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A microinclusion of lower-mantle rock and some other lower-mantle inclusions in diamond

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Abstract

A microcrystalline polymineral aggregate was identified as an inclusion in a diamond from the Rio Soriso area, Mato Grosso State, Brazil. It is composed of iron carbides, ferropericlase (with exsolved magnesioferrite) and two orthorhombic, postspinel phases - Mg-Cr-Fe and Ca-Cr oxides, which are new mineral phases. This association was formed during several stages and may be considered as a rock microfragment of the lower mantle. In addition to the carbide-oxide fragment, some other phases were identified as inclusions in that diamond, such as parascandolaite KMgF_3 (that is stable at pressures of up to 50 GPa) in association with orthorhombic MgO, and porous dolomite occurring together with nanoinclusions of calcite, apatite, spinel, Fe-sulfide, and an assemblage of periclase plus wüstite. These minerals belong to the carbonatitic association and, along with syngenetic nanoinclusions of fluid nitrogen, represent the media of diamond formation. The assemblage of periclase and wüstite within the carbonatitic matrix points to the origin of diamond from a carbonatitic environment within the lower mantle under pressure conditions of $\geq 85\text{--}86$ GPa ($\sim 1,900$ km deep).

Keywords: lower mantle, MgCr_2O_4 , CaCr_2O_4 , parascandolaite, iron carbide, Fe_5SiC , wüstite, nitrogen

Introduction

Over the last two decades, a number of the Earth's lower-mantle minerals have been identified as inclusions within diamond (Kaminsky 2012; Harte & Hudson 2013 and references therein). In accordance with both theory (e.g., Kesson and FitzGerald 1991) and experimental studies (e.g., Wood 2000), ferropericlase $(\text{Mg,Fe})\text{O}$, MgSi-perovskite MgSiO_3 and CaSi-perovskite CaSiO_3 were identified as major mineral phases, characteristic of the upper part of the lower mantle. Some other, accessory minerals, such as CaTi-perovskite, stishovite, Mg- and Mn-ilmenites, native Fe and Ni, and iron carbides were found in this association as well. No lower-mantle rock fragments, however, have been found to date.

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Over the past few years we have studied a variety of diamond from the Juina area, Mato Grosso State, Brazil, and in doing so, identified a series of mineral inclusions from the Earth's lower mantle (Kaminsky et al. 2001, 2009, 2013; Wirth et al. 2007, 2009; Kaminsky & Wirth 2011). Some minerals among these might have originated at the core/mantle boundary; such as wüstite in association with ferropericlasite (Wirth et al. 2009; Kaminsky et al. 2009) and native iron in association with various iron carbides, including Fe_7C_3 (Kaminsky & Wirth 2011). We continue to study diamonds from this area. Here, we report a new, polymineral inclusion in diamond, which may be considered as a rock fragment, originated within the Earth's lower mantle. It is composed of iron carbide, ferropericlasite and two orthorhombic, postspinel phases - Mg-Cr-Fe and Ca-Cr oxides, which are new mineral phases. Some other, new mineral inclusions were identified as well. Some other, new mineral inclusions were found in the same diamond, witnessing its lower-mantle origin.

Sample description and analytical techniques

Diamond crystal #8-108 was collected from the Rio Soriso placer deposit in the Juina area, Mato Grosso State, Brazil, from which some other diamonds with lower-mantle inclusions have previously been identified (Harte et al. 1999; Kaminsky et al. 2001, 2009, 2013). This diamond is a rounded, almost intact, rhombic-dodecahedroid weighing 107.8 mg (Fig. 1a). The diamond does not show any cracks visible with optical microscopy; numerous inclusions were observed, however (Fig. 1b). The inclusions have been studied with the aid of transmission electron microscopy (TEM). All mineral phases within the inclusion were identified by a combination of electron diffraction analysis and energy-dispersive X-ray analysis (EDX) spectra.

In order to gain access to the inclusions, the diamond was polished using a commercial Sn-Co-Cu alloy polishing wheel. During the course of polishing, fragments of the inclusions in diamond broke away and the newly formed cavities were infilled with abrasion material from both the polishing wheel and carbon from the diamond. Such areas could be easily identified, where present, by the occurrence of Sn, Co and Cu in the chemical composition of that part of the stone. Twenty-three electron-transparent foils, with typical dimensions of $15\text{ }\mu\text{m} \times 10\text{ }\mu\text{m} \times 0.150\text{ }\mu\text{m}$, were cut out from the polished diamond for transmission electron microscopy (TEM) investigations, applying the focused ion beam technique (FIB). Focused Gallium ions, accelerated to 30 keV, were used to sputter material from the diamond. Because of the excellent thermal conductivity of diamond, no substantial heating ($T \ll 100^\circ\text{C}$) of the sample occurred during the sputtering process. Detailed descriptions of the FIB foil preparation, especially the use of the selected carbon mill technique SMCTM to enhance the sputtering process with diamond, are given elsewhere (Wirth 2004, 2009).

The foils were studied at GFZ Potsdam with a FEI F20-XTwin TEM equipped with a Schottky field emission gun as electron emitter, and operated at 200 keV. The TEM is equipped with a Fischione HAADF detector for Z-contrast imaging, a Gatan TridiemTM imaging filter, and an EDAX X-ray analyzer with ultrathin window. We studied the samples with various TEM techniques, such as bright-field (BF) and dark-field (DF) imaging, high-angle annular dark-field imaging (HAADF), selected area electron diffraction, high-resolution imaging and electron energy-loss spectroscopy (EELS). Electron diffraction patterns were recorded on image plates or calculated from high-resolution images using Fast Fourier Transform (FFT) software packages. Phase identification of the usually nanometer-sized inclusions was made by measuring the lengths of the different vectors in the diffraction patterns and calculating the

respective d_{hkl} -spacing. Additionally, the angles between adjacent vectors were measured in the diffraction patterns. Comparing the observed d_{hkl} – values with the calculated d_{hkl} – values, based on unit cell parameters from literature data, along with the comparison of the observed angles between adjacent planes and the calculated angles, confirmed or disproved the existence of a particular phase. The d_{hkl} -spacing, measured from image plates is precise to within three decimals of a nanometer, whereas d_{hkl} -spacing, calculated from FFT, is precise only within two decimals because the diffraction spots are not as sharp as on image plates. The angles between the vectors can be determined with an accuracy of 0.5° from image plates and with an accuracy of $1-1.5^\circ$ from FFT because of less sharp diffraction spots. Analytical electron microscopy (AEM) was always performed in the scanning transmission mode (STEM), scanning the electron beam within a preselected area to avoid mass loss during the data acquisition. The size of the area was selected according to the grain size. The foil was tilted between 10° and 15° towards the detector. Acquisition time was 60 or 120 seconds to accumulate enough counts to minimize the error of the counting statistics. Quantitative chemical compositions were calculated from the EDX spectra applying the TIATM software package and using the k_{AB} factors from the software. The quantitative results are given in atomic % and summed to 100 %. The approximate uncertainties are: $\pm 3\%$ for concentrations in the range 30–50 at. %, $\pm 6-12\%$ for concentrations between 5-25 %, $\pm 12-25\%$ for concentrations between 1-5 %, and $\pm 25-100\%$ for concentrations below 1 at. %.

