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Response: Commentary: Is the Neoproterozoic oxygen burst a supercontinent legacy?

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A commentary on

Commentary: Is the Neoproterozoic oxygen burst a supercontinent legacy?
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We thank Nedelec and Borisova (2015) for giving us the opportunity to clarify our data and (derived) conceptual model. The purpose of Macouin et al. (2015) was to propose a new approach to explain the Neoproterozoic Oxygenation Event. It should be recalled that among the recent and abandoned hypotheses for the oxidation of the atmosphere, rise of less reduced gases (or more oxidized) remains one of the most frequently invoked (i.e., Kasting, 2013).

We illustrate our model with data acquired on the Neoproterozoic Socotra biotite granite (SBG) thought to be related to one of the subduction zones that surrounded Rodinia around 780 Ma. The main question raised by Nedelec and Borisova (2015) concerns the primary origin of hematite and ilmenite in this granite and the oxidized character of the emitted gases.

Before discussing the oxide assemblage, we answer on the use of the hematite-magnetite buffer, for which we refer to Sun et al. (2015) and Botcharnikov et al. (2008). Indeed, the magnetite-hematite assemblage does not permit to give a precise value of ΔFMQ, but as stated by these authors, the assemblage is a classical indicator of high oxygen fugacities and hence of an oxidized magma. As mentioned in the comment, it is true that, recently, fO_2 from gas has been shown to possibly diverge from the source magma contrary to what was commonly thought previously (i.e., Burgisser and Scaillet, 2007). Nevertheless, these authors have estimated the deviation from the redox state of the magma source by no more than 1.5 log unit at maximum. In our case, we can still invoke oxidized gases since our estimated fO_2 from sources is significantly higher (ΔFMQ + 4/5).

Concerning the oxide assemblage found in the SBG, we first state that magmatic or late magmatic origin of (titano-poor) hematite has already been reported. For example, Carvalho and Janasi (2012) found hematite in the 610 Ma Pedra Branca syenite (from a magmatic arc) in Brazil. These authors described a primary assemblage of hematite, ilmenite and magnetite. They conclude that this coexistence implies oxidized conditions and probably high oxygen fugacities. One of the authors herself reports an example of magmatic hematite in the unaltered Washita granite (Nedelec et al., 2015). In this publication, the hematite, in the unaltered granite, is interpreted as due to a change in oxygen fugacity in the magma "*without any influence of a hydrous fluid*." Also, contrary to what Nedelec and Borisova (2015) advance in their comment, Broska and Petrik (2011) do not state that hematite is always post magmatic but that the reactions could begin in the magmatic stage.

