Eskolaite associated with diamond from the Udachnaya kimberlite pipe, Yakutia, Russia

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ABSTRACT

The mineral eskolaite (Cr_2O_3) has been discovered in association with natural diamond from the Udachnaya pipe in Yakutia, where it is intergrown with an octahedral diamond, mostly as an inclusion in the diamond, but also exposed at its surface. A detailed study was performed on fragments extracted from the outer surface of the diamond, using single-crystal X-ray diffraction (XRD), high-resolution electron microscopy (HRTEM), analytical electron microscopy (AEM), including line-scan and elemental-mapping, EMP, and SIMS. These applied techniques confirmed the nature of the eskolaite with 86.8 wt% Cr_2O_3 and notable impurities of TiO_2 (3.99 wt%), Al_2O_3 (2.00 wt%), Fe_2O_3 (5.83 wt%), and MgO (1.11 wt%). Trace elements, including V (4900), Mn (129 ppm), Zr (56 ppm), and Nb (32 ppm) were also detected. The entire range of REE is just at or below the limits of detection. A small picrochromite inclusion (X_{Mg} 81.2; Y_{Cr} 94.7) was detected in the eskolaite; its chemistry is typical of chromite diamond inclusions. It also contains minute inclusions of perovskite, corundum, and an unidentified Ti-phase. Nano-sized cavities in picrochromite were determined to consist of carbonate and quench products, including Si, Mg, Ca, P, K, and Cl. This may represent relics of the diamond-forming metasomatic fluids. The eskolaite, containing a picrochromite inclusion, was formed at high pressure within the diamond stability field from C-O-H-bearing fluids containing Ca, K, Cl, P, and possibly even peridotitic (U-type) oxides and silicates.

Keywords: Diamond association, intergrowth, eskolaite, picrochromite, Udachnaya kimberlite pipe, Yakutia, Russia

INTRODUCTION

Eskolaite (Cr_2O_3), identified as the natural counterpart of the synthetic compound Cr_2O_3, was firstly described from the Outokumpo mine, Finland (Kouvo and Vuorelainen 1958). It was approved as a new mineral species representing the Cr analog of corundum. The eskolaite occurred in skarns associated with some Cr-bearing minerals, including chromite, and represented part of a low-pressure, metasomatic assemblage. Later, eskolaite was discovered in a grospydite xenolith from the barren Zagadochnaya kimberlite pipe, Yakutia: gros = grossular; py = pyroxene; di = disthene (kyanite) (Bobrievich et al. 1960; Sobolev et al. 1968; Sobolev 1977), where it appeared to have formed at pressures of up to 3 GPa, but below the diamond stability field. This small xenolith, which also contained Cr-rich kyanite, Cr-rich omphacite, and Ca-Cr-garnet (uvarovite), most probably formed as part of metasomatized, Cr-enriched layers observed rarely in some grospydite xenoliths.

Unusually high Cr-enrichment of ilmenites, reaching 10–14 mol% of eskolaite solid solution, occurs associated with olivines in diamond and also found in kimberlite associated with garnet and chromite. Some diamond occurrences include the Mir, Sputnik, and Mwadui mines (Sobolev 1977; Sobolev et al. 1997; Stachel et al. 1998), dependent mostly on bulk composition and temperature (Green and Sobolev 1975; Haggerty 1991).

In the present study, we report the first occurrence of eskolaite associated with natural diamond, as it occurs not only within the diamond (>1 ct.), but is also exposed at its outer surface. This diamond is from the Udachnaya pipe in Yakutia. Due to the precious nature of this gem diamond, it was not possible to break this diamond; therefore, only fragments of this opaque inclusion were extracted from the outer surface of this sharp-edged octahedral diamond crystal, typical for the majority of Yakutian diamonds (Orlov 1977). Such occurrences of minerals as real inclusions in diamond, yet partly exposed at the surface, have previously been extensively sampled as exposed diamond inclusions (DIs) of garnets and chromites in several Yakutian diamonds (Sobolev 1977). In fact, similar types of diamond inclusions, with a portion exposed at the surface, formed the basis for the study of garnets and chromites in large (10–200 ct.) Yakutian diamonds (Sobolev et al. 2001; Taylor et al. 2003). It has been demonstrated that both major- and trace-element chemistry of exposed inclusions are practically identical to compositions of typical wholly encapsulated inclusions; this was recently shown for inclusions in diamonds of Cr-rich subcalcic pyropes and Cr-rich chromites (Taylor et al. 2003). These minerals have been considered to have

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been formed in equilibrium with diamond.

