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Reply 2 to comment on "Ultra-high pressure and ultra-reduced minerals in ophiolites may form by lightning strikes"

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Reply

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We appreciate the comments by Yang *et al.* (2018) to our recent proposal (Ballhaus *et al.*, 2017) that high pressure and ultra-reduced minerals in ophiolites may form by lightning strikes. We have carried out additional experiments to address the issues raised by Yang *et al.* (2018). We maintain that the ultra-reduced phases in ophiolites are best explained as plasma precipitates generated by lightning strikes.

Yang *et al.* (2018) note that ultra-reduced phases are recovered from chromitite ore sampled tens of meters below the surface. Previously, no information was provided regarding the recovery depth of phases like SiC, presumably because a near-surface origin was not considered. To semi-quantify the penetration depth of lightning bolts in crystalline rocks we measured the specific resistances of various lithologies (Fig. 1a).

We note that chromitites are more conductive by ~2 orders of magnitude than silicate rocks. A rock body with a higher conductivity can provide a guide path for cloud-to-ground discharges more effectively than a lithology with lower conductivity, as cloud-to-ground discharges need a counter-pole capable of accumulating charges. The "semi-conductive" nature of the rock allows the buildup of a high electrical field which is imperative for the formation of a plasma. The penetration depth of a lightning strike is probably determined by many factors; electrical conductivity and the 3D orientation of the target rock, faulting/fracturing, presence or not of H_2O along grain boundaries and fractures. We put to the discussion the possibility that conductive lithologies like chromitite exposed to frequent lightning may accumulate over time appreciable quantities of lightning strike minerals.

A criticism raised is that our experimentally synthesised ultra-reduced minerals are small and anhedral, while grains in ophiolites are large and subhedral. Our ultra-reduced phases are indeed small but can nonetheless be euhedral (Fig. 1b). It is in the nature of experiments that synthetic phases are smaller than their natural analogues. Yang *et al.* (2018) should have commented how in their opinion ultra-reduced phases like moissanite might have formed in lithologies enriched in FeO. Moissanite is only stable at ~ 6 to 8 log-bar units below the iron-wüstite buffer (IW-6 to IW-8; Golubkova *et al.*, 2016) where most (if not all) transition elements are in a reduced metallic state. Podiform chromitites are oxidised to around FMQ which is 12 log units more oxidised than moissanite. There is no way to argue that ultra-reduced phases may have formed and have survived metastably - the diffusivities at ambient temperature in the deep mantle are too high. Oxidation would be inevitable given the FeO content of the mantle and the length of time these phases would have to survive before they reach the surface. Our preferred explanation is that the super-reduced phases precipitated out of a plasma, as did the micro-spherule ejecta found in surface sediments of the Luobusa ophiolite (for refs. see Ballhaus *et al.*, 2017). Plasma condensates are insensitive to the oxidation states of the lithologies within which they precipitate.

We do not see how the presence of moissanite in kimberlites adds to the problem of SiC in ophiolites. Groundmass moissanite in kimberlites must be metastable because kimberlites are FeO bearing. Kimberlites form at 6 to 8 GPa and ascend so rapidly that they may bridge the distance from generation depth to the surface within hours (Wilson and Head III, 2007). A major driving force is CO_2 exsolution. Shiryaev and Gaillard (2014) argued that micro-diamonds may precipitate metastably when the fluids are C-saturated. Moissanite might precipitate as well if decompression is so rapid that this phase has no time to identify FeO in the melt as a thermodynamic problem.

Yang *et al.* (2018) maintain that fulgurites do not carry high pressure phases. That is not correct (*cf.* Carter *et al.*, 2010). We concede though that in fulgurites, high pressure phases are exceptional but this could be owed to the fact that most fulgurites studied occur in surface sediments that do not behave isochorically when lightning strikes. One of our experiments using a felsic granulite as target lithology indeed returned amorphous lamellae within K-feldspar (Fig. 1c). The thermal pulse apparently induced a shockwave sufficient to amorphise the K-feldspar lattice. For comparable lamellae in quartz in a fulgurite in a granite, Chen *et al.* (2017) derived a minimum pressure of 7 GPa, well within coesite stability.

Central to ophiolite genesis is the origin of the diamonds. A lot of the controversy arises because so many questions remain open. We found no clear statement in the literature as to where the diamondiferous ophiolite samples were taken (surface or underground). It seems that the diamonds were separated at the Institute of Mineral Resources, Chinese

