

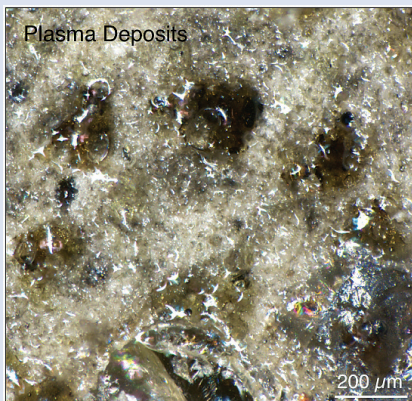
## Ultra-high pressure and ultra-reduced minerals in ophiolites may form by lightning strikes

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### Abstract



Since ultra-high pressure (UHP) minerals have been discovered in ophiolites from Tibet and the Polar Urals, it is speculated that the mantle sections of ophiolites may originate deep within the mantle. The UHP minerals are frequently found together with ultra-reduced silicides, carbides, and nitrides. Consequently, it is argued that the deep mantle, or at least domains within it, must be highly reduced, so reduced that practically all transition elements at depth are present in the metallic state. We find it problematic to rewrite the history of ophiolite complexes based on these observations and suggest we should search for alternative and more realistic modes of origin. Electric discharge experiments at >6000 K reported here show that the UHP and highly reduced phase assemblages may precipitate from plasmas. We argue that the mineral assemblages may originate by lightning strikes. As such, they may not record the origin and emplacement history of the mantle lithologies within which they occur.

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### Introduction

Until recently it was accepted that ophiolites form at low pressure along intra-oceanic spreading ridges (Lago *et al.*, 1982; Zhou *et al.*, 1996; Matveev and Ballhaus, 2002). The identification of ultra-high pressure (UHP) phases in chromitites and harzburgites of ophiolite complexes (Robinson *et al.*, 2004; Yang *et al.*, 2014, 2015) appears to be changing that view. It is now being argued that mantle sections of ophiolites either originate in, or were processed within, the Earth's mantle at depths as great as 600 km (Xiong *et al.*, 2015; Xu *et al.*, 2015; Griffin *et al.*, 2016). Furthermore, these UHP phases are often found associated with ultra-reduced minerals: native metals, silicides, carbides, and nitrides (Dobrzhinetskaya *et al.*, 2009; Xu *et al.*, 2015). Consequently, it is speculated that the mantle source regions of ophiolites must be ultra-reduced.

We question that the UHP and ultra-reduced phases are sufficient evidence to challenge long-established models of ophiolite genesis. Rather, alternative ways should be explored as to how these unusual mineral assemblages may have formed. We suggest that they may be the products of lightning strikes

(Essene and Fisher, 1986; Daly *et al.*, 1993). Novel ultra-high temperature experiments at >6000 K reported here show that ultra-reduced phases can precipitate directly from plasmas. We do not identify diamond because our quench rates are too high, however, we do synthesise concentric shell fullerenes that may serve as nanoscopic pressure cells to vapour-deposited (CVD) diamonds (Banhart and Ayajan, 1996; Sorkin *et al.*, 2011). The Luobusa ophiolite in Tibet where the unusual mineral assemblages are documented in most detail is situated at an altitude in excess of 4000 m, in a region where lightning strikes are frequent (Kumar and Kamra, 2012). The lithologies in which UHP and ultra-reduced minerals are found – serpentinised harzburgite and podiform chromitite – are electrically highly conductive lithologies and prone to attract lightning strikes.

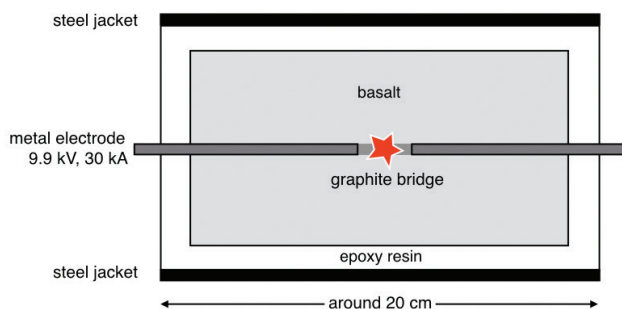
### Experimental Strategy

Basaltic samples are exposed to electric discharges that correspond in terms of current (30 kA) to natural cloud-to-ground lightning strikes (Uman, 1986). The samples are cut in cuboids, set in epoxy resin, and encased by steel sleeves. Tungsten