Results

General observations

All foils show heterogeneous dislocation density in the diamond matrix. In some foils (e.g. #3601 and #3593), there is a high dislocation density, which includes many bent or curved dislocation lines. These features indicate that the diamond was deformed by dislocation glide followed by dislocation climb, which is a thermally activated process requiring thermal annealing at high temperature (Fig. 1c). Other foils contain only a few, mostly straight dislocations.

Two different kinds of inclusions are visible in diamond #8-108 under optical microscopic examination (Fig. 1b): 'large' inclusions 100-300 nm in diameter, and numerous smaller inclusions in the range of 5–50 nm in size. From optical microscopy alone it is not possible to determine if the 'large inclusions' represent single phases or an agglomeration of much smaller inclusions. By their shape, among the inclusions, there are mineral inclusions of irregular shape, and lamellas, which display sharp, straight interfaces with diamond. Micrometer-sized inclusions of irregular shape (in foils ##3576, 3601, 3609, 3611, 3612, 3620, 3621, 3711, and 3713) have phase boundaries with diamond always composed of straight segments. A few foils (#3617 and #3593) contain only small (10-50 nm) idiomorphic inclusions, filled in with nitrogen (Fig. 1d). Nitrogen was identified with EEL spectroscopy. Similar nitrogen-bearing inclusions were found earlier in other diamonds from the same Rio Soriso area (Kaminsky et al. 2013).

Compositionally, three types of inclusions were distinguished in the studied diamond: composite, polyphase oxide-carbide inclusion (foil #3601); plate-like, lamellar inclusions that are composed of iron carbide and graphite (foils #3607, 3619, and 3620); and porous carbonate inclusions with minor amount of other mineral nanoinclusions also present (foils ##3611, 3709, 3713, and 3721). Data on all inclusions are presented in Table 1.

Inclusions in diamond

The most interesting, ***polyphase inclusion was identified in foil #3601***. Its size is approximately 4 μm (Fig. 2a). The upper part of the inclusion has broken apart during the polishing process, and was infilled by particles of the Sn-Co-Cu alloy from the polishing wheel, crushed diamond fragments, and graphite. Fortunately, the major part of the original inclusion still exists. It is composed of an aggregate of iron carbide, ferropericlasite with exsolved magnesioferrite, orthorhombic Mg-Cr-Fe oxide, orthorhombic Ca-Cr oxide, and graphite (Fig. 2a,b). All mineral grains are closely intergrown and extensively resorbed from the external borders. Iron carbide forms straight interfaces with diamond and has straight or slightly curved boundaries with oxides. Ferropericlasite contains tiny nanocrystals of magnesioferrite (Fig. 2c). The graphite matrix consists of polycrystalline graphite aggregate with a grain size of several tens of nanometres, along with patches of non-crystalline, amorphous carbon.

An elemental map (Fig. 3), using the C- K_{α} , O- K_{α} , Mg- K_{α} , Ca- K_{α} , Cr- K_{α} and Fe- K_{α} X-ray intensities, illustrates the locations of the various mineral phases within the assemblage and their different chemical compositions.

EDX spectra of the four phases constituting the mineral assemblage, illustrating their chemical compositions, are presented in Fig. 4. The precise chemical compositions of the minerals, calculated from the EDX spectra, are presented in Table 2. In addition to major elements, EDX spectra demonstrate the presence of minor admixtures: Mg, Al, Ti, V, and Fe in Ca-Cr oxide; Al and V in Mg-Cr-Fe oxide; Cr and Mn in ferropericlasite.

Plate-like, lamellar inclusions, composed of iron carbide and graphite, were identified in foils ##3607, 3619 and 3620. The lamella, penetrating through the entire foil #3607, is between 70 and 150 nm thick. It comprises nanometer-sized iron carbide grains that are elongate, or irregularly shaped grains. Like in the polyphase inclusion, the iron carbide crystals appear to be corroded, with cavities filled with graphite. Lattice fringe images of graphite demonstrate that it is disordered, occurring along with patches of amorphous carbon. EDX analysis of the carbide revealed only Fe and C.

In foil #3619, an approximately 7.15 μm long and 30-50 nm thick iron carbide lamella is exposed (Fig. 5a). The lamella ends in diamond sharply (Fig. 5b,c). Dark-field imaging demonstrates that the lamella is composed of plate-like nanocrystals approximately 50 x 10 nm in size that are stacked on top of each other (Fig. 5b). These overlapping nanocrystals produce moiré pattern in bright-field and dark-field images (Fig. 5b,c). EDX analyses, as well as EEL spectra, show that the lamella has a Fe-C-N composition with a minor (< 0.5 at. %) admixture of Si.

Foil #3620 hosts an inclusion with only relicts of iron carbide in a graphite/amorphous carbon matrix. The iron carbide is strongly corroded or partially dissolved. Its relicts, from EDX spectra, have a Fe-N-Si-C composition.

Inclusions of porous carbonates with minor nanoinclusions of other minerals were found in foils ##3611, 3709, 3713, and 3721. The major mineral component of these inclusions is dolomite, which forms relatively 'large' (up to several micrometres in size) polycrystalline grains, associated with numerous nanocrystals (Fig. 6). The nanocrystals (grain size of less than 100 nm) are predominantly wüstite (with minor admixture of Mg), periclasite (with minor admixture of Fe), spinel - all of these minerals were confirmed by electron diffraction analyses; minor apatite surrounded by calcite, Fe-sulfide with admixture of Ni (Fe = 47.2 at. %; Ni = 0.9 at. %; S = 51.9 at. %), and rarely silicate with a composition of phlogopite. Dolomite grains contain pores, indicating the presence of a fluid prior to the

FIB sample preparation. A high-resolution elemental map (Fig. 7) shows details of the inclusion with individual nanocrystals.

Wüstite and periclase occur together as an irregular assemblage of nanocrystals. In foil #3709 we observed a single crystal of wüstite (140 nm) with the composition $(\text{Fe}_{0.93}\text{Mg}_{0.07})\text{O}$, completely surrounded by polycrystalline periclase, $(\text{Mg}_{0.93}\text{Fe}_{0.07})\text{O}$, with a crystallite grain size of less than 50 nm (Figs. 6 and 7). Spinel nanocrystals have the general composition: Mg-Fe-Ti-Cr-Al-O, with varying proportions of Fe and Mg. Most grains are strongly enriched in magnesium; some are enriched in iron or titanium. Reliable chemical compositions of individual nanograins cannot be presented because their grain sizes are much smaller than that of the foil thickness (approximately 150 nm), resulting in a mixed analysis from different grains. The spinel structure was confirmed by diffraction data (FFT from high-resolution images).

