Diamonds and other unusual phases formed during high-temperature gas phase condensation (CVD) in local microenvironments in volcanic rocks.

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More than 20 years ago Russian geologists reported diamond in bedrock in recent lavas from the active Avacha volcano within the Kamchatka Peninsula (Baikov et al.,1995). These diamonds are aggregates of micro- to nanocrystalline diamond a few hundred micrometre in size. In a recent paper by Kaminsky et al., (2016) these diamonds have been proposed to be carbonado-like diamonds.

A more detailed TEM study of these diamond aggregates and another diamond aggregate from a different locality in Kamchatka reveals the presence of other unusual minerals and phases together with diamond, which have not yet been reported. Electron transparent foils from the aggregates have been prepared applying the focused ion beam (FIB) technique.

Diamond shows a characteristic microstructure of intense twinning after $\{111\}$ and local extremely high dislocation density. The diamond crystals form a kind of framework with some space or porosity between the individual crystals. That space is usually filled with nanocrystalline material but also with amorphous material. The nanocrystalline material includes silicon Si (twinned after $\{111\}$) and a new open-framework allotrope of silicon Si_{24} , SiO_2 quartz and tridymite, carbides such as polymorphs of SiC (cubic, SiC4H, SiCH6), W-carbide and B-carbide, Tilleyite $Ca_5(Si_2O_7)$ ($CO_3)_2$, Calcium carbonate, graphite, silicides such as Mn-Fe-silicides with varying chemical composition and crystal structure (hexagonal and orthorhombic). Calcite crystals are full of bubbles suggesting an early stage of high-temperature decomposition. Decomposition of calcite at ambient conditions starts already at 600° C (Rodriguez-Navarro et al., 2009).

The amorphous material includes SiO₂, carbon and material mainly composed of Ca-Si-O.

All of these phases with exception of calcite have formed by gas phase condensation at high temperature in local microenvironments under highly reducing conditions. Especially, the discovery of the open-framework silicon Si_{24} in rocks confirms the formation of these aggregates from gas phase condensation because the authors of the first synthesis of that material made an important statement in their publication: "low-pressure methods such as chemical vapour deposition could potentially enable larger scale production of Si_{24} " (Duck Young Kim et al., 2015).

Consequently, the observation of diamond in the field such as placer diamond not necessarily documents high-pressure conditions. However, CVD diamond aggregates display unique and characteristic microstructures that allow discriminate them from kimberlitic and metamorphic diamonds.

Baikov, A.I., Anikin, L.P., Dunin-Barkovsky, R.L., 1995. Find of carbonado in volcanic rocks

of Kamchatka. Doklady Akademii Nauk SSSR 343 (1), 72-74 (in Russian).

Duck Young Kim, Stefanoski, S., Kurakevych, O.O., Strobel, T.A. (2015) Synthesis of an open-framework allotrope of silicon. Nature Materials, **14**, 169 –173.

Kaminsky, F., Wirth, R., Anikin, L.P., Morales, L., Schreiber, A., (2016) Carbonado-like diamond from the Avacha active volcano in Kamchatka, Russia. Lithos, 265, 222 –236.

Rodriguez-Navarro, C., Ruiz-Agudo, E., Luque, A., Rodriguez-Navarro, A. B., Ortega-Huertas, M. (2009) Thermal decomposition of calcite:mechanisms of formation and textural evolution of CaO nanocrystals. American Mineralogist, 94, 578 –593.

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