


Reply

Reply to the discussion of Galuskin and Galuskina (2023) “Evidence of the anthropogenic origin of the ‘Carmel sapphire’ with enigmatic super-reduced minerals” by Griffin *et al.* (2023)

Evgeny Galuskin  and Irina Galuskina 

Faculty of Natural Sciences, Institute of Earth Sciences, University of Silesia, Poland

(Received 16 May 2023; accepted 17 May 2023; Accepted Manuscript published online: 25 May 2023; Principal Editor: Roger Mitchell)

Introduction

At the beginning of their discussion, Griffin *et al.* (2023) thank us for our detailed investigation of corundum aggregates from Carmel Mt, Northern Israel, which, in their opinion, is “a useful supplement” to their previous publications. We would also like to thank Griffin *et al.*, whose denial of the existence of ‘white breccia’ (corundum angular fragments of different size in white cement) simplifies our defence of our position.

In our paper (Galuskin and Galuskina, 2023) we provide mineralogical evidence that ‘Carmel sapphire’ has an anthropogenic genesis based on the study of ‘white breccia’, which consists of the waste of electrocorundum (fused alumina, refractory abrasive material) production. It seems if there is no ‘white breccia’, then our evidence of the anthropogenic genesis of Carmel sapphire does not matter. However Griffin *et al.* (2019a) were the first to use the term ‘white breccia’. Both in their scientific publications and in the reporting documents of the *Shefa Yamim* exploration company, there are images of ‘white breccia’ with Carmel sapphire or corundum grains with a white coating (Xiong *et al.*, 2017; Griffin *et al.*, 2021a; Galuskin and Galuskina, 2023, figure S9, supplementary materials).

At this point, we can close the discussion with two brief conclusions: (1) Griffin *et al.* (2023) debate plenty of secondary issues that divert attention from the main object, ‘white breccia’, which is key to solving the problem of Carmel sapphire genesis; (2) ‘white breccia’ (in the form of individual samples) exists and consists of the waste of electrocorundum production. However we decided that readers can draw their own conclusions after reading our paper (Galuskin and Galuskina, 2023) and the discussion connected with it; we answer most of the remarks of Griffin *et al.* (2023) below.

Background information

The total weight of Carmel sapphire extracted by the *Shefa Yamim* company is significantly less than one kilogram (Griffin

et al., 2019a). To obtain a heavy fraction containing corundum grains, hundreds of tons of mainly alluvial materials were re-treated. This material was obtained from shallow pits, trenches or large diameter drill holes. With this extraction technology partial mixing of material taken from different levels cannot be excluded (<https://www.slideshare.net/JamesAHCampbell1/shefa-gems-cpr-2019>), hence the geological background of the Carmel sapphire setting and its “before-anthropogenic” time period confinement (Griffin *et al.*, 2019a, 2023) are subject to doubt. The extraction of sedimentary material by the *Shefa Yamim* company took place in a technologically advanced area with a high level of human activity, where there is presently a series of technoparks with working factories involved in the production of various ceramics and aluminium. To contaminate the Kishon River basin with anthropogenic material containing Carmel sapphire, a few tens of kilograms of disintegrated slag from electrocorundum production would be enough, and these could be transported by both natural and technogenic factors. In addition, small aggregates of Carmel sapphire can be transferred to significantly higher strata in the geological section as a result of multifarious human activity.