Among *other inclusions*, mineral grains from foil #3711 are especially interesting (Fig. 8). Among the phases observed in this inclusion are idiomorphic, cubic crystals of a parascandolaite KMgF_3 up to 1 μm in size, intergrown with graphite and a nanocrystalline Al-rich phase, which has a spinel-type structure (hercynite?). Parascandolaite crystals were confirmed in electron diffraction patterns and through chemical analysis. The electron diffraction patterns shows a single crystal cubic pattern with $a_0 = 0.39892\text{ nm}$, which corresponds to the patterns of natural mineral, isotypic to cubic perovskite (Demartin et al. 2014) and synthetic KMgF_3 (Muradyan et al. 1984), both with space group $Pm-3m$. However, all diffraction intensities are smeared out, appearing as if they are slightly rotated around a common zone axis $[0-10]$ (Fig. 8b). The smeared out reflections suggest a mosaic structure in the identified mineral. Such kind of diffraction patterns can be the result of an assembly of many nanocrystals that are slightly tilted or/and rotated against each other. Although fluorperovskite KMgF_3 is an important technological compound used in electro-optical applications, it was discovered in the natural environment only recently as a volcanic sublimate at Vesuvius volcano, Italy (Demartin et al. 2014). According to experimental data, it is stable up to at least 40-50 GPa, keeping the cubic perovskite structure (Vaitheeswaran et al. 2007; Aguado et al. 2008).

In the opposite part of the inclusion (upper right in Fig. 8a), parascandolaite is intergrown with a ‘large’ (2 μm) single crystal of almost pure MgO , which has only minor admixtures of Fe and Ca. The empirical formula of this mineral is $(\text{Mg}_{0.953}\text{Fe}_{0.033}\text{Ca}_{0.013})\text{O}$. Surprisingly, the electron diffraction patterns of that crystal could not be indexed as a cubic, rock-salt periclase structure, or as a hexagonal wurtzite structure (Fan et al. 2008) (Table 3). It has unit cell parameters $a_0 = 2.14078\text{ nm}$, $b_0 = 0.61099\text{ nm}$, $c_0 = 0.42597\text{ nm}$ (calculated from diffraction pattern), which could only be indexed using the orthorhombic crystal structure, published by Zwijnenburg and Bromley (2011) with the unit cell parameters $a_0 = 2.15903\text{ nm}$, $b_0 = 0.61608\text{ nm}$, $c_0 = 0.42143\text{ nm}$. A comparison of the measured d -spacing and the angles between adjacent planes is presented in Table 3. The agreement between the observed data and the data calculated from the structure published by Zwijnenburg and Bromley (2011) is compelling. This contradicts experimental data, according to which periclase maintains the rock-salt cubic structure up to at least 227 GPa (e.g., Duffy et al. 1995). However, theoretical calculations demonstrate that other than cubic MgO , low-energy polymorphs (including orthorhombic) may be energetically more preferable (Zwijnenburg and Bromley 2011 and references therein).

Parascandolaite, associated with orthorhombic MgO , shows a polycrystalline state with nanometer-sized individual crystallites. In the electron diffraction pattern, nanometer-sized parascandolaite is represented as weak intensities forming Debye-Scherrer rings in the single crystal patterns of orthorhombic MgO .

Major rock-forming minerals identified from the polyphase inclusion

All mineral phases in this inclusion (foil #3601) were identified by electron diffraction analysis and based upon their chemical composition. EDX spectra of the phases are presented in Fig. 4, and chemical compositions of the oxide phases in Table 2.

Ferropericlasite is one of the major minerals in the lower mantle (e.g. Kaminsky 2012 and references therein). In foil #3601, it is intergrown with two orthorhombic oxides, Mg-Cr-Fe-oxide and Ca-Cr-oxide (Fig. 2a,b). Its chemical composition is (at. %): Mg = 63.08; Fe = 31.10; Mn = 5.52; Cr = 0.30, with $mg = Mg/(Fe+Mg) = 0.670$, which is quite common for ferropericlasite from the Rio Soriso area in Brazil. Only the Mn content in the studied mineral is unusually high; the usual MnO content in other known lower-mantle ferropericlasite rarely exceeds 1 wt. %.

The characteristic feature of the studied ferropericlasite is the presence of **magnesioferrite** crystals, 10-50 nm in size, which form idiomorphic (cubic and octahedral) grains along dislocation lines (Fig. 2d). The oriented precipitation of magnesioferrite from ferropericlasite is documented in the electron diffraction patterns in Fig. 9. The unit cell parameter of magnesioferrite ($a_0 = 0.858$ nm) is approximately twice that of ferropericlasite ($a_0 = 0.422$ nm). The electron diffraction pattern in Fig. 9 illustrates rows of very intense spots representing the ferropericlasite matrix and rows of much weaker spots always half distance in between, which are attributed to magnesioferrite. There is a precise orientation relationship between both phases: $(022)_{M.F.} // (022)_{F.P.}$; $(11-1)_{M.F.} // (11-1)_{F.P.}$; the zone axis for both phases is $[2-11]$. The much weaker intensity of magnesioferrite diffraction spots evidences that the volume of magnesioferrite exsolved from ferropericlasite is significantly smaller than that of the ferropericlasite host.

Magnesioferrite exsolution along ancient dislocation lines has been recently reported and described in detail from a ferropericlasite inclusion in another deep-seated diamond from Juina (Wirth et al. 2014).

Mg-Cr-Fe oxide with orthorhombic structure has the chemical composition (in at. %): Mg = 30.09; Cr = 45.78; Fe = 12.92; Mn = 6.08; V = 3.55; Al = 1.58, which makes its empirical formula as the following: $(Mg_{0.90}Mn_{0.18})_{1.08}(Cr_{1.37}Fe^{3+}_{0.39}V_{0.11}Al_{0.05})_{1.92}O_4$. Its mg index (0.700) is close to ferropericlasite. It is a chemical analogue to magnesian chrome spinel. Diffraction patterns from two different zone-axis orientations, both from this particular grain were acquired at (Fig. 10a,b). The observed d -spacing (d_{hkl}) and the angles between adjacent planes were compared with those calculated from orthorhombic CT phase (Chen et al. 2003b), orthorhombic $CaCr_2O_4$ phase (Hörkner and Müller-Buschbaum 1976), and cubic chromite (Chen et al. 2003b) (Table 4). The observed diffraction patterns cannot be indexed as cubic chromite. The studied Mg-Cr-Fe oxide has an orthorhombic structure. Its diffraction patterns can be indexed based either on the structure data given by Hörkner and Müller-Buschbaum (1976) (labeled H in Fig. 10a) or based on the CT polymorph structure (Chen et al. 2003b) (labeled CT in Fig. 10b); they fit better to the CT phase $FeCr_2O_4$, obtained by Chen et al. (2003b) in experiments under pressure conditions above 20 GPa.

