Ultra-reduced phases in ophiolites cannot come from Earth’s mantle

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ABSTRACT

Several recent papers have purported to find ultra-reduced minerals—as natural examples—within ophiolitic mantle sections, including SiC moissanite, Fe-Si alloys, various metal carbides, nitrides, and borides. All those phases were interpreted to be mantle derived. The phases are recovered from mineral concentrates and are assigned to the deep mantle because microdiamonds and other ultrahigh-pressure (UHP) minerals are also found. Based on these findings, it is claimed that the mantle rocks of ophiolite complexes are rooted in the transition zone (TZ) or even in the lower mantle, at redox states so reduced that phases like SiC moissanite are stable.

We challenge this view. We report high-temperature experiments carried out to define the conditions under which SiC can be stable in Earth’s mantle. Mineral separates from a fertile lherzolite xenolith of the Eifel and chromite from the LG-1 seam of the Bushveld complex were reacted with SiC at 1600 K and 0.7 GPa. At high temperature, a redox gradient is quickly established between the silicate/oxide assemblage and SiC, of ~12 log-bar units in fO₂.

Reactions taking place in this redox gradient allow us to derive a model composition of an ultra-reduced mantle by extrapolating phase compositions to 8 log units below the iron-wüstite equilibrium (IW-8) where SiC should be stable. At IW-8 silicate and oxide phases would be pure MgO end-members. Mantle lithologies at IW-8 would be Fe° metal saturated, would be significantly enriched in SiO₂, and all transition elements with the slightest siderophile affinities would be dissolved in a metal phase. Except for the redox-insensitive MgAl₂O₄ end-member, spinel would be unstable. Relative to an oxidized mantle at the fayalite-magnetite-quartz (FMQ) buffer, an ultra-reduced mantle would be enriched in enstatite by factor 1.5 since the reduction of the fayalite and ferrosilite components releases SiO₂. That mantle composition is unlike any natural mantle lithology ever reported in the literature. Phases as reduced as SiC or Fe-Si alloys are unstable in an FeO-bearing, hot, convecting mantle. Based on our results, we advise against questioning existing models of ophiolite genesis because of accessory diamonds and ultra-reduced phases of doubtful origin.

Keywords: Ultra-reduced minerals, moissanite, ultra-reduced mantle, ophiolites, oxidation state

INTRODUCTION

Until recently, it was thought that ophiolites form by spreading of oceanic lithosphere at shallow (~50 km) depth (Nicholas 1999; Pearce and Robinson 2010; Dilek and Furnes 2014), most commonly above intra-oceanic subduction zones (Miyashiro 1973; Robertson 2002). The discovery of UHP minerals in ophiolites worldwide (Robinson et al. 2004; Yang et al. 2015) challenges that view. New models now propose that the mantle lithologies of ophiolites are rooted in the transition zone (TZ) or even in the lower mantle (Griffith et al. 2016a). Some authors even claim that the characteristic ores of supra-subduction zone ophiolites—podiform chromite mineralizations—are enriched at TZ pressure when chromite is in the post-spinel stability field (Xiong et al. 2015).

But how credible are those models? Do microdiamonds in ophiolite lithologies justify rewriting the entire history of ophiolite genesis? The problem is that ophiolitic diamonds are found almost exclusively in heavy mineral concentrates of harzburgite and chromitite bulk samples up to 1000 kg in size (Robinson et al. 2004; Xu et al. 2015; Yang et al. 2015). The risk of contamination during sample processing is high. Except for three dubious examples (Yang et al. 2007, 2015; Das et al. 2017)—two of the in situ diamonds occur in carbon glass—no cases are reported where diamonds were found intergrown with mantle minerals.

In addition to diamonds, the mineral separates return ultra-reduced minerals, including SiC, Fe-Si alloys, metal nitrides, carbides, and borides (Fig. 1). These phases also pose a problem. Ophiolites are lithologies that crystallize at oxygen fugacities (fO₂) around FMQ. Silicon carbide and Fe-Si alloys, by contrast, afford fO₂ conditions of ~IW-8 (Barin 1995). At this relative fO₂ mantle silicates should be FeO-free, should coexist with (Fe,Ni) metal, and Cr₂O₃ in chromite would be reduced to metallic Cr.