The purpose of the present study was to confirm the nature of this first discovery of eskolaite associated with diamond, using sophisticated analytical instrumentation to examine its crystal structure, homogeneity, possible submicroscopic inclusions, and to compare the major- and trace-element compositions of eskolaite, and provisional included minerals, with other known natural occurrences.

ANALYTICAL METHODS

Single-crystal X-ray diffraction (XRD) analysis was performed on one of the eskolaite fragments; crystal-structural study and refinement were performed with a Stoe STADI-4 diffractometer (graphite-monochromated Mo$K\alpha$ radiation; scintillation counter) at GFZ Potsdam. Lattice constants were refined by centering of 36 reflections (13 independent) in the 15.3 < °2θ < 33.2 range. A total of 1206 diffraction intensities were collected up to 20–65 < °2θ for the triclinic symmetry. The intensity distribution revealed a trigonal symmetry, and the observed systematic extinctions indicated space group, $R\bar{3}c$. The crystal structure was solved using SHELXS-97 (Sheldrick 1997a) and then, refined using SHELXL-97 (Sheldrick 1997b).

The focused ion beam (FIB) tool was used to prepare site-specific transmission electron microscopy (TEM) foils for subsequent analysis by TEM (Wirth 2004) of submicroscopic inclusions in eskolaite. TEM investigations were performed at GFZ Potsdam with a TECNAI F20 X-TWIN instrument operating at 200 kV with a field-emission gun electron source. The TEM is equipped with a GATAN Tridiem filter, an EDAX Genesis X-ray analyzer with an ultrathin window and a Fishione high-angle annular dark-field detector (HAADF). TEM techniques were applied, such as electron diffraction, analytical electron microscopy (AEM), including line-scan and elemental-mapping, as well as high-resolution electron microscopy.

Major-element compositions of eskolaite were determined with a fully automated JEOL 8100 electron microprobe (EMP) at the Institute of Geology and Mineralogy in Russia. EMP analytical conditions employed an accelerating potential of 15 kV, 30 nA beam current, 5 μm beam size, and standard ZAF correction procedures. Counting times were 20 s for the majority of elements.

Trace-element analyses of the eskolaite were performed with a modified CAMECA IMS-3f ion microprobe at Washington University in St. Louis, Missouri. Details of the analytical procedures are described by Zinner and Crozaz (1986a, 1986b), Alexander (1994), Hsu (1995), and Fahey et al. (1987). Detection limits are variable, depending on the element analyzed.

RESULTS

Considerable analyses of this eskolaite were performed, leading to its detailed characterization. Experimental details for the single-crystal XRD data collection, and structure refinement of the eskolaite are presented in Table 1. An M-O distance of 1.9928 Å, which was calculated as a sum of ionic radii (Shannon and Prewitt 1969), is in agreement with the experimental value. Previous structural investigations of Cr_2O_3 were performed on synthetic samples (Battle et al. 1988; Finger and Hazen 1980; Newnham and de Haan 1962; Rekhi et al. 2000; Sawada 1994). Ranges of unit-cell parameters for those determinations are practically identical: a = 4.951–4.961 Å; c = 13.566–13.599 Å; c/a ratio values of 2.740–2.742. The a parameter of the Yakutian sample exceeds slightly the values of synthetic samples; similarly, the c parameter lies near the experimental upper values. In comparison with natural eskolaite from Outokumpu (Kouvo and Vuorelainen 1958), the a parameter of our sample appears less, whereas the c parameter is noticeably larger. However, these distinctions are well within the estimated standard deviations and are not considered real differences.

Several fragments of eskolaite were mounted in epoxy, polished, and checked for homogeneity. A total of 28 spots on different fragments were analyzed by EMP (Table 2). Major

impurities detected in the studied eskolaite sample are represented by Fe_2O_3 (5.82 wt%), TiO_2 (3.99 wt%), Al_2O_3 (2.0 wt%), and MgO (1.11 wt%). SIMS trace-element analyses (Table 2) revealed the abundant presence of Ti, V, and Mn, and notable levels of Zr (55–57 ppm) and Nb (31–32.6 ppm). Extremely low abundances of LREE and MREE were determined, close to the limits of detection, however, the HREEs were non-detectable. One of the analyzed spots (area 1; Fig. 2a) possibly included some secondary products or relics of fluids, as indicated by higher Ba abundances with higher LREE values.

