

## Comment

## Comment on Volodichev et al. Archean Zircons with Omphacite Inclusions from Eclogites of the Belomorian Province, Fennoscandian Shield: The First Finding. *Minerals* 2021, *11*, 1029

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**Abstract:** Volodichev et al. (Volodichev et al., 2021) reported on the first finding of omphacite (23%–25% Jd) inclusions in 2.68 Ga metamorphic zircons from Gridino eclogites and presented it as evidence for Archean eclogite-facies metamorphism in the Belomorian Mobile Belt. We believe that the Archean age of the garnets referred to by the above authors was estimated incorrectly. Our interpretation is that omphacite origin is related to Archean high-pressure granulite-facies metamorphism.

**Keywords:** eclogite; zircon; omphacite; geochronology; geochemistry; mineral inclusion; Gridino eclogites; Belomorian Mobile Belt

Eclogites in the Belomorian mobile belt (BMB) provide the key for the geodynamic reconstruction of not only BMB but also the entire Fennoscandian Shield. One of the major problems in the study of BMB eclogites is determining the timing of their formation. Some researchers interpret BMB eclogites as Archean, thus applying modern geodynamic plate tectonic mechanisms to this Archean crust segment. Available geochronological data on BMB eclogites are interpreted in various ways. The dominant point of view of the Paleoproterozoic age of BMB eclogites is based on the results of a set of independent isotopic-geochemical dating methods, such as the local U–Pb method for heterogeneous zircons with magmatic cores and eclogite paragenesis. All three methods independently show that eclogite-facies metamorphism is of Svecofennian age and yield the same value,  $\sim$ 1.9 Ga [1–7].

Therefore, the authors [8] believe that the omphacite inclusion in zircon of Archean age from an eclogite boudin found on Stolbikha Island in the Gridino area is an indisputable argument in favor of the Archean age of BMB eclogites. However, the attentive reader of the above contribution can notice that the evidence obtained by the authors, as well as the results of earlier studies, are misrepresented.

1. The above authors strongly argue that the Archean age for garnets from BMB eclogites was estimated earlier using the U–Pb method [9]. However, it is clear from the source referred to (an abstract) that no concordant age values for the analyzed garnets (21 samples) have been obtained (Figure 1). A discordia line with an age of  $1866 \pm 44$  Ma was plotted for some of the analytical points, and another discordia line with an age of  $2747 \pm 52$  Ma was constructed for other points. An MSWD value for both discordia lines was not given. The plot only shows figurative points rather than ellipses of mistakes, which can be analyzed to check the validity of the evidence presented.



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**Figure 1.** U–Pb diagram for garnets from eclogites of BMB (modified after [9]). Filled diamonds are garnets from Salma eclogites, white diamonds are garnets from Gridino eclogites.

With respect to the U–Pb method used for the analysis of the garnets, it should be noted that the garnets were treated with warm 2N HCl for 20 min prior to a dissolving procedure, which could result in a considerable loss of lead. The experiments (unpublished data IPGG RAS) have shown that the treatment of garnets with 0.05N HCl and 0.25N HCl solutions for one hour at 80 °C results in the loss of 30% to 40% of lead. Thus, the discordance of the analyzed samples is assumed to have been caused by the disturbance of the U–Pb system of the garnets during the preliminary treatment of the mineral. This assumption is supported by the «zero» intersection of the plotted discordia lines (Figure 1). Furthermore, the garnets were dissolved in a mixture of HF and HNO<sub>3</sub> at ~200 °C for 48 h. It is known that such sample preparation conditions are commonly used for the dissolving of zircons. Therefore, it is assumed that micron-sized zircon inclusions were dissolved or at least affected. As garnets from BMB eclogites contain no radiogenic lead (Skublov, unpublished data), they cannot be used as a U–Pb geochronometer. The age of  $2747 \pm 52$  Ma is, in fact, the age of zircon inclusions analyzed in garnet. This age practically coincides with that of zircons from the same eclogite boudin found on Stolbikha Island in the Gridino area ( $2743 \pm 10$  Ma), whose age was interpreted as the timing of granulite-facies metamorphism, which preceded ~1.9 Ga eclogite-facies metamorphism [6].

The results of the Sm–Nd dating of the garnets seem to be more valid, because the possible presence of zircon in the garnet does not affect the behavior of the Sm–Nd system [10]. We dated garnets from Gridino eclogites using the Sm–Nd method with a preliminary treatment of the garnets with high-purity H<sub>2</sub>SO<sub>4</sub> based on the technique described in [11]. As a result, we obtained an isochrone with an age of 1911 ± 11 Ma (MSWD = 0.61), which coincided with the age of eclogite zircons from the same sample [2]. The dating of garnets from Gridino eclogites using the Lu–Hf method also yielded ages of 1937 ± 8 Ma and 1892 ± 10 Ma [3]. Similar ages of 1.96–1.92 Ga were obtained by garnet Lu–Hf geochronology for Gridino eclogites [5].

Thus, we believe that the Archean U–Pb age of Gridino eclogites is not strictly proven. It contradicts the results of garnet dating by other methods (Sm–Nd, Lu–Hf) and seems to be consistent with the age of micron-sized zircon inclusions in garnet; therefore, it cannot indicate the time of eclogite formation.

2. The authors' conclusions are based on the scarcity of their data. Only two (!) omphacite inclusions were found in the cores of Archean zircons. The biggest inclusion,

 $\sim$ 5  $\times$  20 µm in size, is in the zircon (grain 7), which the authors did not date. It is, therefore, incorrect to draw conclusions about the age of the zircon and, hence, the age of the omphacite inclusion in it solely from the «similarity» of the CL-image of the zircon to other dated zircon. The other omphacite inclusion, only 3.8  $\times$  1.9 µm in size (grain 13), is too small to be reliably analyzed by SEM-EDS method.

