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Syngenetic phlogopite inclusions in kimberlite-hosted diamonds: implications for role of volatiles in diamond formation

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Abstract

We discuss the chemistry of exceptionally rare phlogopite inclusions coexisting with ultramafic (peridotitic) and eclogitic minerals in kimberlite-hosted diamonds of Yakutia, Arkhangelsk, and Venezuela provinces. Phlogopite inclusions in diamonds are octahedral negative crystals following the diamond faceting in all 34 samples (including polymineralic inclusions). On this basis phlogopite inclusions have been interpreted as syngenetic and in equilibrium with the associated minerals. In ultramafic diamonds phlogopites coexist with subcalcic high-Cr_2O_3 pyrope and/or chromite, olivine and enstatite (dunite/harzburgite (H) paragenesis) or with clinopyroxene, enstatite, and/or olivine and pyrope (lherzolite (L) paragenesis). Ultramafic phlogopites have high Mg# [100·Mg/(Mg+Fe)] from 92.4 to 95.2 and Cr_2O_3 higher than TiO_2 in H-phlogopites (1.5–2.5 wt.% versus 0.1–0.4 wt.%, respectively) but lower in L-phlogopites (0.15–0.5 wt.% versus 1.3–3.5 wt.%, respectively). Eclogitic (E) phlogopites show Mg# from 47.4 to 85.3 inclusive, and very broad ranges of TiO_2 up to 12 wt.%. The primary syngenetic origin of phlogopite is indicated, besides other factors, by its compositional consistency with the associated minerals. The analyzed phlogopites are depleted in BaO (0.10–0.79 wt.%), and their F and Cl contents are highly variable reaching 1.29 and 0.49 wt.%, respectively. The latter is in line with high Cl enrichment in some unaltered kimberlites and in nanometric fluid inclusions from diamonds. The presence of syngenetic phlogopite in kimberlite-hosted diamonds provides important evidence that volatiles participated in diamond formation and that at least a part of diamonds may have been related to early stages of kimberlites formation.

Keywords: phlogopite; diamond; mineral inclusions; olivine; pyroxene; paragenesis

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Introduction

Understanding the role of volatiles is a key point in the formation of diamond, which is still an enigmatic mineral (Sobolev, 1960). Kimberlite-hosted diamonds are time capsules (Taylor and Anand, 2004) as carriers of inclusions that represent the mantle diamond-forming environment (Harris, 1992; Meyer, 1987; Navon, 1999; Sobolev, 1974; Sobolev et al., 1969 a,b; Sobolev et al., 2004, 2009; Stachel and Harris, 2008). Experimental results synthesized in explicit overviews (Palyanov et al., 2007; Safonov et al., 2007), along with data on multiphase fluid and mineral inclusions of micrometric and submicrometric sizes found in many diamonds worldwide (Guthril et al., 1991; Izraeli et al., 2001, 2004; Klein BenDavid et al., 2009; Logvinova et al., 2007, 2008; Navon, 1999; Reutskii and Zedgenizov, 2007; Tomlinson et al., 2006; Zedgenizov et al., 2004), show ultrapotassic fluids/melts to be an essential agent in diamond formation in the upper mantle.

Micas, which are the repository of hydrogen, fluorine, and chlorine, have not received much attention in the course of years-long studies of mineral inclusions in diamonds. The reason is that they are very rare and their paragenesis is uncertain (Meyer, 1987). Few finds of phlogopite inclusions in diamonds (Giardini et al., 1974; Gurney et al., 1979; Meyer and McCallum, 1986; Prinz et al., 1975; Williams, 1932) were either underestimated or interpreted as epigenetic species (Harris, 1992; Meyer, 1987).

Identifying primary or secondary origin of phlogopite of peridotitic and eclogitic xenoliths in kimberlites, including diamond-bearing samples, is quite difficult (Beard et al., 1996; De Stefano et al., 2009; Kushiro and Aoki, 1968; Misra et al., 2004). That is the case of phlogopites found in numerous alkali basalt- and kimberlite-hosted spinel and pyrope peridotite xenoliths (Menzies and Hawkeswotrh, 1987), in granular and deformed peridotite xenoliths from kimberlites of Yakutia (Sobolev et al., 1997c; Solovjeva et al., 1997, 2008; Tychkov

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et al., 2008) and South Africa (Griffin et al., 1999), as well as in diamond-bearing eclogite xenoliths from the Udachnaya kimberlite pipe (Misra et al., 2004; Sobolev et al., 1999). Most of those phlogopites were identified as late secondary phases for the lack of major-element consistency with the associated minerals (Menzies and Hawkesworth, 1987; Sobolev et al., 1997c), and for their compositional proximity to typical phlogopite macrocrysts in kimberlites. Representative mineralogical data on peridotitic xenoliths in South African kimberlites restrict the compositions of primary phlogopites to a narrow domain according to Cr_2O_3 and TiO_2 contents (Erlank et al., 1987). Phlogopite is a kimberlitic mineral which, unlike garnet, chromite, picroilmenite, or clinopyroxene, rarely occurs in kimberlite pipe haloes (Afanas'ev et al., 2008).