It should be emphasised that we failed to find scientific literature concerning the study of inclusions in the electrocorundum of different producers or literature describing processes related to fused corundum production in electric furnaces. A paper by Litasov *et al.* (2019a) is the only modern study containing a detailed description of inclusions in a few types of electrocorundum, and it assumes an anthropogenic genesis of Carmel sapphire. In open access sources on the internet and in patents one can find information on electric furnace design and even YouTube movies showing all the stages of electrocorundum production. The websites of companies producing and selling electrocorundum report that to synthesise corundum with different properties, a calcinated bauxite furnace charge with various additives is used. This leads to wide variation in the composition of both corundum and any inclusions. Technological processes of fused corundum production in electric furnaces result in gravitative differentiation of the melt. Broadly speaking, when a melt is cooling, slags of FeSi (+Ti, C, Mn...) alloys form in the lower part of the furnace, light slags (for example, containing hibonite and diaoyudaoite) are generated in the upper part, and corundum aggregates crystallise in the central part. It should be underlined that the fused corundum production process is ‘dirty’, with an abundance of waste material. Corundum from the bottom part

Corresponding author: Evgeny Galuskin, Email: evgeny.galuskin@us.edu.pl; Irina Galuskina, Email: irina.galuskina@us.edu.pl

Cite this article: Galuskin E. and Galuskina I. (2023) Reply to the discussion of Galuskin and Galuskina (2023) “Evidence of the anthropogenic origin of the ‘Carmel sapphire’ with enigmatic super-reduced minerals” by Griffin *et al.* (2023). *Mineralogical Magazine* 87, 635–638. <https://doi.org/10.1180/mgm.2023.39>

of the furnace, with a great number of inclusions, is used as a secondary raw material.

We consider that the geochemical evidence for the natural genesis of Carmel sapphire provided in the discussion (Griffin *et al.*, 2023), which is based on a comparison of the chemical characteristics of inclusions in Carmel sapphire and electrocorundum used for sandpaper production by only two producers (Litasov *et al.*, 2019a), cannot be used to draw conclusions about other types of electrocorundum produced using different types of furnace feeds.

Comments and responses to Discussion by Griffin *et al.* (2023)

Below we use numbering corresponding to those in the Discussion by Griffin *et al.* (2023).

1. The material received by us for investigation does not have a precise location of origin; it was extracted in the valley of the Kishon River near Elro'i, Northern Israel.

2. It must be admitted that we did not plan to write a critical paper on the genesis of Carmel sapphire. We only wanted to compare osbornite from phosphide-bearing breccia from the Hatrurim Complex (Galuskin *et al.*, 2022) with osbornite from Carmel sapphire (Griffin *et al.*, 2021b). In the material that we studied from Carmel, the grains of Carmel sapphire have different sizes (from 1 μm to ~ 1 cm) and are in a white cement. The investigation of this specific 'white breccia' showed that it is a furnace charge (calcined bauxite) for electrocorundum production mixed with waste from its production. That led us to write a critical paper on the genesis of Carmel sapphire (Galuskin and Galuskina, 2023).

We do not understand Griffin's remark about the incorrect description of Carmel sapphire fragments cemented by a white mass as 'white breccia', as Griffin himself regards the presence of such breccia as an indication of the natural origin of Carmel sapphire (Griffin *et al.* 2019a, direct quote): "*Evidence of volcanic provenance. The CS grains from the pyroclastic deposits, and even from the alluvial beds, commonly are coated in glass, but even more commonly by a fine-grained white breccia, consisting of carbonate-cemented volcanic ash. This cement is a result of eruption of the ashes on a shallow marine carbonate platform, and the subsequent covering of the ash beds by thick carbonate sequences.*" We provide an optical image of the polished mount of 'white breccia' with Carmel sapphire that we studied (Galuskin and Galuskina, 2023, Fig. S4, supplementary materials), and also an image of a typical sample of 'white breccia' extracted by Shefa Yamim (Galuskin and Galuskina, 2023, fig. S9, supplementary materials).