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metal electrodes are drilled into the front faces of the cuboids and bridged in the centre by a 10 mm long graphite rod (Fig. 1). The electrodes are then connected to a surge-current generator charged to 9.9 kV. The generator has a capacity of 2140  $\mu\text{F}$  and produces a current surge of 30 kA for  $\sim 120 \mu\text{s}$ . Both the graphite rod and the tips of the W electrodes are vapourised upon electric discharge. A plasma is generated. The minimum temperature is given by the boiling point of metallic W ( $\sim 6000 \text{ K}$ ). The samples shatter as a result of thermal expansion. Along the cracks, plasma jets escape and condense on the crack surfaces. The condensates carry ultra-reduced phases identical to those recovered from the Luobusa and Ray-Iz ophiolites.

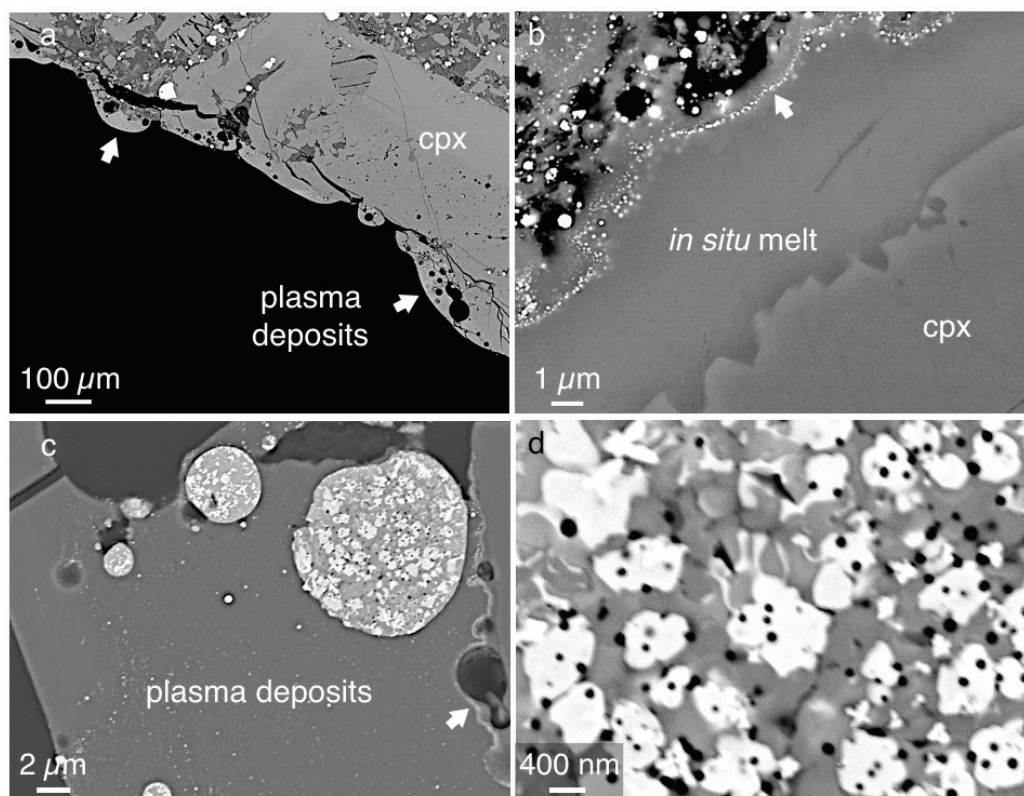


**Figure 1** Experimental arrangement. A basalt cuboid surrounded by a 7 mm thick steel sleeve. The epoxy resin serves as electric insulator to prevent the current from short circuiting around the sample through the steel sleeve. Current pulses are generated with a pulse generator of the type SSG 10 kV/100 kJ (Haefely). The capacity of the pulse generator is 2140  $\mu\text{F}$ . It can be charged to 10 kV. The energy achievable is 100 kJ. The pulse width depends on the load and is of the order of a few hundred microseconds.

## Results

The plasma deposits tend to be up to 100  $\mu\text{m}$  wide (Fig. 2a), consist of silicate glass with dispersed metal beads, and are distinctly zoned (Fig. 2b). On the thermally resorbed mineral surfaces (here a cpx phenocryst) we note an inclusion free *in situ* glass rim around 5  $\mu\text{m}$  wide. Within analytical error, these *in situ* glasses have the same compositions as the minerals on which they rest. Then follows a chain of metal globules  $\sim 20 \text{ nm}$  wide (arrow in Fig. 2b), separating the *in situ* glass layer from glass deposits rich in voids and metal blebs. The glasses above the metal chain are extremely heterogeneous on the micron scale:  $\text{SiO}_2$  from 15 to 67 wt. %,  $\text{TiO}_2$  from 0 to 6.6 wt. %,  $\text{FeO}$  from 0.6 to 62 wt. %,  $\text{MgO}$  from 0 to 52 wt. %, and  $\text{CaO}$  from 0.3 to 23 wt. %.