We have come across very few phlogopite inclusions when studying, for years, the chemistry and parageneses of diamond-related minerals from deposits in Russia and abroad (less than 0.1% of the samples). The phlogopite inclusions most often exist either as aggregates with other minerals (polymineralic inclusions) (Sobolev, 1974; Sobolev et al., 1988, 1997a, 1998) or as isolated crystals among multiple other mineral inclusions (Sobolev et al., 1997b). These are the aggregates, in which minerals are in contact and in equilibrium, that constitute a basic component of the collection we studied. This paper summarizes our published and unpublished data on 34 samples of phlogopites discovered in diamonds, mainly in association with other minerals (Table 1).

Samples and methods

Below we present new unpublished data on compositions and parageneses of phlogopite inclusions in diamonds from the kimberlite pipes Mir, Udachnaya, Komsomolskaya (Yakutia) and from the Guaniamo kimberlites (Venezuela), in addition to previously reported few examples of syngenetic phlogopites in diamonds of the Sputnik pipe, Yakutia (Sobolev et al., 1997a), Pionerskaya pipe, Arkhangelsk diamond province (Sobolev et al., 1997b), and of Guaniamo kimberlites, Venezuela (Sobolev et al., 1998). Many samples contain phlogopite as part of aggregates (Table 1) with intergrowing chromite (Fig. 1) and clinopyroxene (Figs. 2 and 3). Especially interesting are several phlogopites grown in with clinopyroxene we discovered during preanalytical treatment of extracted omphacite inclusions (Figs. 2 and 3). All discussed phlogopites coexist with other ultramafic or eclogitic minerals in diamonds.

The selected monomineralic and polymineralic phlogopite inclusions in diamonds are octahedral negative crystals (see Figs. 1, 2, 3 for elements of this faceting in six selected polymineralic samples). This is the octahedral negative faceting, with the inclusion facets along the octahedral facets of the diamond host, that has been currently the universally accepted evidence for the syngenetic origin of inclusions (Harris, 1992; Stachel and Harris, 2008). Octahedral negative habits were observed previously in garnets, pyroxenes, and olivines from Yakutian (Sobolev et al., 1970, 1972) and South African diamonds (Prinz et al., 1975), and in synthetic species (Bakumenko et al., 1984).

Phlogopite-bearing diamonds (Table 1) look like colorless or poorly colored crystals of octahedral or transitional octahedral-dodecahedral shapes and are similar to other diamonds common to the Yakutian (Orlov, 1973) and Guaniamo (Kaminsky et al., 2000; Sobolev et al., 1998) localities, respectively. Note that three samples belong to typical polycristalline aggregates (framesites) reported from many kimberlite pipes (Kirkley et al., 1994; Orlov, 1973; Sobolev, 1974).

Unlike the analyzed rare phlogopite parageneses in diamonds, phlogopite is a common mineral phase in nanometric inclusions of high density fluids (HDF) found as negative crystals in diamonds from the Internatsionalnaya and Yubileinaya pipes in Yakutia (Logvinova et al., 2007, 2008). An example of such inclusions, in which phlogopite and dolomite coexist with other problematic phases in a cloudy central part of diamond from the Yubileinaya pipe (Logvinova et al., 2007), is shown in Fig. 4.

In most of ultramafic samples (Table 1), phlogopite occurs together with minerals of clearly dunite-harzburgite or lherzolite parageneses. In order to highlight this division based on specially developed criteria (Sobolev, 1974; Sobolev et al., 1973), the phlogopite compositions are reported below in comparison with the compositions of all associated minerals (Tables 2 and 3). Of special importance are inclusions (Table 1) in which phlogopite is grown in (touching) with other minerals, such as chromite (Fig. 1), or grows in with clinopyroxenes (Fig. 2, 3). Altogether we discuss phlogopites and associated minerals from 19 ultramafic and 15 eclogitic diamond samples (Table 1).

Phlogopites, along with associated minerals, were extracted through diamond crushing, and in some cases were discovered only after clinopyroxene inclusions had been polished before analysis (see Figs. 2 and 3 for the phlogopite-clinopyroxene relations and note that phlogopite is subordinate in almost all polymineralic inclusions).

The major-element composition of mineral inclusions was determined by EPMA on a *Cameca Camebax-micro* and a *JEOL JXA-8100* electron microprobes following the standard procedure (Korolyuk et al., 2008; Lavrent'ev et al., 1987). Special attention was given to impurities, such as Na_2O in garnets, K_2O in clinopyroxenes, and Cr_2O_3 in olivines (Sobolev, 1974). Impurities in phlogopites (Ba, F, Cl) were determined only in a few samples (Tables 1, 2, and 4). Each phlogopite inclusion was analyzed at 5 to 10 points, depending on its size.

Results

The compositions of the analyzed inclusions of phlogopite and associated minerals in diamonds are listed in Tables 2 and 3. Their parageneses are identified according to common signatures of mineral assemblages and their compositions (Meyer, 1987; Sobolev, 1974; Sobolev et al., 1973). The