In the natural environment, a similar mineral with an experimental formula $(Fe_{0.87}Mg_{0.13}Mn_{0.01})_{1.01}(Cr_{1.62}Al_{0.25}Ti_{0.08}V_{0.02})_{1.97}O_4$ was identified in the shock vein of the Suizhou meteorite, China and termed 'xieite' (Chen et al. 2008). Chemically xieite is analogous to chromite and has an ideal formula $FeCr_2O_4$. It has an orthorhombic structure and lattice parameters of: $a_0 = 0.9462$ nm; $b_0 = 0.9562$ nm; $c_0 = 0.2916$ nm, which are similar to the parameters of the synthetic orthorhombic CT phase ($a_0 = 0.9467$ nm; $b_0 = 0.9550$ nm; $c_0 = 0.2905$ nm). Minor differences of the calculated parameters

for the investigated phase ($a_0 = 1.0654$ nm; $b_0 = 0.9401$ nm; $c_0 = 0.2907$ nm) are obviously caused by its different chemical composition, the isomorphic replacement of Fe^{2+} with Mg.

Ca-Cr oxide with an orthorhombic structure is another new orthorhombic phase, found in the studied sample. Its chemical composition is (in at. %): Ca = 35.72; Cr = 57.02; Fe = 1.93; Mg = 0.79; Mn = 0.69; Al = 0.80; Ti = 1.09; V = 1.96; which results in the following empirical formula:

$(\text{Ca}_{1.07}\text{Mg}_{0.02}\text{Mn}_{0.02})_{1.11}(\text{Cr}_{1.71}\text{Fe}^{3+}_{0.06}\text{V}_{0.06}\text{Ti}_{0.03}\text{Al}_{0.03})_{1.89}\text{O}_4$, with $mg = 0.290$.

Diffraction data based on the FFT from high-resolution images together with electron diffraction patterns are presented in Table 5. The cubic crystal structure for that phase can be excluded based on the electron diffraction patterns. The d -spacing along with the angles between adjacent planes of the Ca-Cr oxide phase match orthorhombic postspinel structures, such as CaFe_2O_4 , CaTi_2O_4 and CaCr_2O_4 (Hörkner and Müller-Buschbaum 1976; Chen et al. 2003a,b; 2008). The best fit (based on the angles between the adjacent planes) is with a synthetic pure CaCr_2O_4 postspinel phase (Hörkner and Müller-Buschbaum 1976). Minor angular differences might be due to the admixtures of Fe, V, Ti, Al, Mg and Mn in the studied phase. Therefore, the observed Ca-Cr oxide is another ***postspinel phase with the ideal formula, CaCr_2O_4*** . This is the first find of such a compound in the natural environment.

Iron carbide, in foil #3601, forms an intergrowth with all three oxides (ferropericlaase and orthorhombic Mg-Cr-Fe Ca-Cr oxides). From the outer edge of the inclusion, it is resorped and infilled with graphite aggregate (Fig. 2b). Lamellar, polycrystalline iron carbide inclusions in foils #3607 and #3619 are also corroded and partly replaced by graphite (Fig. 5). Quantitative EEL spectroscopy of the Fe-carbide lamellae is limited because we cannot fully exclude a contribution to the carbon C-K edge from the host diamond. However, even in this case, most analyses show the values of the Fe/(C+N) atomic ratio from 1.5 to 2, implying the composition close to Fe_2C , Fe_7C_3 (chalypite), or Fe_9C_4 (yarlongite). In one analysis, Fe/(C+N) ratio was 2.52 suggesting the presence of cohenite (Fe_3C) as well. All grains have very high nitrogen impurity, from 12.8 to 18.42 at. % (Fig. 11). N/(C+N) atomic ratio varies from 0.37 to 0.60, showing that in some cases nitrogen predominates over carbon, and the mineral should be called *nitrocarbide* or even *carbonitride*. In addition to nitrogen, minor admixtures of silicon were recorded in some EDX spectra.

Diffraction patterns of iron carbide grains (Fig. 12, Table 6) confirm the presence of three mineral species, nitrogen-containing analogues of chalypite, cohenite, and yarlongite. The first one, *chalypite* is Fe_2C or Fe_7C_3 (Kaminsky and Wirth 2011). The studied sample has d -spacings, which are similar to both Fe_2C (chalypite) and Fe_3C (cohenite). The lattice parameters fit both carbide varieties, and angles between adjacent planes are closer to the values for Fe_3C (Table 6).

Diffraction patterns for the iron carbide grain from foil #3619 (Fig. 12b) match parameters of the synthetic $\text{Fe}_3(\text{N}_{0.8}\text{C}_{0.2})_{1.395}$, a trigonal iron carbonitride (Leinenweber et al. 2001). This compound is similar to Cr-Fe-Ni carbide, *yarlongite*, discovered in chromitites from the Luobasha ophiolite in Tibet (Shi et al. 2009), and which has a general formula of $(\text{Cr,Fe,Ni})_9\text{C}_4$. Our mineral, containing 17.5 at. % of N in its cation part ($\text{N}/(\text{C}+\text{N}) = 0.47$), by its composition is closer to synthesized $\text{Fe}_3(\text{N}_{0.80}\text{C}_{0.20})_{1.38}$ (Leinenweber et al. 2001).

In foil #3620, the studied grain does not show a structural similarity to carbides, but instead to orthorhombic phases. It is orthorhombic, with lattice parameters ($a_0 = 1.1094$ nm; $b_0 = 0.7656$ nm; $c_0 = 0.7423$) close those of silicocarbide, Fe_5SiC , which is well known among nanocomposite materials (Lomaeva et al. 2005), but never before has it been identified in the natural environment (Table 7).

Discussion and Conclusions

Arguments for a lower mantle origin of some of the inclusions in this diamond.