Interestingly, dark moissanite crystals were also found in rock resembling 'white breccia' (Griffin *et al.*, 2021a, fig. OM4, Supplementary figures), which is described as Miocene carbonate-cemented beach placer, i.e. as sandstone. In figure OM4, fragments of moissanite grains up to 2 mm in size and quartz grains up to 0.5 mm in size are visible in white cement. An analogy can be drawn here: 'Carmel sapphire' is cemented with aluminium hydroxides (the main components of the charge for the production of electrocorundum), and Carmel moissanite is cemented with material with a large number of quartz grains (the main component of the charge for the production of corundum). In the part of the discussion dealing with the geological evidence for the natural origin of Carmel sapphire, Griffin *et al.* (2023) write about large moissanite crystals up to 4 mm in size, which are a lot larger than any corundum abrasive grains and, in their opinion, cannot be synthetic.

Indeed, nobody would use fragments of SiC of 4 mm in grinding powder or sandpaper. However, the technological process of corundum production in an electric furnace can produce a large druse of SiC crystals a few centimetres in size (https://www.reddit.com/r/chemistry/comments/8yig3t/huge_iridescent_silicon_carbide_crystals_found_in/), which typically have a tarnish analogous to the tarnish on SiC crystals from Carmel (Griffin *et al.*, 2016).

3. Osbornite in Carmel sapphire forms characteristic skeletal crystals typical of cubic symmetry (Griffin *et al.*, 2021b; Galuskin and Galuskina, 2023, fig. S5, Supplementary materials). If osbornite was formed as a result of crystallographically controlled voids in corundum, the trigonal symmetry of corundum would be inherited. Growth of skeletal osbornite with the melting point 2930°C is explained by the crystallisation of the mineral in a viscous melt (the melting point of corundum is 2072°C). Osbornite formation at a lower temperature is only possible as a result of physical or chemical vapour deposition processes (Azadi *et al.*, 2016).

4. We agree with this remark. Though why do the authors refer to skeletal osbornite formation here, and not to how it fills voids in early corundum?

5. We failed to perform a full identification of the böhmite-like phase. This phase strongly diffuses light, so a Raman spectrum was not obtained. A powder-diffraction pattern was not produced because of a limited amount of böhmite-like material and its partial amorphisation. In figures 8d and 8f (Galuskin and Galuskina, 2023) one can see the differences between the EDS spectra for corundum (Al_2O_3 with trace of Ti) and the böhmite-like phase ($\sim\text{AlOOH}$). We agree that the identification of this phase is incomplete, however the data obtained undoubtedly indicate the presence of aluminium hydroxide, which we think was a main component of the charge in electrocorundum production. In fig. 5 in the paper of Xiong *et al.* (2017), an optical microphoto of breccia with Carmel sapphire and C and Al element maps is shown. In addition to phases enriched in Al (hydroxides), the cement contains increased carbon content (coke remains). Here, it should be emphasised that corundum is a stable mineral and its replacement in low-temperature conditions by a böhmite-like phase, as proposed by Griffin *et al.* (2023), is highly improbable, particularly as there are unaltered corundum fragments and porous böhmite-like minerals nearby in breccia (Galuskin and Galuskina, 2023, figs 8 and S5D, supplementary materials). Moreover, it is impossible to transform volcanic ash to bauxite.

6. Indeed, there are cases where skeletal osbornite crystals can be found completely inside corundum. In our samples, osbornite is typically confined to glass inclusions (Galuskin and Galuskina, 2023, figs S5D, S6C, supplementary materials).

7. Here, the term 'unstable composition' does not have any thermodynamic meaning. Probably, we used an unfortunate term to underline the wide variation of osbornite composition (TiN–TiC–TiO system) in Carmel sapphire. Even two-phase monocrystalline TiC–TiN segregations were detected in Carmel sapphire (Galuskin and Galuskina, 2023, fig. S6d, supplementary materials). We believe that the enrichment in carbon of the central part of osbornite skeletons, which was established in both osbornite from Carmel sapphire (Galuskin and Galuskina, 2023, fig. 3) and in osbornite from electrocorundum (Galuskin and Galuskina, 2023, fig. S3, supplementary materials), is the main indication of the anthropogenic origin of osbornite. Such enrichment is explained by the character of the electrocorundum production process, when in corundum melt at temperatures

higher than 2000°C and with relatively high carbon activity during the initial stage of the process (carbon is added to the charge as coke), osbornite enriched in carbon crystallises.

