*, 2019a) contains much less Ti and no Mg, however it has significant contents of Fe, Ni, Mn, Ca, K, Th and P, which are absent or present only at low trace-element levels in 'Carmel Sapphire'.
- TiC in the fused abrasives analysed by Litasov *et al.* (2019a) contains no Fe, whereas that in 'Carmel sapphire' typically contains Fe at *ca* 1 wt.% levels, reflecting equilibrium partitioning with coexisting Fe–Si melts (Griffin *et al.*, 2021a, 2022).
- The most reduced of the Mt Carmel parageneses (corundum + hibonite + grossite + native vanadium) requires an atmosphere dominated by H_2. To our knowledge, this does not occur in the production of alumina or Al_2O_3-based abrasives, because Al_2O_3 would be reduced to the metal, which is undesirable. However, it is a predictable result of the ascent and partial oxidation of COH fluids from a metal-saturated mantle (Griffin *et al.*, 2018b, 2019a).
- The oxygen-isotope composition of Carmel Sapphire ranges from $\delta^{18}O = +7$ to $+13$‰, with a mean around +10 (Oliveira *et al.*, 2021). Natural corundum shows a range of $\delta^{18}O$ from –27 to +23‰. In contrast, commercial synthetic-alumina products produced by a range of processes have $\delta^{18}O = +23$ to +32‰, reflecting the interaction of the material with air ($\delta^{18}O = 23.9 \pm 0.3$ ‰) during processing (Pack, 2021). This difference is critical in distinguishing natural corundum derived from mantle/magma-related processes from a synthetic product.
- U-rich thorianite $[(Th,U)O_2]$ occurs with ziroite (ZrO_2), mizraite-(Ce) $[Ce(Al_{11}Mg)O_{19}]$ and Ti-sulfide in one melt inclusion in a Carmel Sapphire. EMPA Th–U–Pb age determination of the largest 1-μm thorianite crystal using a JEOL JXA-iHP200F Field Emission EPMA and the Probe for EPMA program yields an age of 13±2 Ma (Ma *et al.*, pers com.), making it unlikely that the corundum host was produced by humans.

This evidence indicates that there is no scientific basis for the authors' conclusion that "the contamination of geological samples with anthropogenic material has led to popularisation of biased views". The responsibility for "popularisation of biased views" must lie solely with those who refuse to consider straightforward *geological* and *geochemical* evidence for the natural origin of the Mt Carmel samples.

References

Ballhaus C., Helmy H.M., Fonseca R.O.C., Wirth R., Schreiber A. and Jöns N. (2021) Ultra-reduced phases in ophiolites cannot come from the Earth's mantle. *American Mineralogist*, **106**, 1053–1063.

Ballhaus C., Wirth R., Fonseca R.O.C., Blanchard H., Pröll W., Bragagni A., Nagel T, Schreiber A., Dittrich S., Thome V. *et al.* (2017) Ultra-high pressure and ultra-reduced minerals in ophiolites may form by lightning strikes. *Geochemical Perspectives Letters*, **5**, 42–46.

Fukai Y. (2005) *The Metal-Hydrogen system. Basic Bulk Properties.* Springer-Verlag Berlin, 505 pp.

Galuskin E. and Galuskina I. (2023) Evidence of the anthropogenic origin of the "Carmel sapphire" with enigmatic super-reduced minerals. *Mineralogical Magazine*, **87**, https://doi.org/10.1180/mgm.2023.25

Griffin W.L., Gain S.E.M., Adams D.T., Huang J-X., Saunders M., Toledo V., Pearson N.J. and O'Reilly S.Y. (2016) First terrestrial occurrence of tistarite (Ti_2O_3): Ultra-low oxygen fugacity in the upper mantle beneath Mount Carmel, Israel. *Geology*, **44**, 815–818, https://doi.org/10.1130/G37910.1.

Griffin W.L., Gain S.E.M., Bindi L., Toledo V., Camara F., Saunders M. and O'Reilly S.Y. (2018a) Carmeltazite, $ZrAl_2Ti_4O_{11}$, a new mineral trapped in corundum from volcanic rocks of Mt Carmel, northern Israel. *Minerals*, **8**, 601–612.

Griffin W.L., Huang J-X., Thomassot E., Gain S.E.M., Toledo V. and O'Reilly S.Y. (2018b) Super-reducing conditions in ancient and modern volcanic systems: Sources and behaviour of carbon-rich fluids in the lithospheric mantle. *Mineralogy and Petrology*, **112**, Supplement 1, 101–114.

Griffin W.L., Gain S.E.M., Huang J-X., Saunders M., Shaw J., Toledo V. and O'Reilly S.Y. (2019a) A terrestrial magmatic hibonite-grossite-vanadium assemblage: desilication and extreme reduction in a volcanic plumbing system, Mt Carmel, Israel. *American Mineralogist*, **104**, 207–217.