Minerals of the spinel group, AB_2O_4 , are widely known in upper mantle rocks, where they occur as accessory minerals, and exhibit a wide compositional range in their kimberlites, lamproites and alkali basalt hosts (e.g. Barnes and Roeder 2001). Reid and Ringwood (1969, 1970) proposed orthorhombic $CaFe_2O_4$ -type (CF) and $CaTi_2O_4$ -type (CT) structures, which are denser than spinel, as top candidates for postspinel phase transitions in the Earth's mantle. The CF and CT structures contain dodecahedral and octahedral sites; the difference between the two structures only lies in slight modifications of the polyhedral linkage. Experimental investigations demonstrated, that: (a) the $CaAl_2O_4$ and $MgAl_2O_4$ structures transform to a CF structure at pressures of above 26.5 GPa; and (b) the $MgAl_2O_4$ structure transforms into a CT structure at pressures in excess of 40 GPa (Chen et al. 2003a and references therein). Until recently, the only natural orthorhombic postspinel polymorph (CF) of chromite, with an ideal formula of $FeCr_2O_4$, was discovered in shock veins of the Suizhou meteorite and termed xieite (Chen et al. 2003b, 2008). In addition to the Cr, Al, Mg, and Fe substitution in natural chromite, the CF and CT phases are likely to incorporate Ca, Ti, Fe, Na, Si (as in $CaFe_2O_4$, $CaTi_2O_4$ and $NaAlSiO_4$), and possibly other divalent and trivalent transition elements and rare earth elements, and thus can have a major effect on element partitioning of the deep Earth geochemistry (Chen et al. 2003a,b).

In our sample we found two postspinel mineral phases with orthorhombic-type structures. One has an experimental formula $(Mg_{0.90}Mn_{0.18})_{1.08}(Cr_{1.37}Fe^{3+}_{0.39}V_{0.11}Al_{0.05})_{1.92}O_4$, isomorphic to magnesian chrome spinel from kimberlites (e.g. Barnes and Roeder 2001); it is similar to xieite, with Mg instead of divalent Fe in its composition. The other mineral has an empirical formula of $(Ca_{1.07}Mg_{0.02}Mn_{0.02})_{1.11}(Cr_{1.71}Fe^{3+}_{0.06}V_{0.06}Ti_{0.03}Al_{0.03})_{1.89}O_4$. Ca-rich, cubic-structured spinels are well known as magnetic insulators, but as orthorhombic compounds are not known in nature to date. These two newly identified postspinel oxides are new lower-mantle minerals. The existence of these phases suggests the following pressure range relating to their formation: chromite CT (> 20 GPa) equivalent to the upper part of the lower mantle (approximately 680 km).

The occurrence of a parascandolaite $KMgF_3$ further suggests extreme pressure conditions, such that this mineral may be stable at pressures of up to 50 GPa (Aguado et al. 2008). However, the stability range is not yet known and might even exceed 50 GPa.

In foil #3709 we observed a single crystal of wüstite (140 nm) with composition $Mg_{0.07}Fe_{0.93}O$ completely encapsulated by polycrystalline periclase ($Mg_{0.93}Fe_{0.07}O$). The dissociation of ferropericlase into almost pure wüstite ($Fe_{0.985}Mg_{0.001}O$) and an Mg-rich phase ($Fe_{0.211}Mg_{0.789}O$) at 86 GPa and 1000 K was reported from a diamond anvil experiment (Dubrovinsky et al. 2000). Pure wüstite holds rock salt structure (B1) until 200 GPa and 3,200 K (Ozawa et al. 2010). Our observation would support the idea of dissociation of ferropericlase under very high pressure conditions. As such, this provides a third high-pressure marker for the inclusions within diamond: 86 GPa ($\geq 1,900$ km).

It should be noted that not only these oxides, but other minerals, comprising the inclusion suite in the same diamond, have orthorhombic structures. Iron silicocarbide, Fe_5SiC in foil #3620 is orthorhombic as well (see Table 5). Some grains of almost pure MgO, intergrown with parascandolaite in foil #3711, also have an orthorhombic-type structure, according to electron diffraction pattern data (Table 3). Low-energy orthorhombic polymorphs of MgO, although of much lower density than those with a rock-salt

cubic structure, are lower in enthalpy and may be energetically preferable (Zwijnenburg and Bromley 2011). Such polymorphs may exist not only for MgO, but for other binary compounds.

In summary, the observed inclusions in diamond suggest an origin from within the lower mantle or even at the base of the mantle.

Rock fragment from the lower-mantle?

Several intergrowths of lower-mantle mineral phases have been previously identified as inclusions in diamond (Kaminsky 2012 and references therein). However, the inclusion in foil #3601, that comprises iron carbide with oxide phases, may be considered as a fragment of a lower-mantle rock that unveils at least three different stages in its formation.

The first stage is the formation of the mineral assemblage iron carbide + oxides with an orthorhombic structure (postspinel phases) in the lower mantle. All mineral grains are closely intergrown, demonstrating their single-stage origin. A tiny piece of this parent rock was trapped by upwelling mantle material in a hot spot or plume. In the second stage, while still in the lower mantle the upwelling material encountered a carbonatitic melt, whereby diamond starts to nucleate and grow. One of these diamonds overgrew the lower mantle microxenolith, together with some remaining fluid or melt (carbonatitic melt), that facilitated the continued growth of diamond. A third stage is the continued ascent of the encapsulating diamond, until pressure and temperature conditions reached those in which graphite was stable. Here, the fluid started reacting with iron carbide leading to dissolution of the latter, as evidenced in the observed present-day corrosion microstructure. But what happened to the remaining iron from the dissolved iron carbide? In this context it is important to note that a FIB foil represents only a small volume of the total inclusion. It might well be that Fe precipitated in another part of the inclusion as native iron. In support of this, we note that within another Juina area diamond inclusion, where partially resorbed iron carbide has been observed, we reported the presence of iron carbide and graphite in association with native iron (Kaminsky & Wirth 2011).

These facts demonstrate a prolonged history in the formation of the mineral assemblage, observed in foil #3601. This inclusion may be considered as a microfragment of rock, formed under lower-mantle conditions. Moreover, it demonstrates, that the composition of the lower mantle is not limited by three major minerals (ferropericlase, MgSi-perovskite and CaSi-perovskite), but may in fact be more variable, including other phases, such as a variety of postspinel phases having an orthorhombic crystal structure.

Syngenetic nitrogen in diamond

Of particular interest is the presence, in the same diamond, of a carbonatitic inclusion (foil #3709) and syngenetic nitrogen (foils ##3617 and 3593), that are similar to earlier found carbonatitic and nitrogen lower-mantle inclusions in other diamonds from this area (Kaminsky et al. 2009, 2013) (Fig. 1d). The analogues to octahedral inclusions with nitrogen, termed ‘voidites’, have previously been identified within diamond, though were considered as defects, formed as a result of decomposition of platelets or as a final stage of nitrogen aggregation in diamond (e.g. Barry et al. 1987; Kiflawi and Bruley 2000, and references therein). However, our inclusions are different for a number of reasons: (1) They are much larger (10-50 nm, sometimes up to 100 nm) than voidites (usually 7-10 nm). (2) Unlike voidites, they do not form clusters. (3) The inclusions do not associate with platelets, dislocations or phase boundaries, like most voidites. (4) They do not have moiré patterns, caused by presence of crystalline phase within

voidites. (5) They do not show strain induced diffraction contrast around them in the diamond matrix, which is common for voidites. The nitrogen inclusions reported upon earlier by Kaminsky et al. (2013), and in the current study, are not defects but represent monophase fluid inclusions. Their fluid character was determined based on rapidly changing mass absorption contrasts when focusing the electron beam on an inclusion. Density fluctuations in the fluid caused by the electron beam are responsible for the contrast fluctuations. By their morphology, orientation in host diamond, and relationship to the host diamond, where these are without any traces of stress tension, the studied nitrogen inclusions are syngenetic to the formation of diamond and represent the high concentration of nitrogen in diamond-forming media within the lower mantle. The carbonatitic association and nitrogen represent the media of the diamond crystallization, while the polymineral inclusion is a microxenolith of the mantle rock. We cannot exclude the presence of NH_3 in the identified fluid inclusions, and this will be subject to future investigations.