8. Here we agree that we over-simplify by only calling the glass silicate.

9. See response to point 2.

10. In this case we provided a photo of a thin glass plate to stress the point that it cannot be preserved when 'white breccia' is formed in the conditions of a shallow sea (see citation of Griffin *et al.* in point 2).

11. We know well the work of Griffin *et al.* (2019b) on hibonite and aluminates and also consider them to be fragments of slags of electrocorundum or special ceramics production. These mineral associations probably correspond to light slags.

12. Unfortunately, Griffin *et al.* (2023) did not note that in addition to inclusions of mullite in glass, we describe mullite inclusions in cristobalite (Galuskin and Galuskina, 2023, fig. 4F, supplementary materials). We agree with Griffin that the mullite crystallised at low pressure, but in an electric furnace, where light slags are generated, and not during a volcanic eruption.

13. Indeed, in super-reduced systems at relatively low temperatures (~1200–1400°C) there is Fe–Si (+Ti) melt and volatile components can influence the melt temperature drop. However in this case, we should consider a system of two immiscible melts – metallic and corundum. Corundum has a high melting point 2027°C, and only at temperatures of ~2000°C does the corundum melt have properties that cause the mobility of the melted metal drops and possibly lead to its gravitational removal from the system. This process is demonstrated well by the sample of zonal slag from the bottom part of a furnace shown in fig. S2 (Galuskin and Galuskina, 2023, supplementary materials). Also, we direct the reader to the paper by Ballhaus *et al.* (2021), where they showed that SiC and Fe–Si alloys are unstable under the conditions proposed in a model of Carmel sapphire formation (Xiong *et al.*, 2017; Griffin *et al.*, 2021a).

14. There is no doubt about the rapid solidification of the corundum melt from which the Carmel sapphire was formed. In the technological process of electrocorundum production, rapid hardening takes place in air, as is reflected in the formation of non-equilibrium morphological forms of growing crystals. In Carmel sapphire, these are skeletal osbornite crystals (Galuskin and Galuskina, 2023, fig. S5A, supplementary materials), and also corundum manifested the specific growing zonation (Oliveira *et al.*, 2021; Galuskin and Galuskina, 2023, fig. 11).

15. We understand the disillusionment of mineralogists who put a great deal of effort into the investigation and description of new super-reduced 'minerals' from Carmel. But the most important criterion of the CNMNC–IMA when considering whether something is a new mineral is its natural genesis. We consider that the evidence we have presented of the anthropogenic origin of Carmel sapphire and other super-reduced minerals allows us to pose questions about the potential discrediting of minerals from Carmel approved by the CNMNC–IMA.

We did not propose in our paper that minerals from Carmel should be discredited purely because they are anthropogenic phases. There are many cases of CNMNC–IMA approval of minerals from burnt coal dumps, which are *de facto* anthropogenic phases. But these minerals formed in processes which are analogous to natural ones (natural fires, pyrometamorphic rocks, etc.). We consider that Carmel sapphire is a product of electrocorundum production which does not have an analogue

in Nature. This is an additional argument supporting our proposition that the anthropogenic minerals from Carmel should be discredited.

Additional comments

In the discussion the authors passed over the most important parts of our paper concerning the evidence for the anthropogenic origin of Carmel sapphire (Griffin *et al.*, 2023). Points 2 and 9 of the discussion contradict the fact that the source of Carmel sapphire is 'white breccia', which in our opinion is the waste of electrocorundum production. Interestingly, in the discussion with Litasov *et al.* (2019a, 2019b) on the natural origin of Carmel sapphire, the 'white breccia' with Carmel sapphire grains was described as evidence of its natural origin (Griffin *et al.*, 2019a).