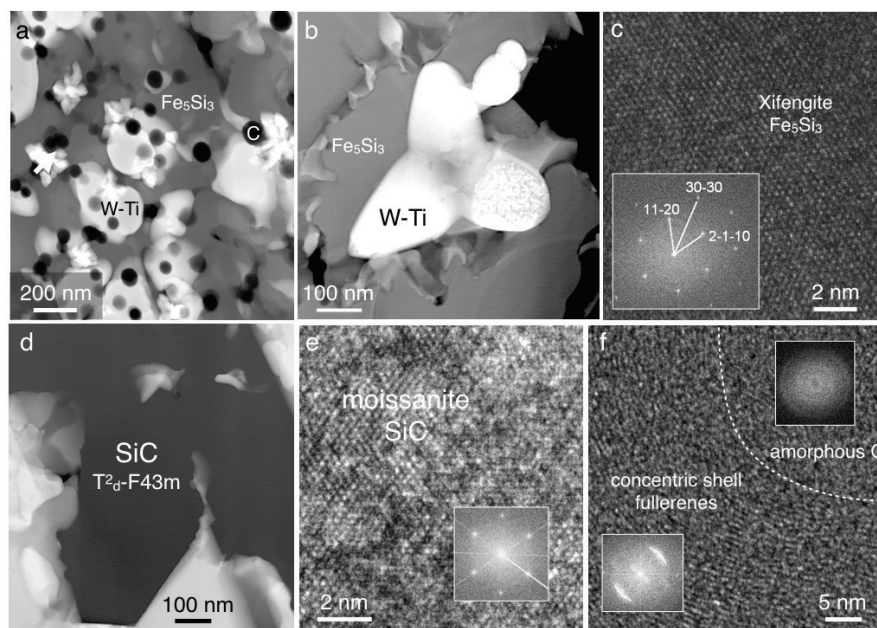
We scanned the larger metal blebs (Fig. 2c) in wavelength dispersive (WDS) mode for their major elements: W, Fe, and Si, as well as minor Ti and P. Tungsten is derived from the electrodes, Fe, Si, and P from the basaltic target rock, and Ti from titanomagnetite groundmass crystals of the basalt. Larger metal globules are polyphase (Fig. 2d), apparently because after liquefaction they exsolve. Two bright phases are identified as carriers of W and Ti, plus several medium grey phases enriched in Fe and Si with minor P. In addition, the metal globules are peppered by tiny dark spherules enriched in low atomic number elements, also found in the heterogeneous silicate glasses. Wavelength dispersive scans on the metal globules with the oxygen sensitive LDE-1 crystal show that the globules are oxide-free.



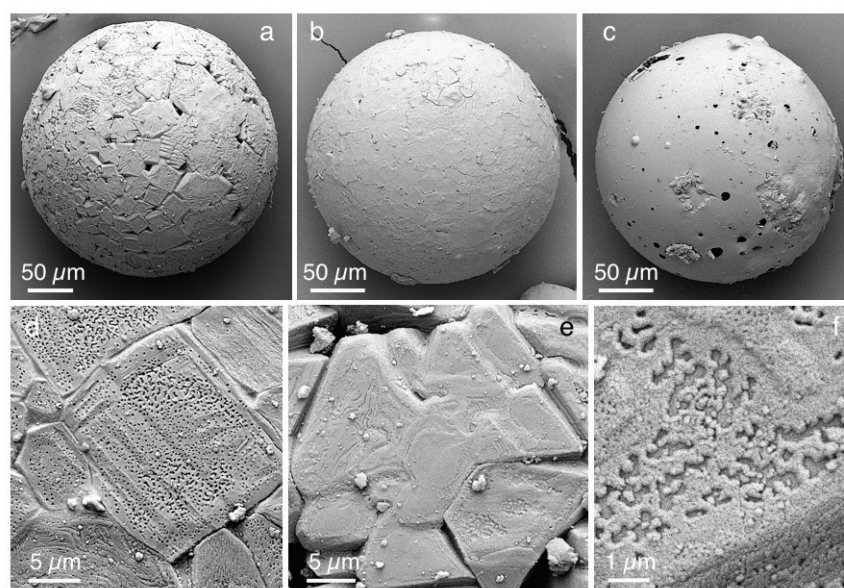
**Figure 2** Images in BSE mode of plasma deposits. (a) Cross section of a crack covered by an up to 100  $\mu\text{m}$  wide porous glass rim, resting upon a cpx phenocryst from the basaltic target rock. (b) Thermally resorbed cpx covered by inclusion-free glass (*in situ* melt), a chain of metal beads (arrow), and porous metal-bearing silicate glasses to the upper left (see text). (c) Larger exsolved metal globule within silicate glass; *in situ* glass to the right of the metal chain (arrow). (d) A metal globule in detail; bright quench phases are W-Ti metal, medium grey are Fe silicides, darker grey are SiC, and dark spherules are carbon condensates.