Griffin W.L., Toledo V. and O'Reilly S.Y. (2019b) Discussion of "Enigmatic super-reduced phases in corundum from natural rocks: Possible contamination from artificial abrasive materials or metallurgical slags" by Litasov et al. *Lithos*, **348–349**, 105122.

Griffin W.L., Gain S.E.M., Camara F., Bindi L., Shaw J., Alard O. Saunders M., Huang J-X., Toledo V. and O'Reilly S.Y. (2020a) Extreme reduction: mantle-derived oxide xenoliths from a hydrogen-rich environment. *Lithos*, **358–359**, 105404.

Griffin W.L., Gain S.E.M., Saunders M., Bindi L., Alard O., Toledo V. and O'Reilly S.Y. (2020b) Parageneses of TiB_2 in corundum xenoliths from Mt Carmel, Israel: Siderophile behaviour of boron under reducing conditions. *American Mineralogist*, **105**, 1609–1621.

Griffin W.L., Gain S.E.M., Saunders M., Alard O., Shaw J., Toledo V. and O'Reilly S.Y. (2021a) Nitrogen under super-reducing conditions: Ti oxynitride melts in xenolithic corundum aggregates from Mt Carmel (N. Israel). *Minerals*, **11**, 780.

Griffin W.L., Gain S.E.M., Saunders M., Cámara F., Bindi L., Spartà D., Toledo V. and O'Reilly S.Y. (2021b) Cr_2O_3 in Corundum: ultra-high contents under reducing conditions. *American Mineralogist*, **106**, 1420–1437.

Griffin W.L., Gain S.E.M., Saunders M., Huang J-X., Alard O., Toledo V. and O'Reilly S.Y. (2022) Immiscible metallic melts in the upper mantle beneath Mount Carmel, Israel: Silicides, phosphides and carbides. *American Mineralogist*, **107**, 532–549.

Huang J-X., Xiong Q., Gain S.E.M., Griffin W.L., Murphy T.D., Siryaev A.A., Li L., Toledo V., Tomshin M.D. and O'Reilly S.Y. (2020) Immiscible metallic melts in the deep Earth: Clues from moissanite (SiC) in volcanic rocks. *Science Bulletin*, **65**, 1479–1488.

Litasov K.D., Kagi H. and Bekker T.B. (2019a) Enigmatic super-reduced phases in corundum from natural rocks: Possible contamination from artificial abrasive materials or metallurgical slags. *Lithos*, **340–341**, 181–190.

Litasov K.D., Bekker T.B. and Kagi H. (2019b) Reply to the discussion of "Enigmatic super-reduced phases in corundum from natural rocks: Possible contamination from artificial abrasive materials or metallurgical slags" by Litasov et al. (*Lithos*, 340–341, p.181–190) by W.L. Griffin, V. Toledo and S.Y. O'Reilly. *Lithos*, **348–349**, 105170.

Litasov K.D., Kagi H., Voropaev S.A., Hirata T., Ohfuji H., Ishibashi H., Makino Y., Bekker T.B., Sevastyanov V.S., Afanasiev V.P. and Pokhilenko N.P. (2019c) Comparison of enigmatic diamonds from the Tolbachik arc volcano (Kamchatka) and Tibetan ophiolites: Assessing the role of contamination by synthetic materials. *Gondwana Research*, **75**, 16–27.

Oliveira B.B., Griffin W.L., Gain S.E.M., Saunders M., Shaw J., Toledo V. Afonso J.C. and O'Reilly S.Y. (2021) Ti^{3+} in corundum: tracing crystal growth in a highly reduced magma. *Scientific Reports*, **11**, 2439.

O'Reilly S.Y. and Griffin W.L. (2010) Rates of magma ascent: Constraints from mantle-derived xenoliths. Pp. 116–124 in: *Timescales of Magmatic Processes: From Core to Atmosphere* (Dosetto, A., Turner, S. and Van Orman, J.A., editors). Blackwell Publishing Ltd., Hoboken, New Jersey, USA.

Pack A. (2021) Isotopic traces of atmospheric O_2 in rocks, minerals and melts. Pp. 217–240 in: *Triple Oxygen Isotope Geochemistry* (I.N. Bindeman and A. Pack, editors). Reviews in Mineralogy and Geochemistry, **86**. Mineralogical Society of America and the Geochemical Society, Chantilly, Virginia, USA.

Roup A., Kamanovitch E., Baykov Y and Toledo V. (2009) Moissanite discovery by Shefa Yamin. *Geological Society of Israel Annual Meeting*, Abstract, p. 111.

Weitzer F., Schuster J., Naka M., Stein F. and Palm M. (2008) On the reaction scheme and liquidus surface in the ternary system Fe-Si-Ti. *Intermetallics*, **16**, 273–282.

Xiong Q., Griffin W.L., Huang J-X., Gain S.E.M., Toledo V., Pearson N.J. and O'Reilly S.Y. (2017) Super-reduced mineral assemblages in "ophiolitic" chromitites and peridotites: The view from Mt Carmel. *European Journal of Mineralogy*, **29**, 557–570.