Furthermore, Griffin *et al.* (2023) did not pay attention to the enrichment by carbon of central parts of osbornite from Carmel sapphire that is characteristic of osbornite from electrocorundum and is related to the specificity of its production. Neither did they address the presence of numerous metallic droplets in Carmel sapphire (Galuskin and Galuskina, 2023, fig. S5A, supplementary materials), which for gemmologists is a characteristic of crystal grown under laboratory conditions.

In the last part of the discussion, Griffin *et al.* (2023) present geological and geochemical arguments which, according to them, exclude the anthropogenic origin of Carmel sapphire. They partially repeat the evidence they used in the discussion with Litasov (Griffin *et al.*, 2019a; Litasov *et al.*, 2019b). Moreover, Griffin *et al.* write about numerous investigations of similar mineral associations in ophiolites, but do not remember that in all cases micron-sized objects from mineral separates (heavy fractions) were investigated, a finding which, in our opinion, is connected with the contamination of geological samples.

We agree with Griffin *et al.* (2023) that the similarity of products of laboratory and industrial synthesis with natural materials is key for the interpretation of natural processes and cannot be the definitive criterion used to establish the anthropogenic origin of material. However this principle is at work on both sides. The petrological experiments of Ballhaus *et al.* (2021) show that it is impossible for super-reduced minerals to exist under the *P–T* conditions proposed in models of Carmel sapphire formation (Xiong *et al.*, 2017; Griffin *et al.*, 2019b, 2021a).

We are not petrologists; our scientific interests lie in the field of new minerals, crystal chemistry and the ontogeny of minerals. We studied the mineral composition of the 'white breccia' and the growing zonation of osbornite and corundum and drew a conclusion about the anthropogenic origin of Carmel sapphire.

We will not discuss concrete geological and geochemical evidence of the natural origin of Carmel sapphire, which is partially considered by us in the introduction to our responses to the discussion. We deal only with key evidence in the discussion of Griffin *et al.* (2023). The first point concerns oxygen isotopes, which is not an argument as there are no factual data on how the oxygen isotope ratio changes in the vertical cross-section of an electric furnace in the process of electrocorundum production. Moreover, we did not find data on oxygen isotopes in the paper cited here (Oliveira *et al.*, 2021).

The more important point, in our opinion, is the determination of a radiometric age of 13(±2) Ma for thorianite inclusions in Carmel sapphire, performed on very small grains of 1 µm in size using the CHIME (chemical Th–U-total Pb isochron method) method (Ma, pers com. to Griffin; unfortunately, these

data have yet to be published). We can only congratulate the authors on determining this ‘young’ age with such high accuracy using microprobe measurements on a very small thorianite crystal and overcoming known methodical problems connected with interference of the U and Th lines. However, the measurements were probably performed on the relics of a primary thorianite from the furnace charge for electrocorundum production. Thorianite has a very high melting point of 3390°C, and it must remain as a relic in melted corundum. Zirconia-bearing minerals are present in Carmel sapphire; they should contain impurities of radioactive elements. Surely, more reliable age determination could be performed using relatively bigger grains of carmelitazite, $ZrAl_2Ti_4O_{11}$, or zirconite, ZrO_2 . Here, it should also be emphasised that the 13 (± 2) Ma of thorianite in Carmel sapphire is significantly younger than those proposed for xenoliths (a source of Carmel sapphire) from the pyroclastic ejecta of Cretaceous (99–85 Ma) intraplate basaltic volcanoes exposed on Mt. Carmel (Griffin *et al.*, 2020).