Visual examination of several polished eskolaite fragments under the microscope resulted in the discovery of a minute, roughly hexagonal inclusion of picrochromite, about 10×15 μm (Fig. 1a), and its analysis is given in Table 2. To verify the detection of the picrochromite and check the homogeneity of eskolaite, a TEM study was performed close to the interface between the eskolaite and picrochromite inclusion. Electron-diffraction data confirmed the presence of both minerals (Figs. 1b and 1c), with a sharp interface between them. Additional examination of the picrochromite inclusion by TEM resulted in detection of some submicroscopic phases within the eskolaite matrix, as well as the microporosity in the mineral foil. The pore at the lower end of the foil shows a Ca-carbonate crystal, identified by chemical composition (area 2; Figs. 2a and 2c). There are other materials with gray contrast surrounded by nanocrystalline corundum in a C-rich matrix (area 1; Figs. 2a and 2e). Apparent quench products (area 3; Figs. 2a and 2f), containing C-Na-Mg-Al-Si-P-Cl-K-Ti, were found in another inclusion. The presence of these elements was confirmed by the EDS spectrum shown in Figure 2f. Corundum and perovskite nano-inclusions within picrochromite, but outside of the nanoinclusion pockets, were also confirmed by spectral data (area 1; Figs. 2a, 2d, and 2e). Among unidentified

TABLE 1. Chemistry, crystallographic data, and refinement parameters of eskolaite

Chemical formula	$(Cr_{10.37}Fe_{0.74}Ti_{0.46}Al_{0.35}Mg_{0.25}Si_{0.01})^{[6]}_{\Sigma 12.18}O^{[4]}_{18}$
Z	1
Crystal system	Trigonal
Space group	$R\bar{3}c$
a (Å)	4.9696(11)
c (Å)	13.597(4)
V (Å³)	290.81(13)
Crystal size (mm³)	$0.15 \times 0.07 \times 0.03$
d (g/cm³)	5.099
$F(000)$	424
Scan type	ω–2θ
$h_{min,max}$; $k_{min,max}$; $l_{min,max}$	−7,7; 7,7; −20,20
μ (Mo$K\alpha$) (mm⁻¹)	10.384
Number of I_{hkl} measured	1206
Number of unique F^2_{hkl}	120
R_{int}	0.0609
Number of variables	10
R factors for observed reflections [$I > 2\sigma I$]	$R1 = 0.0291$, $wR2 = 0.0779$
R factors for all data	$R1 = 0.0298$, $wR2 = 0.0790$
Residual electron density (e/Å³)	1.873, −0.910