To identify the phases we investigated focussed ion beam (FIB) sections (Wirth, 2009) from metal condensates with TEM (Fig. 3). The bright phases in Figure 3a and b are cubic Ti-bearing metallic W carrying still brighter dendritic quench phases that are enriched in Ti. Evidently, at ultra-high temperature Ti condenses as a metal species. Note that Ti-Fe-Si alloys and Ti carbides are reported from the Luobusa ophiolite and the Ray-Iz complex in the Polar Urals (Yang *et al.*, 2007, 2014, 2015). The medium grey phase (Fig. 3c) is hexagonal  $\text{Fe}_5\text{Si}_3$  xifengite with minor P. Various Fe silicides including xifengite are reported from chromite-rich lithologies of Luobusa (Robinson *et al.*, 2004) and Ray-Iz (Yang *et al.*, 2015). A minor phase is cubic SiC beta-moissanite (Fig. 3d,e),

also known from Luobusa and Ray-Iz. In the experimental deposits, moissanite tends to form crystals sharply faceted against Fe-Si alloys. The dark rounded blebs are composed of carbon. The blebs imaged by TEM have amorphous cores surrounded by graphene units in concentric arrangement, known as onion shell fullerenes (Banhart and Ajayan, 1996). The spacing of the graphene layers ( $\sim 0.357 \pm 0.001$  nm) is somewhat wider than the spacing of graphene layers in the graphite lattice (0.335 nm). Amorphous carbon is also reported from Luobusa (Yang *et al.*, 2014) and Ray-Iz (Yang *et al.*, 2015), commonly around diamond but not documented structurally on the nano-scale.



**Figure 3** Transmission electron (TEM) images of a metal globule. (a) Overview; bright Ti bearing W metals coexisting with  $\text{Fe}_5\text{Si}_3$  xifengite, SiC moissanite (darker grey), and black carbon spherules (C). (b) Dark field image of W-Ti alloy in contact with xifengite. (c) HRTEM image of xifengite and fast Fourier transform (FFT) as inset. (d) Beta-SiC intergrown with Fe silicides. (e) HRTEM image of SiC with FFT as inset. (f) Amorphous carbon surrounded by graphene layers in concentric arrangement around amorphous cores, possibly shell fullerenes; FFTs as insets.



**Figure 4** Images of plasma spherules in secondary electron (SEM) mode, sputtered with Au. (a) and (b) Oxide spherules; surfaces composed of porous Fe-O oxide platelets. (c) Silicate glass spherule. (d) and (e) Surface crystals of Fe oxide spherules (? wüstite) in detail. (f) A quench oxide crystal on edge, apparently composed of multiple layers of nano-spherules. Note that all spherules shown are from an experiment where metallic Fe metal electrodes were used instead of W metal.

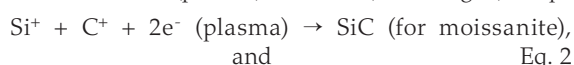
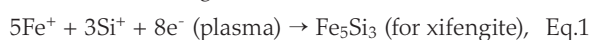
All electric discharges produce spherule ejecta (Fig. 4). We interpret these spherules as condensates of plasma jets that escape along cracks and are quenched in air. We document them here because similar spherules are reported, albeit not explained, from samples of Luobusa (Xu *et al.*, 2015; Griffin *et al.*, 2016). Many spherules are highly porous. Principal quench phases are non-stoichiometric Fe oxides, Fe metal phases, and silicate glass. The crystals on the surface of oxide spherules appear to be composed of packages of nanometre-sized droplets. The similarities to spherules from Luobusa and from fulgurites (Clocchiatti, 1990) are striking.