Carbon, nitrogen and other light elements in the core/mantle boundary

As with our previous works (Kaminsky et al. 2009, 2013; Kaminsky and Wirth 2011), the current study demonstrated the presence of carbon-containing minerals, such as carbides and carbonates among inclusions in diamond. The studied carbides contain a significant proportion of nitrogen, from 12.8 to 18.42 at. %, with $\text{N}/(\text{C}+\text{N})$ ratio varying from 0.37 to 0.60. These minerals, in fact, are not carbides but nitrocarbides and carbonitrides. Nitrogen forms as well fluid inclusions in diamond, as has been established previously (Kaminsky et al. 2013); it is also found in this study (Fig. 1d). These facts suggest a great importance of carbon and nitrogen in the lower mantle.

It is assumed, that approximately 5-10 % of the core should be composed of elements lighter than Fe and Ni (e.g. Stixrude et al. 1997; McDonough 2003). The best candidates for such elements, based on their cosmic abundances, are C, N, O, H, S, and Si. The abundance of carbon in the Earth's core, calculated by different methods, is suggested to be within the range of 0.1 to 4 wt.% (e.g. Zhang and Yin 2012 and references therein). Based on mass balance calculations and experiments (Dasgupta et al. 2013), carbon took part in the core-forming processes, and its content in the early Earth's core was approximately 0.20-0.25 wt. %. Studies of the carbon behavior in the Deep Earth suggested a subsequent process of carbon outgassing from the core, is needed to produce the current estimates of mantle carbon (e.g. Dasgupta et al. 2013). In doing so, this process supports the presence of a significant amount of carbon in the lower mantle.

Our results demonstrate that in addition to the presence of carbon, nitrogen has a key role to play in the lower mantle. The behaviour of nitrogen in the inner parts of the Earth remains enigmatic. There is a 'missing nitrogen' problem for the mantle because it is believed that its concentration in the Earth is depleted relative to the outer planets (Bebout et al. 2013). Nitrogen is considered as a trace element in the major silicate reservoirs (Busigny and Bebout 2013), even as "a useless element in mantle geochemistry" (Cartigny and Marty 2013, p. 359) because of the extensive nitrogen outgassing during the Earth's early history (e.g. Goldblatt et al. 2009). The existing estimates recognize two major reservoirs of nitrogen in the Earth: mantle (mainly lower mantle) with 56.7-61.4 % and atmosphere with 27.0-30.1 % of the total Earth's nitrogen balance, excluding the core and the D" layer from this total (Goldblatt et al. 2009; Palya et al. 2011). As a result, in the estimation of the bulk Earth element inventory, nitrogen is estimated at one order of magnitude less than for the other volatile elements (when normalized to a chondritic composition), with the value of bulk Earth/carbonaceous chondrite ratio equal to 0.11 % (e.g. Marty 2012). On the other hand, high concentrations of nitrogen in taenite from some iron meteorites (Sugiura

1998) provide a potential base in considering the Earth's core as a major reservoir to nitrogen, in which its abundance approached ~0.5 wt.%, and the amount of nitrogen might be sequestered at 2.5×10^4 times that present in the atmosphere (Adler and Williams 2005).

Geochemical estimates of the abundances of nitrogen in the mantle vary over two orders of magnitude, from 0.26 to 36 ppm (Cartigny and Marty 2013 and references therein). The variations of the nitrogen estimate in the core are even greater, within 3-75 wt. ppm (McDonough 2003; Zhang and Yin 2012). However, the existing suggestions are speculative because of the lack of direct observations and experimental data.

Our observations imply that nitrogen may play a greater role in the Earth's core and lower mantle. The earlier found carbides, attributed to the D" layer have 7.3-9.1 at. % N and were suggested to be nitrocarbides (Kaminsky and Wirth 2011). In this study, we observed an even greater concentration of nitrogen in iron nitrocarbides, from 12.8 to 18.42 at. % N. In some grains nitrogen prevails over carbon, and these mineral can be termed iron nitrocarbide or carbonitride.

In addition to nitrocarbides-carbonitrides, nitrogen is concentrated within the diamond lattice, where it comprises the major structural impurity, in the amounts from 20 to 2000 at.ppm (e.g. Kaminsky and Khachatryan 2001). It forms, as well, syngenetic fluid inclusions in diamond (see Fig. 1d; Kaminsky et al. 2013). One may suggest that nitrogen exists in the mantle and the core in higher abundances than previous estimates.

McDonough (2003) suggests the N metal core/silicate mantle enrichment at ~40. This suggestion has a confirmation from experiments at pressure conditions in a range from 1.5 GPa to 18 GPa, which demonstrated the partition coefficient of N between metal and silicate, within this pressure range, of up to 10-30 and that this increases with pressure (Bouhifd et al. 2010; Kadik et al. 2011, 2013; Roskosz et al. 2013). In this case, the 'missing nitrogen' can be concentrated in the Earth's core, where it may be dissolved in the metal phase behaving as a siderophile element, which then forms trivalent N^{3-} groups during crystallization in carbides, nitrides and intermediate compounds. A possible concentrator of nitrogen in the core, based upon the experimental studies of the Fe-N system, is iron nitride Fe_7N_3 , which is stable at pressure conditions of greater than 50.8 GPa (in contrast to another iron nitride, roaldite - Fe_4N) (Adler and Williams 2005). Hexagonal closepacked iron nitrides would be more stable than cubic closepacked roaldite - Fe_4N under pressure regimes of the deep Earth. In addition, ϵ - Fe_7N_3 is more anisotropic than ϵ -Fe: a axis of ϵ - Fe_7N_3 is more compressible than the c axis, with the difference at approximately 6.4 % (Adler and Williams 2005), while pure ϵ -Fe have only 3.5 % difference between a axis and c axis (Stixrude and Cohen 1995). This allows for the consideration of Fe_7N_3 as a better material to satisfy the observed anisotropy in the inner core (Morelli et al. 1986), with substantially less texturing than inferred for a pure iron assemblage. Our observations indicate that neither pure iron carbide Fe_7C_3 nor pure iron nitride Fe_7N_3 , but nitrocarbide-carbonitride $Fe_7(C,N)_3$ should be considered as the most probable concentrator of nitrogen and carbon in the deep Earth.