Even if the omphacite in the zircon core was analyzed correctly, we do not think that it was derived under eclogite-facies conditions. The 25% Jd content of the omphacite is similar to the lower limit for omphacite [12]. Omphacite-hosting zircon has a  $^{207}$ Pb/ $^{206}$ Pb age of 2694.1 ± 8.1 Ma (Table 1, spot 13.1; [8]). The age of ~2.7 Ga, estimated from the zircon cores, was interpreted by us as the timing of granulite-facies regional metamorphism in BMB [6]. The formation of omphacite under high-pressure granulite-facies metamorphic conditions has been repeatedly proven, for example, for Bohemian Massif (up to 27% Jd, [13]) and Western Sudetes (up to 32.6% Jd, [14]) granulites. The parameters of metamorphism for Gridino eclogites (14 kbar and 750 °C [15]), calculated from omphacite inclusions in garnet with 23% Jd, are also consistent with high-pressure granulites rather than eclogites [16].

The paragenesis of the rock-forming minerals corresponding to ~2.7 Ga granulitefacies metamorphism are obscured in this part of BMB by active ~1.9 Ga eclogite-facies metamorphism. Therefore, a correct interpretation of geochronological data for zircons is critical. The typical geochemical characteristics of typical eclogite-facies zircons are well-known [17,18]. An anomalously low Th content (no more than 3 ppm on average) and Th/U value (0.03 on average), much lower REE (less than 22 ppm) and especially LREE (less than 2 ppm) contents, and a lowered Y (34 ppm on average) are generally observed. REE distribution spectra for eclogite zircons display a well-defined flat HREE pattern, no or poorly defined negative Eu-anomaly, and a strongly reduced positive Ce-anomaly [18].

The zircon core with a micron-sized omphacite inclusion contains 275 ppm REE (131 ppm LREE and 144 ppm HREE), 126 ppm Y, 48 ppm Th and a Th/U ratio = 0.21 (Tables 1 and 2, Spot 13.1; [8]). A comparison of these parameters with median values for typical eclogite zircons [18] shows that they are inconsistent. The inconsistency is especially obvious from the Th concentration and the Th/U ratio. A zircon core (grain 13) with such a composition cannot be interpreted as eclogitic.

Furthermore, the authors do not rule out the magmatic origin of the zircon cores but define some cores as eclogitic due to the presence of omphacite inclusions.

3. There are other considerable inconsistencies in the paper discussed [8]. Micronsized garnet inclusions were found only in Svecofennian ~1.9 Ga zircon rims (Figure 4, grains 4 and 11; [8]). Why have no garnets, occurring together with omphacite, been found in zircon cores of Archean age? When describing the composition of the garnets, andradite end-member is described. More detailed comments are needed because Fe<sup>3+</sup> cannot be analyzed by the SEM-EDS method.

The authors [8] reported that garnet in massive eclogites contains both omphacite and amphibole inclusions. Figure 3 shows that omphacite with 28%–30% Jd is in the rock matrix (Figure 3a) and that compositionally similar omphacite occurs as inclusions in the garnet together with chlorine-bearing pargasite (Figure 3b). Figure 4 shows that the zircon core (grain 19) contains a high-Mg hornblende inclusion. Similar cores (grains 7 and 13) were shown to contain omphacite (23%–25% Jd). Does this mean that amphibole and omphacite are in equilibrium and were trapped simultaneously? Garnet-omphacite-amphibole paragenesis is unlikely for classical eclogites. How, then, does this agree with the fact that pargasite in zircon (grain 13) is in ~1.9 Ga zircon rim. According to the phase correspondence theory [19], as pressure increases, the reaction  $Cpx^{Fe} + Amp^{Mg} = Cpx^{Mg} + Amp^{Fe}$  is shifted to the right, i.e., high-Fe rather than high-Mg amphibole would be in equilibrium with high-Mg clinopyroxene, as follows from the authors' data.

The authors argue that the peak stage parameters of eclogite-facies metamorphism are ~18.5 kbar  $\mu$  695–755 °C. However, in accordance with the reaction Ab = Jd + Qz, at such a pressure the rock is expected to contain practically pure jadeite [20], but only 23%–25% Jd omphacite is reported.

Thus, the authors [8] have drawn a far-reaching conclusion about the existence of Archean eclogites in BMB on the basis of only two finds of micron-sized omphacite inclusions in zircon. The authors' conclusions are largely supported by earlier U–Pb dating of garnets, which, when analyzed in detail, is completely unsubstantiated. The composition of Archean zircons has nothing in common with that of typical zircons from the world's eclogite complexes [18]. The authors ignore the option that an omphacite inclusion and the ~2.7 Ga zircon that hosts it may indicate high-pressure granulite-facies metamorphism, in which omphacite with a moderate Jd content may be present.

It should be added that the interpretation of the origin of a rock on the basis of micron-sized mineral inclusions alone may lead to incorrect results. Some time ago, the journal Nature reported the finding of Hadean diamonds in zircon from Jack Hills, Western Australia [21]. This was assumed to be a major discovery in geology. However, it was proven later that the diamonds were the result of contamination during sample preparation [22]. Of course, the omphacite found in zircon is a fact, but the interpretation of this fact, as well as the results of earlier studies, do not support the Archean age of the eclogites.

The above evidence has led us to conclude that the paper [8] is interesting but debatable. The Archean age of BMB eclogites can only be estimated by dating rock-forming and accessory minerals by independent isotopic geochemical methods, as has been done to support the Paleoproterozoic age of BMB eclogites (e.g., [2,3,6,7]).

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