## Discussion

It is obvious that the phases identified here are plasma precipitates. At temperatures where W metal is vapourised (*ca.* 6000 K) a gas consists to a large extent of positively charged species in an electron cloud which by definition is a plasma (Bittencourt, 2013).

The zonation pattern in Figure 2b illustrates how plasmas may evolve with cooling. Following the electric impulse, the plasma expands fracturing the sample. Some proportion of the plasma is ejected to air and condenses to oxide and silicate spherules (Fig. 4). Under natural conditions, such plasma jets could ignite and trigger ball lightning (Abrahamson and Dinniss, 2000). While passing along the fractures, the plasma causes *in situ* flash melting. Note that the *in situ* glasses are inclusion-free on the TEM scale, notably free of W metal droplets. Apparently, when they form, the plasma is too hot to condense even its most refractory component (W metal), suggesting that temperatures could have exceeded the condensation point of W vapour (6000 K) by a comfortable margin. The first plasma condensates are refractory W-Fe-Si metal melt beads that form chains on top of the *in situ* glass rims. Most of the plasma is then liquefied and deposited in the form of multiple layers of a heterogeneous silicate melt (now glass), still with nano-sized metal and carbon spherules in suspension.

Inside the metal beads we find highly reduced phases like Fe<sub>5</sub>Si<sub>3</sub> and SiC. Apparently, the first condensation reactions are recombinations of positively charged gaseous species with electrons, according to



In formulating these schematic reactions we assume (but do not insist) that the prevailing oxidation state of the cations in the plasma is 1+. The first condensates are highly refractory, ultra-reduced native metals and alloys, commonly Fe-Si alloys because FeO and SiO<sub>2</sub> are major oxides in most lithologies and relatively easily ionised. Recombinations with oxygen do not seem to be important at least in the early stages of condensation (Jones *et al.*, 2005) since oxides are less refractory than silicides and carbides. Our first and highest temperature condensates – W-Fe-Si metal beads – are oxygen free. At lower temperatures though, reaction with oxygen is commonplace. Most of the plasma is then deposited as heterogeneous silicate melt layers, likely as superheated liquids but now present as a metal-bearing, highly heterogeneous and porous glass.

Our experiments produce phases identical to those found in “high pressure” ophiolites, including Fe-Si alloys, moissanite, metallic Ti within W-Ti alloys, amorphous carbon,

and spherulitic ejecta. Some of the phases are highly reduced, however, because plasmas can condense on any type of substrate, their redox states (Golubkova *et al.*, 2016) are not diagnostic of the redox states of the rocks within which they occur. Our experiments also produce potential precursors to diamond. Concentric onion shell fullerenes, when they contract during cooling, can reach internal nano-scale pressures so high that they may nucleate diamond in their cores (Banhart and Ayajan, 1996). Other high pressure phases like coesite and stishovite may also form even though they are not found here: a dunite flash-heated to only 2100 K experiences a pressure pulse of 7 GPa (Liu and Li, 2006) if heating is isochoric. Our plasmas reach temperatures in excess of 6000 K and therefore potentially much higher pressures. That we do not find diamond or other high pressure phases may have experimental reasons: (1) the basalt cuboids disintegrate during discharge hence heating is not isochoric, and (2) the quench rates of our experimental plasmas are extremely short (milliseconds), much shorter than quench rates of natural fulgurites. Naturally generated lightning channels may be hotter, may be isochoric if they penetrate deep in solid rock, and may cool more slowly, leaving more time to nucleate high pressure phases.

For the shell fullerenes produced here the carbon source is the graphite rod bridging the W electrodes. In natural diamonds and carbides of ophiolites the carbon source may be roots and soils. Indeed, diamonds and carbides from ophiolites have rather light and variable  $\delta^{13}\text{C}$  (Trumbull *et al.*, 2009; Yang *et al.*, 2015) and highly positive  $\delta^{15}\text{N}$  ratios (Howell *et al.*, 2015), matching in principle the respective isotope ratios of extant plant materials (Evans, 2001; Bowling *et al.*, 2008). In the Luobusa diamonds, nitrogen is not aggregated (type 1B) unlike in diamonds with long residence times in the mantle (Cartigny *et al.*, 2014). Howell *et al.* (2015) calculated an aggregation age of around 100 years. It would seem sensible then to analyse Luobusa diamonds and carbides for <sup>14</sup>C. Should <sup>14</sup>C be detected its presence would be the most convincing argument yet for a latter day origin of the UHP and highly reduced phases.

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## Additional Information



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