Nitrogen can occur in the mantle as well if segregations of metallic iron are also present (Frost and McCammon 2008 and references therein). Accepting the Dasgupta et al. (2013) model the involving H_2O , from deeply subducted slabs taken down to the D" layer that may initiate carbon outgassing, the suggested outgassing process in the lower mantle, starting from the D" layer, may have the following form:

Quantitative estimates of nitrogen abundances both within the core and the mantle seem too speculative and premature at this time. Further direct observations of N-containing phases from the deep

Earth are needed, as are experimental data on the solubility of nitrogen in Fe-Ni alloys under core conditions, and their relation to N partitioning between such alloys and oxide melts, under core-mantle conditions.

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Tables

Table 1. List of mineral inclusions in diamond #8-108 from Rio Soriso, Juina area, Brazil.

Table 2. Chemical compositions of oxides in a polyphase mineral inclusion from foil #3601 (at. %).

Table 3. Structural characteristics of the MgO inclusion.

Table 4. Structural characteristics of the Mg-Cr-Fe oxide.

Table 5. Structural characteristics of the Ca-Cr oxide.

Table 6. Structural characteristics of the iron carbide

Table 7. Structural characteristics of the N- and Si-containing carbides

Captions to figures

Fig. 1. Diamond #8-108. a - General view. b – Polished surface of the diamond with inclusions. Arrows indicate four out of twenty-three FIB cutting sites. Foil #3601 with a rock microxenolith was cut from one of the small inclusions within the circled area. c - Bright field TEM image of the host diamond. Numerous dislocations and platelets are observed. Foil #3601. d – A group of syngenetic fluid inclusions of nitrogen in diamond. Bright field TEM image. Foil 3593.

Fig. 2. Polyphase mineral inclusion in diamond #8-108, foil #3601. a – General view. Scale bar is 1 μm . b – Assemblage of major mineral phases in the inclusion. Scale bar 800 nm. c – Magnesioferrite grains, developed along ancient dislocations. Dark field TEM image. Scale bar 50 nm. d – Magnesioferrite crystals in ferropericlase.

Fig. 3. Elemental map of the polyphase inclusion in foil #36018.

Fig. 4. EDX spectra of minerals from inclusion #8-108, foil #3601.

Fig. 5. Lamella of iron carbide in foil #3619. a – General view. Bright field TEM image. Scale bar 50 nm. b – Detail: end of the lamella. Dark field TEM image. Scale bar 20 nm. c – High resolution bright field image. Scale bar 5 nm.

Fig. 6. Porous carbonatitic inclusion in diamond #8-108, foil #3709. Square indicates the area of the elemental map (Fig. 7). Polycrystalline dolomite contains nanoinclusions of sulfide, apatite, calcite, and wüstite, surrounded by periclase.

Fig. 7. Elemental map of porous carbonatitic inclusion from foil #3709.

Fig. 8. Mineral inclusion in foil #3711. a – General view. Cubic crystals of parascandolaite KMgF_3 , intergrown with hercynite(?) and graphite (left), and with orthorhombic MgO (right). b - Indexed electron-diffraction patterns (FFT) of parascandolaite, obtained from HREM image.

Fig. 9. Indexed electron-diffraction patterns (FFT) from HREM images of ferropericlase (F.P.) with the exsolved magnesioferrite (M.F.). Foil #3601.

Fig. 10. Indexed diffraction patterns for the Mg-Cr-Fe oxide. A - Diffraction pattern 3. B Diffraction pattern 4. (See data in Table 4). Indices H and CT correspond to structural data for orthorhombic CaCr_2O_4 phase (Hörkner and Müller-Buschbaum, 1976) and an orthorhombic CT structure (Chen et al., 2003b) respectively.

Fig. 11. Deconvoluted EEL spectrum of iron nitrocarbide from foil #3619. C and N intensities are equal.

Fig. 12. Indexed electron-diffraction patterns (FFT) from HREM images of iron carbides. a- Fe_2C or Fe_3C . Foil #3601. The weak and diffuse additional spots in between are due to graphite or disordered graphite that replaces the Fe_2C grain. However, the aperture that limits the area of electron diffraction was not small enough to show only Fe_2C . b – $\text{Fe}_9(\text{C,N})_4$ in foil #3619. In addition to diffuse spots from carbide, two sharp spots are from the diamond matrix, which are 111 reflections with a calculated d -spacing of 0.2059 nm and a measured d -spacing of 0.206 nm. This provides an additional, internal standard for our measurements.

Foil #	Microinclusions	Nanoinclusions	Size, nm	Note
Microxenolith:				
3601	Nitrocohenite Fe ₃ (C,N)	Magnesioferrite MgFe ₂ O ₄	10-50	May be nitrochalypite Fe ₇ (C,N) ₃ or Fe ₂ (C,N)
	Ferropericlase (Mg,Fe)O			New mineral
	Orthorhombic MgCr ₂ O ₄			New mineral
	Orthorhombic CaCr ₂ O ₄			
	Graphite			
Lamellar inclusion:				
3619	Nitroyarlongite Fe ₉ (C,N) ₄		10 × 50	Polycrystalline
	Graphite			
3620	Iron carbide Fe-C			Polycrystalline
	Orthorhombic Fe ₅ SiC			New mineral
	Graphite			
Porous carbonatitic inclusion				
3709		Wüstite FeO (core)	70-140	Single spherical inclusion
	Dolomite CaMg(CO ₃) ₂	Periclase MgO (rim)	<100	
		Phlogopite?		
	Calcite CaCO ₃	Apatite		
	Spinel (Mg,Fe)(Ti,Cr,Al) ₂ O ₄			
	Fe-sulfide			
	Pores			
Fluoride-oxide inclusion:				
3711	Parascandolaite KMgF ₃			New mineral
	Hercynite? FeAl ₂ O ₄			
	Orthorhombic MgO			
	Graphite			
Liquid nitrogen inclusions:				
3593		Liquid N	10-50	
3617		Liquid N	10-50	
3773		Liquid N	10-50	

Elements	Ferropericlas	Orthorhombic Mg-Cr-Fe oxide	Orthorhombic Ca-Cr oxide
Mg	63.08	30.09	0.79
Al	-	1.58	0.80
Ca	-	-	35.72
Ti	-	-	1.09
V	-	3.55	1.96
Cr	0.30	45.78	57.02
Mn	5.52	6.08	0.69
Fe	31.10	12.92	1.93
Total	100,00	100,00	100.00
$mg =$ $Mg/(Fe+Mg)$	0.670	0.700	0.290