Positional parameters for the structure of eskolaite sample

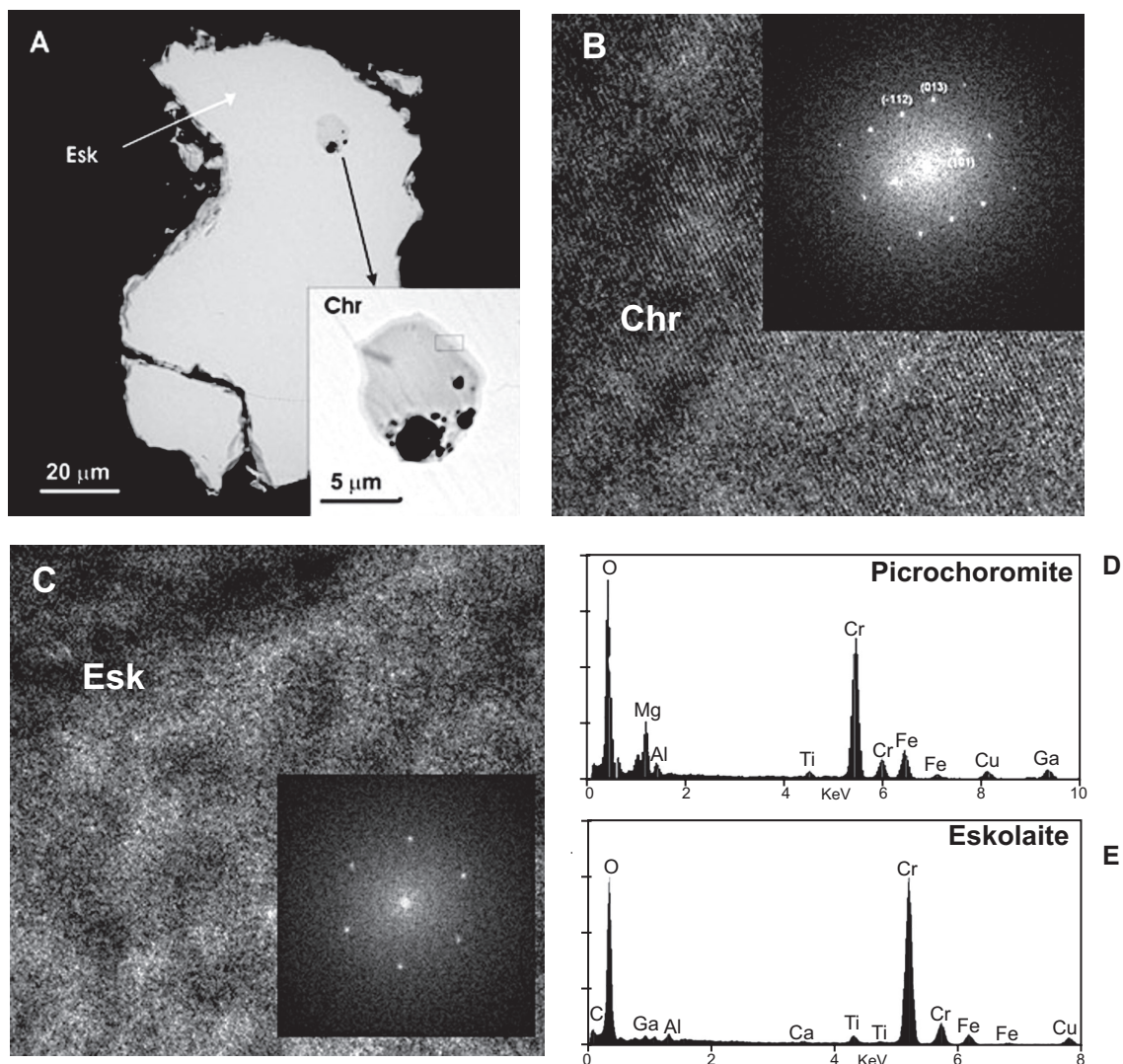| M^{VI} (12 c)	z	0.34834 (4)
	U_{eq}	0.0031 (4)
O (18 e)	x	0.3055 (3)
	U_{eq}	0.0047 (5)
M-O distances (Å)		
M-O (3×)		1.9635 (8)
M-O (3×)		2.0230 (12)
mean		1.9933

FIGURE 1. (**a**) Back-scattered-electron (BSE) image of an eskolaite (Esk) fragment, containing a small picrochromite (Chr) inclusion, in a polished epoxy mount; the rectangle indicates the location where the TEM foil was cut away permitting the TEM imaging; (**b**) energy-filtered TEM lattice-fringe images of the picrochromite diffraction pattern; also of (**c**) eskolaite. An AEM spectra from (**d**) picrochromite and (**e**) eskolaite. The Ga intensity in the spectra is due to implanted Ga during FIB sample preparation; the Cu intensity is from the copper grid.

inclusions, a Ti-phase and an Mg-Si amorphous inclusion were also found, with locally strong variations of the Si/Mg ratio. This inclusion most probably represents a quench product of the fluid that formerly filled the pores.

DISCUSSION

The eskolaite investigated in this study, with the picrochromite inclusion, is similar to that described from the type locality by Kouvo and Vuorelainen (1958). However, some important compositional differences were observed. The major-element composition, determined by EMP, contains elemental substitutions that effectively lower the Cr_2O_3 end-member abundance down to 86.8 wt%, from the theoretical value of 100%. The most abundant secondary oxide in the Outokumpu eskolaite (Kouvo and Vuorelainen 1958) is V_2O_3 (4.58 wt%), with only 0.55 wt%

Fe_2O_3. In the Yakutian diamond inclusion, the reverse is the case, with only 0.25 wt% V_2O_3 and 5.83 wt% Fe_2O_3.

