

The Occurrence of Diamond in the HPHT Metal-Chromite-Carbon System: Implications for Diamond in Ophiolites

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Introduction

The origin of micro-diamond crystals extracted from various ophiolites has long been controversial (Dobrzynetska et al. 2022). Up to now, predecessors have successively separated a considerable number of micro-diamonds from ophiolites close to orogenic belts globally (Yang et al. 2014, 2021). In addition, several in-situ diamond crystals have been found in podiform chromite and mantle peridotite of Luobusha, Ray-Iz, and Indus ophiolites (Yang et al. 2015; Das et al. 2017). One micro-diamond sized ~6 μm is associated closely with a silicate phase and the syngenetic inclusion occurs in an Os-Ir alloy grain separate from Luobusha chromitites (Yang et al. 2007). Another two in-situ diamond grains sized ~300 and ~400 μm are found to occur in small patches of carbon hosted in chromite grains from the Polar Urals (Yang et al. 2015). Besides, an in-situ octahedral diamond crystal sized ~50 μm is occurs as inclusion along with nitrogen (N_2) in ortho-enstatite from Nidar ophiolite (Das et al. 2017). The presence of cooled NiMnCo alloy, orthorhombic- Al_2O_3 , Ca-perovskite, coesite, and other high-temperature and high-pressure (HPHT) mineral inclusions inside micro-diamonds suggest that these diamond particles may have formed in deep-mantle environment (Lian et al. 2017; Yang et al. 2021). Chromite is the most important associated minerals of ophiolite-hosted diamond, but almost no chromite inclusion has been found in ophiolite-hosted diamond. As a comparison, manganese-rich mineral inclusions represented by NiMnCo alloy, tephroite, and spessartine are widely existed in micro-diamonds from ophiolite (Liu et al. 2021; Yang et al. 2021). The incompatibility between diamond, chromite, and NiMnCo alloy, as well as the reason why diamond particles are enriched in podiform chromite, remain unknown. The high temperature and high pressure (HPHT) experiments provides a new pathway for exploring the relationship between micro-particles of diamond and chromite, NiMnCo alloy.

Experimental section

In this work, natural chromite, NiMnCo alloy, and graphite at various compositions were selected as initial materials to crystallize diamonds under typical upper mantle P-T conditions of ~5.5 GPa and ~1350°C. The initial composition of NiMnCo alloy, graphite, and chromite was 1: 1: 0 (D-1), 1: 1: 0.8 (D-2), 1: 1: 1.6 (D-3), and 1: 1: 3.2 (D-4), respectively. After the synthesis process of 2 h, the quenched blocks were encapsulated into resin targets and polished to the surface. The occurrence of micro-diamond in the quenched blocks were obtained by SEM-EDS system worked at 15.0 KV.

Results

As shown in Figure 1, abundant micro-diamond crystals occur in the quenched blocks of D-1 to D-3, whereas no diamond crystallization was observed in quenched block D-4. It indicates that the addition of high content of chromite to the initial NiMnCo-C-chromite system is unfavorable for the crystallization of

micro-diamonds. In block D-1 with no chromite added to the NiMnCo-C system, massive micro-diamonds are surrounded by cooled alloy catalyst, similar crystallization was also observed in blocks D-2 and D-3. We attributed the crystallization of diamond in the metal to the chemical-potential-difference or film growth mechanism (Kanda 2005). Besides, in blocks D-2 and D-3 with chromite added to the initial NiMnCo-C system, we found many micro-diamonds distributed at the junction between chromite and metal catalyst. The formation of these diamonds is probably related to the oxygen fugacity difference between chromite and metal catalyst under high-temperature and high-pressure conditions (Palyanov et al. 2013). However, we did not find micro-diamonds directly crystallized from the interior of chromite particles.