Undoubtedly, in industrial areas such as the Kishon River basin there is a high probability of contamination by anthropogenic material of a large region, and this could be caused even by a relatively small amount of waste, the transport of which may be the result not only of natural forces but also of human activity. Griffin *et al.* (2023) conclude in their discussion that we do not take into consideration their geological and geochemical evidence that Carmel sapphire is a natural phase, and thus argue that there are no grounds for talking about the popularisation of incorrect scientific views. For us, the main geological and geochemical evidence of the anthropogenic origin of Carmel sapphire is the ‘white breccia’, which contains fragments of Carmel sapphire cemented by material predominantly consisting of aluminium hydroxides. We hope that after considering our paper (Galuskin and Galuskina, 2023), readers will agree with the evidence we present confirming that ‘white breccia’ is waste from electrocorundum production.

Acknowledgements. Investigations of Carmel sapphire were supported in part by the National Science Center (NCN) of Poland, grant 2021/41/B/ST10/00130.

Competing interests. The authors declare none.

References

- Azadi M., Sabour Rouhaghdam A. and Ahangarani A. (2016) A review on titanium nitride and titanium carbide single and multilayer coatings deposited by plasma assisted chemical vapor deposition. *International Journal of Engineering, Transactions B: Applications*, **29**, 677–687.
- 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 Earth’s mantle. *American Mineralogist*, **106**, 1053–1063.
- 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>.
- Galuskin E., Galuskina I.O., Kamenetsky V., Vapnik Ye., Kusz J. and Zieliński G. (2022) First *in-situ* terrestrial osbornite (TiN) in the pyrometamorphic Hatrurim Complex, Israel. *Lithosphere*, **2022**, 81277447.
- Griffin W.L., Gain S.E.M., Adams D.T., Toledo V., Pearson L.J. and Y. O’Reilly, S. (2016) Deep-earth methane and mantle dynamics: insights from northern Israel, southern Tibet and Kamchatka. *Journal & Proceedings of the Royal Society of New South Wales*, **149**, 17–33.
- Griffin W.L., Toledo V. and O’Reilly S.Y. (2019a) 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*, v. 340–341, p. 181–190). *Lithos*, **348–349**, 191–122.
- Griffin W.L., Gain S.E.M., Huang J.-X., Saunders M., Shaw S., Toledo V. and O’Reilly S.Y. (2019b) A terrestrial magmatic hibonite-grossite-vanadium assemblage: desilication and extreme reduction in a volcanic plumbing system, Mount Carmel, Israel. *American Mineralogist*, **104**, 207–219.
- Griffin W.L., Gain S.E.M., Cámara F., Bindi L., Shaw J., Alard O., Saunders M., Huang J.-X., Toledo V. and O’Reilly S.Y. (2020) Extreme reduction: mantle-derived oxide xenoliths from a hydrogen-rich environment. *Lithos*, **358–359**, 1–8.
- Griffin W.L., Gain S.E.M., Saunders M., Cámara F., Bindi L., Spartà D., Toledo V. and O’Reilly S.Y. (2021a) Cr_2O_3 in corundum: ultrahigh contents under reducing conditions. *American Mineralogist*, **106**, 1420–1437.
- Griffin W.L., Gain S.E.M., Saunders M., Alard O., Shaw J., Toledo V. and O’Reilly S.Y. (2021b) Nitrogen under super-reducing conditions: Ti oxynitride melts in xenolithic corundum aggregates from Mt Carmel (N. Israel). *Minerals*, **11**, 780.
- Griffin W.L., Toledo V. and O’Reilly S.Y. (2023) Discussion of paper by Galuskin and Galuskina, “Evidence of the anthropogenic origin of the “Carmel Sapphire” with enigmatic super-reduced minerals”, *Mineralogical Magazine*, **87**, <https://doi.org/10.1180/mgm.2023.39>.
- 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*, v.340–341, p. 181–190) by W.L. Griffin, V. Toledo and S.Y. O’Reilly). *Lithos*, **348–349**, 105170.
- Oliveira 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 traces crystal growth in a highly reduced magma. *Scientific Reports*, **11**, 2439.
- Xiong Q., Griffin W.L., Huang J.-H., 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 Mount Carmel. *European Journal Mineralogy*, **29**, 557–570.