Eskolaites from both localities are associated with Cr minerals, such as chromite. However, no analytical data are available on Outokumpu chromite associated with eskolaite, whereas the picrochromite inclusion in the diamond eskolaite sample is characterized by exceptional values of X_{Mg} (= 0.912) and Y_{Cr} (= 0.947), even exceeding those in other diamond inclusions from Yakutia (Sobolev et al. 2004). Elevated TiO_2 content in picrochromite (0.98 wt%) is consistent with the TiO_2 content in the associated eskolaite (Table 2). In general, these compositional features are within the range of compositions of chromites associated with diamonds (Sobolev 1977; Meyer 1987; Harris 1992; Taylor et al. 2003; Kirkley et al. 1991). These assemblages occur both as inclusions and as intergrowths with diamond monocrystals,

Table 2. Major- (wt%) and trace-element (ppm) compositions of eskolaite, and included picrochromite, diamond inclusion from the Udachnaya Kimberlite

Udachnaya Sample U-505		
	Eskolaite	Picrochromite
No. of analyses	28	2
SiO_2	<0.03	0.11
TiO_2	3.99 (8)*	0.98
Al_2O_3	2.00 (3)	1.37
Cr_2O_3	86.8 (5)	73.1
Fe_2O_3	5.83 (6)	7.73‡
MnO	<0.03	0.16
MgO	1.11 (5)	16.5
CaO	0.01 (1)	0.06
NiO	0.03 (1)	<0.03
V_2O_3	0.25 (1)	0.05
Total	100.02	100.06

Spots	1	2	3	Formula moles based on 4 O atoms	
Na	13	7.24	8.18	Si	0.004
P	1.45	0.16	0.29	Ti	0.024
Sc	3.12	2.98	3.02	Al	0.053
Ti	46587	41928	42918	Cr	1.894
V	4807	4903	4899	Fe^{3+}	0.025
Mn	243	124	129	Fe^{2+}	0.187
Rb	0.03	0.02	0.02	Mn	0.004
Sr	0.64	0.02	0.03	Mg	0.806
Y	0.02	0.01	0.003	Ca	0.002
Zr	57	56	55.3	Ni	0.000
Nb	31.7	31.1	32.6	Total	2.029
Ba	0.49	0.04	0.08	X_{Mg}‡	0.812
La	0.70	0.01	0.007	Y_{Cr}	0.947
Ce	1.21	0.01	0.007		
Pr	0.11	0.003	0.002		
Nd	0.37	0.038	0.005		
Sm	0.05	bdl†	bdl		
Eu	0.01	bdl	bdl		
Gd	0.03	bdl	bdl		

* Numbers in parentheses are the one-sigma variance in analyses for the least unit cited.
† Below detection limits.
‡ Total iron recalculated as FeO; X_{Mg} = Mg/(Mg + Fe); Y_{Cr} = Cr/(Cr + Al).

penetrating them, and with polycrystalline diamond aggregates (framesites). Thus, the picrochromite is a signature indicative of its U/P-type (ultramafic) diamond environment.

The only other reported occurrence of eskolaite to date is from the Zagadochnaya kimberlite in Yakutia, where it coexists with a set of eclogitic (E-type) Cr-enriched minerals, including kyanite, omphacite, and Ca-rich garnet, in a grospydite assemblage (Sobolev 1977). This eskolaite contains considerably lower Cr_2O_3 (75.5 wt%) and higher Al_2O_3 (15.5 wt%) contents than those from Finland or Udachnaya, and clearly demonstrates even more solid solution toward corundum.

In contrast to the eskolaite from the low-pressure skarn assemblage in Finland, eskolaite from the Zagadochnaya high-pressure grospydite (Sobolev 1977) and the one from our diamond study both contain higher TiO_2 contents of 1.3 and 4.0 wt%, respectively. No TiO_2 was reported for eskolaite from the type locality. This difference in TiO_2 content possibly reflects a positive correlation with pressure. Another difference is the high content of Al_2O_3 (2.0 wt%), which may also be a function of pressure.

At high pressures of 3.0–5.5 GPa, present during the formation of the Yakutian eskolaites (Sobolev 1977; Sobolev et al. 2000), both associated with grospydite and diamond, the structural constitution of eskolaite is mainly a function of regular compression only (Finger and Hazen 1980; Rekhi et al. 2000).