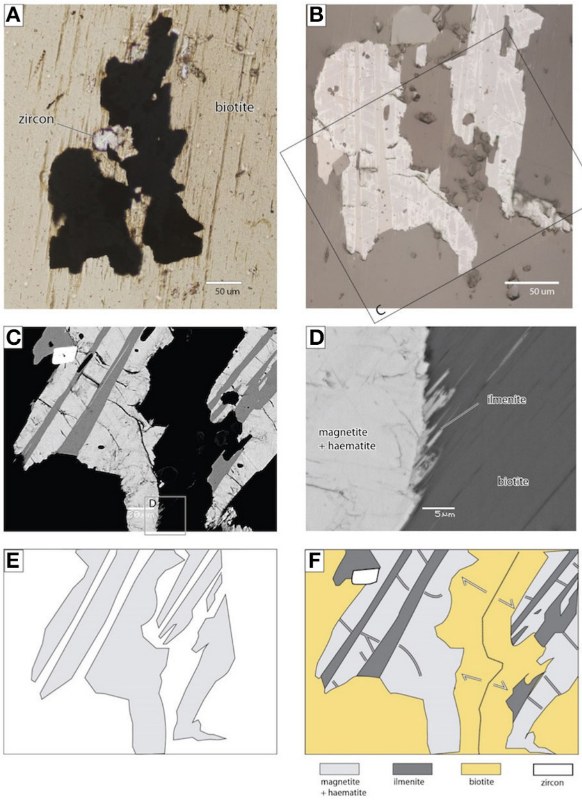

FIGURE 1 | Corrected caption of Figure 7 of Macouin et al. (2015). Photomicrographs of magnetite from CS46 sample (Socotra Biotite Granite, Neoproterozoic terrains, Oman) **(A)** Photomicrographs of subhedral crystals of magnetite (black minerals) trapped in a poikiloblast crystal of biotite (brown mineral). **(B)** Recognition of treillis-like shaped hematite within the crystal of magnetite under reflected light microscopy. Note that hematite is present in the ilmenite and at the fringe of the ilmenite lamellae **(C)** Back-scattered electron imaging on the internal structure of oxide, using a scanning electron microscope (SEM), reveals multiple grains of magnetite-hematite separated by elongated crystals of ilmenite. **(D)** Oriented needles or patches of ilmenite outline the contact with biotite. **(E,F)** Interpreted magmatic events depicted from microscopic and SEM observations. Ilmenite and hematite lamellae developed along cleavage planes of magnetite, due to magmatic oxy-exsolution processes. Magnetite was fractured and divided.

Nedelec and Borisova (2015) affirm that liquidus phase hematite was uniquely found in an experimental peralkaline residual (Edgar, 1974), and therefore not possible with natural samples. More recent literature reports formation of liquidus phase hematite on both, for example, I-type Chinese granite, remelted and recrystallized (Liaw et al., 2006) and a synthetic analog of a ferrobasaltic melt of the Skaergaard intrusion (Botcharnikov et al., 2008). These authors even demonstrate that they produce hematite in their experiments only at high oxygen fugacities ($fO_2 > 2.5$). Both these experiments involve formation of titano-poor hematite (and not of stoichiometric hematite) as it is interpreted in the SBG. This interpretation is strongly suggested by the reversible behavior of the thermomagnetic curves with Néel temperatures on the order of 620°-630°C (see samples CS27-CS30 from Figure 4, Macouin et al., 2015) combined with the petrological observations.

We are aware that hematite can be secondary in granites due to oxygenated fluids. Such secondary hematite has been described in different forms described in Nedelec et al. (2015), or associated with chloritized biotite (Just and Kontny, 2012). A typical mark of hematitization (maghemitization) of titano-magnetite is to display a progression from rims toward core center (often with the core untouched) or along the fractures (Figure 4H of Broska and Petrik, 2011). Curved cracks are also a typical feature of maghemitization (Figure 15 of Haggerty, 1991; Figure 3C of McEnroe and Brown, 2000). It is worth noting that in the SBG, the hematite does not appear into any of these forms and marks of alteration are absent (**Figure 1**).

In the SBG, as described by Haggerty (1991), the C4 stage is probably reached in the samples presenting the assemblage of magnetite-ilmenite-hematite. It is difficult to assess whether the hematite lamellae replaced previous thin ilmenite lamellae (as expected for C4 stage) or are secondary as Nedelec and Borisova (2015) argue. Nevertheless, in **Figure 1B**, thick ilmenite lamellae are seen to both contain hematite and be fringed by hematite, indicating the C4 stage. While we think that this stage was attained during the formation of the granite, late magmatic deuteric oxidation (above 600°C) could not completely be excluded. In this case, such a high temperature alteration would indicate high fugacity of oxygen at least in the fluids that were involved during the end or just after the crystallization as likely occured in the Malani red rhyolites described by Torsvik et al. (2001).

Furthermore, contrary to what Nedelec and Borisova (2015) claim, porphyries generally present hematite-magnetite assemblages and their primary origin has recently been evoked by Sun et al. (2013, 2015). As stated by Sun et al. (2013), intergrowths of magnetite-hematite, such as the ones we exposed in our paper (Macouin et al., 2015), are not often studied and may represent a challenge. It appears clearly that their occurrences are rare and therefore represent an unusual feature. The fact that hematite is ignored or systematically referred as secondary might be a bias in the studies.

Finally, the hematite in the SBG seems to be likely primary and our model remains a possible valid explanation for the NOE. This interesting discussion emphasizes the need to scrutinize this type of mineralogical assemblage in further studies. Additional methods could be used for that, such as paleomagnetic direction to decipher the synchronicity in hematite and magnetite formation or in-situ geochemistry.

AUTHOR CONTRIBUTIONS

All authors listed, have made substantial, direct and intellectual contribution to the work, and approved it for publication.

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