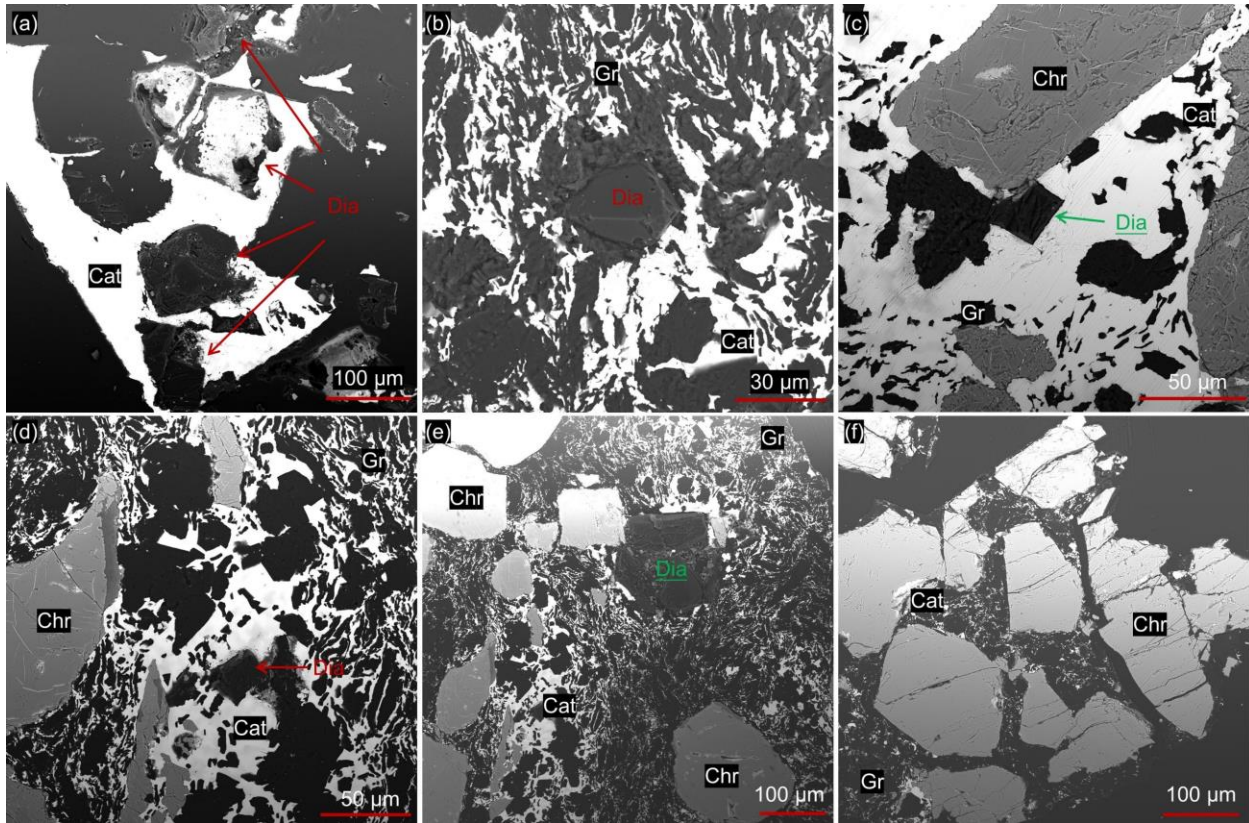


Figure 1. The occurrence of micro-diamonds inside blocks synthesized from various NiMnCo-chromite-C system. initial NiMnCo: C: chromite value = 1: 1: 0 (a), 1: 1: 0.8 (b) and (c), 1: 1: 1.6 (d) and (e), 1: 1: 3.2 (f). Cat: catalyst; Chr: chromite; Dia: diamond crystal grown from metal film; Dia: diamond crystal grown at the junction between chromite and metal catalyst; Gr: graphite.

Discussion

The occurrence of micro-sized diamonds in the quenched NiMnCo-C-chromite blocks after HPHT experiment facilitates discussion on the relationship between chromite, micro-diamond, and NiMnCo alloy. The direct crystallization of diamond inside was not observed in the quenched blocks. For natural in-situ diamond in ophiolites, we noticed that the in-situ micro-diamonds from the Polar Urals is not completely enclosed within chromite grains. Instead, two in-situ micro-diamonds are surrounded by an amorphous carbon pocket, and the pocket is connected to cracks in chromite (Yang et al. 2015). Currently, there is no evidence of in-situ diamond enclosed within chromite grains. Therefore, we believe that the absence of diamond crystallization inside chromite in our experiment is not contradictory to the presence of natural in-situ diamonds within fractures of chromite in the Polar Urals.

The components of inclusion in ophiolite-hosted diamonds provide the most direct evidence of its formation environment. NiMnCo alloy, tephroite, spessartine and Mn-spinel, and other manganese-bearing minerals, are the most representative inclusion components of ophiolite-hosted diamonds, while chromite components are basically absent. In contrast, iron-bearing minerals such as wüstite, magnetite, ilmenite, FeNi, and FeTi alloys are common in the abnormal minerals separated from podiform chromite, wherever manganese-bearing minerals is not dominant (Xu et al. 2009). Based on these observations, we speculate that ophiolite-hosted diamonds cannot directly crystallize from podiform chromite. Instead, it is more likely to crystallize from a metal-bearing deep mantle environment at first. The formation mechanism of micro-diamonds may be related to the film growth or the oxygen fugacity difference caused by the reaction between chromite and Mn-rich metal. In this case, the inclusions inside the ophiolite-hosted diamonds basically do not contain chromite, but are rich in manganese minerals formed in the environment. Since the nitrogen impurities inside ophiolite-type diamonds are mostly in unaggregated state, we prefer that ophiolite-hosted diamonds are formed due to the oxygen fugacity difference caused by the reaction between chromite and Mn-rich alloy. In this non-equilibrium state, diamonds tend to form rapidly and then be captured and transported by the later upwelling chromite.

Conclusion

The controversial origin of micro-diamonds in ophiolites is explored by combined HPHT experiments, the occurrence of natural in-situ diamonds in ophiolites, and their typical inclusions. Micro-diamonds can crystallize from the NiMnCo-C-chromite system by film growth or oxygen fugacity difference mechanism. The absence of diamond crystallization within chromite in our experiment aligns with natural occurrences of in-situ diamond, indicating that ophiolite-hosted diamonds likely crystallize from a metal-bearing deep mantle environment at first and then be captured and transported by the later upwelling chromite.

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