As c/a ratio varies within a narrow interval, the changes of unit-cell metrics are close to isotropic. At 5.68 GPa, the decrease of unit-cell volume is only 2.2% (Finger and Hazen 1980). Such changes may be compensated by the synchronous heating to 1000 °C. Thus, eskolaite crystal chemistry might be used for estimating the conditions of its formation. However, at present, sufficient data does not exist with respect to the effects of cation substitution due to the eskolaite-corundum solid solution.

The presence of the picrochromite inclusion in the eskolaite is indicative of ultramafic, i.e., U/P-type diamond P-T-X environment (Sobolev 1977; Meyer 1987). In addition, some typical minerals expected for such an assemblage include Cr-rich clinopyroxene and forsteritic olivine. The inhomogeneous Si-Mg quench products found in one of the cavities within the picrochromite may represent altered olivine. Clinopyroxenes associated with chromites representing a diopside-jadeite-kosmochlor ($NaCrSi_2O_6$) solid solution have been reported in a series of polycrystalline diamond aggregates (framesites) from the Mir and Jwaneng pipes (Sobolev et al. 1975; Kirkley et al. 1991). Both these pyroxenes and chromites are similar to those included in diamonds (Meyer 1987; Sobolev et al. 2004). Chromites from kimberlite the groundmass of Udachnaya contain considerably higher TiO_2 (0.43–5.0 wt%) and lower Cr_2O_3 within the range of 42.8–45.3 wt% (Sobolev et al. 1989), and thus cannot be considered a source of the studied picrochromite inclusion in eskolaite. That is, this inclusion in the eskolaite must have formed in the diamond P-T environment, adding to the fact that this eskaloaite, even though not exposed at the surface of the diamond, is a true diamond inclusion, not a low-temperature alteration product.

In spite of this first report of eskolaite formed within the diamond stability field, the other end-member of the Al_2O_3-Cr_2O_3 series, namely corundum, has been found as a red-ruby single inclusion in diamond (Meyer 1987; reviewed in Taylor and Anand 2004), as well as a part of multiple inclusions with garnet and omphacite in Venezuela E-type diamond (Sobolev et al. 1998). Rare diamondiferous corundum eclogites are also known (e.g., Sobolev 1977). The rarity of corundum in equilibrium with diamond may be explained by the rare occurrence of Si-under-saturated compositions in mantle diamond-forming environment (e.g., Sobolev et al. 1999; Taylor and Anand 2004).

Nano-sized cavities in the picrochromite inclusion in the eskolaite (Fig. 2f) contain quench products, including Si, Mg, Ca, P, K, and Cl along with carbonates. These may represent relics of the diamond-forming metasomatic fluids, similar to those described in diamonds from South Africa (Izraeli et al. 2001), Canada (Klein-BenDavid et al. 2006, 2007; Tomlinson et al. 2006), and Siberia (Logvinova et al. 2003, 2006; Zedgenizov et al. 2004), as well as in experimental studies on diamond growth (e.g., Pal'yanov et al. 2005, 2007).