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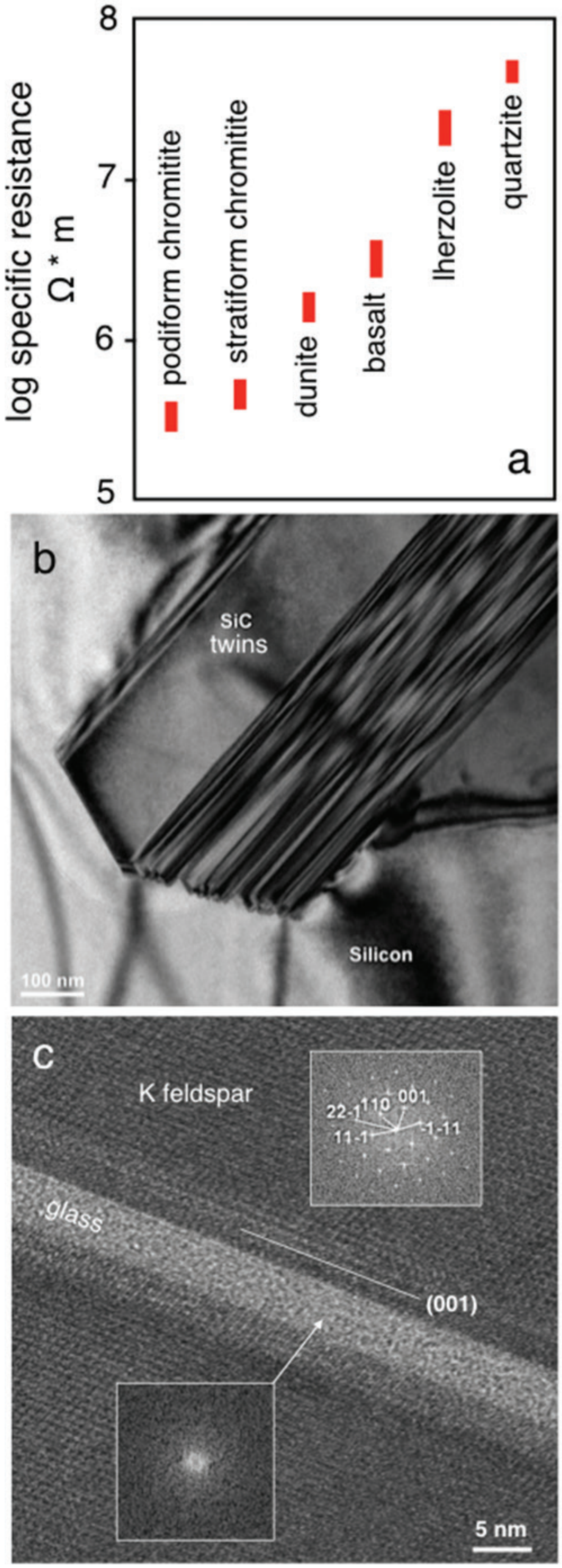

Figure 1 **(a)** Specific resistivities of various lithologies measured with an EG & G 5210 Lockin Amplifier (AC, 12 Hz). Rocks were cut to 8 cm^3 sized cubes, then dried at 80 °C overnight to remove water films along grain boundaries. Electrodes were polyether-polyuretane fabrics impregnated with electrically conductive latex, pressed onto opposing sides of the rock cubes. Lithologies: podiform chromitite (serpentinised) from Cyprus; stratiform UG-1 chromitite from the Bushveld Complex, South Africa; FeO-rich dunite from the Mooihoek pipe, Bushveld Complex; primitive alkali basalt from the Eifel; fresh lherzolite xenolith from the Eifel; and a hydrothermally silicified sandstone from a Lower Cretaceous hot spring in Tunisia. **(b)** Bright-field image of a euhedral moissanite twin inside metallic Si to illustrate that experimentally generated ultra-reduced phases can be euhedral. **(c)** An amorphous glass lamella in K-feldspar parallel to (001), with Fast Fourier Transforms (FFTs) as insets.

Academy of Science, an organisation that processes a wide range of ore samples for the mining industry (Xu *et al.*, 2015). If hundreds of kilos of podiform chromite are processed to recover tens of grains of diamond and SiC, how can contamination be ruled out? Little information exists on nano-structures of ophiolitic diamonds although nano-structures (*e.g.*, twinning, nano-inclusions) are diagnostic to discriminate between natural and artificial origins. Are single crystal diamonds recovered from concentrates identical in terms of nano-structures to diamonds enclosed in chromite (*cf.* Yang *et al.*, 2014)? Why are ophiolitic diamonds characterised by 1b nitrogen aggregation states (Howell *et al.*, 2015) when they had a long residence time within the deep mantle? The Ni-Mn-Co metal inclusions are also problematic. How could a mantle with 8 wt. % FeO and 0.14 wt. % MnO precipitate metals rich in Mn but poor in Fe? When MnO is reduced to Mn, FeO is alo reduced to metallic Fe.

Yang *et al.* (2018) ignore the genetic significance of the spherule ejecta (Ballhaus *et al.*, 2017 and refs. therein). This might be a mistake. Karpov (2014) described diamonds from volcanic tuffs of the Tolbachik fissure in Kamchatka, and those diamonds are also associated with spherules, identical in shape to our experimental spherules and those reported from Luobusa. Electrical discharges can also occur in volcanic ash plumes, and here too plasmas are produced in lightning channels. When volcanic plumes are CO_2 rich, why should diamonds, perhaps even carbonados, not form when the plasmas condense? One should therefore not rule out a CVD origin of diamonds in ophiolites. For the ultra-reduced phases we see no real alternative to plasma precipitation because they are not in redox equilibrium with the FeO and Cr_2O_3-bearing lithologies within which they occur.

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Additional Information

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