Summary

Eskolaite, the Cr-rich end-member of the Al_2O_3-Cr_2O_3 join, has been identified for the first time as an inclusion in an octahedral diamond, as well as partly exposed at its surface. The primary mantle origin of this eskolaite is confirmed by a picrochromite in the eskolaite with a composition typical for chromites only included in diamonds worldwide. Such a discovery represents an
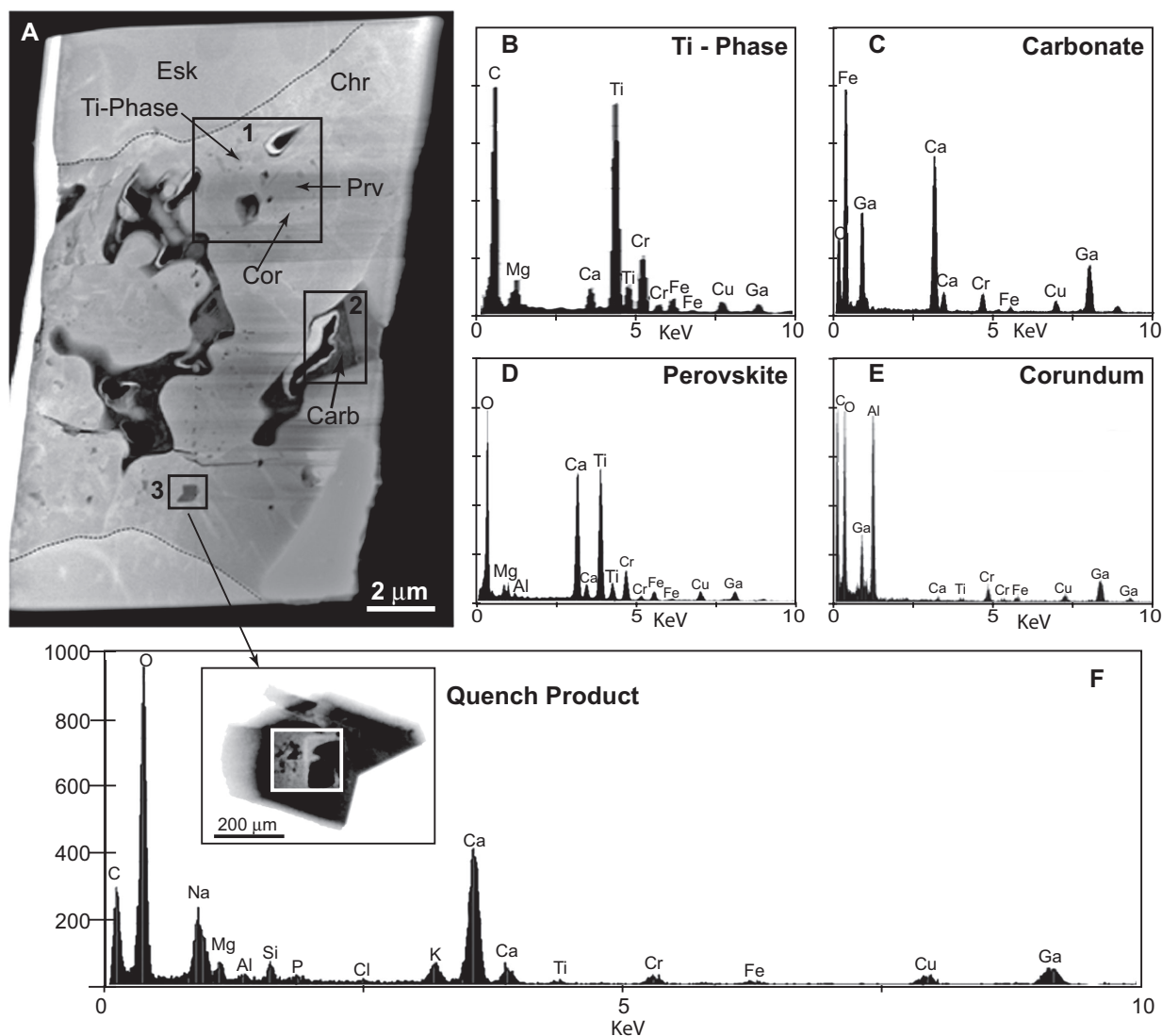
FIGURE 2. Observed mineral phases and quench products within the picrochromite. (**a**) HAADF image of foil 1080 with investigated areas 1, 2, and 3 indicated; AEM spectra: (**b**) Ti-phase, (**c**) carbonate, (**d**) perovskite, (**e**) corundum, and (**f**) fluid quench product. Abbreviations: Esk = eskolaite; Chr = picrochromite; Prv = perovskite; Cor = corundum; Carb = carbonate. Thin solid lines in **a**, on the upper and lower parts of the foil, mark the contacts between eskolaite and picrochromite.

important contribution to a limited list of the identified primary mineral species associated with diamond (Meyer 1987; Harris 1992). The present integrated study of this eskolaite inclusion also resulted in the discovery of a series of nanoinclusions within this picrochromite. Some of these inclusions, in particular perovskite, are considered as primary; others, like carbonate, corundum, an unidentified Ti-phase, and an Si-Mg-rich inhomogeneous inclusion, are considered secondary, possibly being entrapped in the process of evolution of the kimberlite melt (Kamenetsky et al. 2004). Irregular, submicroscopic pockets, containing relict fluids enriched in Ca-K-Cl-P, were identified in picrochromite, thereby demonstrating the significance of such elements in diamond-forming fluids. No indications of any late-secondary alteration were found in the eskolaite. This feature is possibly caused by the unique freshness of the Udachnaya kimberlite, containing no serpentine at all (e.g., Kamenetsky et al. 2004).

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