MgO inclusion foil #3711 This work, observed data	MgO Orthorhombic structure (Zwijnenburg and Bromley, 2011)	Synthetic periclase MgO Cubic structure (Hazen, 1976)	MgO Hexagonal wurtzite structure (Fan et al., 2008)
<i>Lattice parameters, nm</i>			
a₀ = 2.14078	a₀ = 2.15903	a ₀ = 0.42110	a ₀ = 0.32786
b₀ = 0.61099	b₀ = 0.61608		
c₀ = 0.42597	c₀ = 0.42143		c ₀ = 0.48736
<i>d-spacings d_{hkl}, nm</i>			
0.34945	0.34784 (011)		
0.27044	0.27088 (511)		0.28394 (01-10)
0.24871	0.25077 (520)	0.24351 (111)	0.24534 (10-11)
0.1907	0.18937 (502)	0.18863 (210)	0.18492 (01-12)
<i>Angles between planes</i>			
31.96°	(502)/(511)	31.49°	
42.6°	(502)/(0-11)	42.12°	
62.1°	(-5-20)/(0-11)	62.04°	
43.2°	(-5-20)/(-5-1-1)	43.76°	

Note: The indicative parameters are shown in bold.

Natural Mg-Cr-Fe oxide, foil #3601 This work, observed data	Synthetic FeCr ₂ O ₄ (CT polymorph) Orthorhombic structure SG: <i>Cmcm</i> (Chen et al., 2003b)	Synthetic β -CaCr ₂ O ₄ Orthorhombic structure SG: <i>Pbnm</i> (Hörkner and Müller- Buschbaum, 1976)	Natural FeCr ₂ O ₄ (chromite) Cubic structure (Chen et al., 2003b)
<i>Lattice parameters, nm</i>			
a₀ = 1.0654 ± 0.0123	a₀ = 0.9467	a₀ = 1.0639	
b₀ = 0.9401 ± 0.0187	b₀ = 0.9550	b₀ = 0.9094	
c₀ = 0.2907 ± 0.0004	c₀ = 0.2905	c₀ = 0.286	
<i>d-spacings d_{hkl}, nm</i>			
0.3280	0.33617 (220)	0.3304 (310)	
0.2948	0.29963 (310)	0.29153 (130)	0.2947 (022)
	0.29050 (001)	0.29600 (001)'	
0.250	0.24818 (021)	0.24159 (121)	0.2514 (131)
		0.24879 (211)	
0.2456	0.24759 (201)	0.24807 (021)	0.2407 (222)
	0.24007 (121)		
	0.23967 (211)		
0.2193	0.2198 (221)	0.22047 (311)	0.2228 (213)
	0.21373 (301)		
0.181	0.18105 (141)	0.18183 (331)	0.1819 (412)
		0.18188 (050)	
		0.18141 (421)	
0.160	0.1559 (051)	0.15496 (051)	0.1604 (511)
		0.16072 (341)	
	0.15897 (431)		
	0.15862 (501)		
0.1599	0.15959 (051)		
0.1595	0.15924 (341)		
<i>Angles between planes</i>			
Diffraction pattern 3 (Fig. 10a)	Calculated	Calculated	Calculated
35.4°	(431)/(310) 37.40°	(341)/(130) 36.48°	(151)/(022) 35.26°
29.9°	(431)/(121) 29.12°	(341)(211) 30.49°	(151)/(13-1) 29.50°
49.9°	(121)/(-211) 47.19°	(211)/(1-21) 49.70°	
30.0°	(-211)/(-501) 28.99°	(1-21)/(0-51) 28.36°	
35.9°	(-501)/(-3-10) 37.30°	(0-51)/(-1-30) 34.98°	
Diffraction pattern 4 (Fig. 10b)	Calculated	Calculated	
60.3°	(301)/(220) 61.25°	(311)/(3-10) 60.59°	
40.2°	(301)/(1-21) 38.76°	(311)/(021) 40.85°	
32.9°	(-1-41)/(1-21) 32.03°	(331)/(021) 32.64°	
46.1°	(-1-41)/-2-20) 47.96°	(331)/(310) 45.92°	

Note: The indicative parameters are shown in bold.

Ca-Cr oxide, foil #3601 This work, observed data	Synthetic β -CaCr ₂ O ₄ Orthorhombic SG: <i>Pbnm</i> (Hörkner and Müller- Buschbaum, 1976)	Meteoritic FeCr ₂ O ₄ (xieite) Orthorhombic SG: <i>Bbmm</i> (Chen et al., 2003a, 2008)	Synthetic FeCr ₂ O ₄ Orthorhombic (CF polymorph) SG: <i>Pnma</i> (Chen et al., 2003b)	Synthetic FeCr ₂ O ₄ Orthorhombic (CT polymorph) SG: <i>Cmcm</i> (Chen et al., 2003b)	Synthetic CaTi ₂ O ₄ Orthorhombic (CT polymorph) SG: <i>Bbmm</i> (Bright et al., 1958)
<i>Lattice parameters, nm</i>					
a₀ = 1.0170	a₀ = 1.0639	a ₀ = 0.9462	a ₀ = 0.8955	a ₀ = 0.9467	a ₀ = 0.973
b₀ = 0.9017	b₀ = 0.9094	b ₀ = 0.9562	b ₀ = 0.2985	b ₀ = 0.9550	b ₀ = 0.999
c₀ = 0.2874	c₀ = 0.2960	c₀ = 0.2916	c ₀ = 0.9909	c ₀ = 0.2905	c ₀ = 0.314
<i>d-spacings d_{hkl}, nm</i>					
0.4508	0.4547 (020)	0.47310 (200)	0.44775 (200)	0.47335 (020)	0.4437 (120)
0.2693	0.26597 (400)	0.26754 (111)	0.27228 (111)	0.26667 (111)	0.26584 (021)
0.2450	0.24879 (211)	0.24824 (201)	0.24091 (211)	0.23967 (211)	0.24325 (400)
		0.24076 (121)			
		0.24027 (211)			
		0.23905 (040)			
0.19597	0.19676 (231)	0.19542 (321)	0.20644 (311)	0.19544 (231)	0.19597 (150)
0.19179	0.19332 (411)				0.19101 (510)
<i>Angles between planes</i>					
50.1°	(231)/(020)	(321)/(200)	(311)/(100)	(231)/(010)	cannot be indexed
	49.53°	51.72°	46.24°	52.13°	
24.5°	(231)/(211)	(321)/(121)	(311)/(111)	(231)/(211)	cannot be indexed
	24.6°	23.54°	26.05°	23.34°	

Note: The indicative parameters are shown in bold.

Iron carbide, foil #3601 This work, observed data	Fe ₂ C Orthorhombic SG: <i>Pnnm</i> (Hirotsu & Nagakura, 1972)	Fe ₃ C Orthorhombic SG: <i>Pnma</i> (Wood et al., 2004)
<i>Lattice parameters, nm</i>		
a₀ = 0.4712 / 0.5009*	a₀ = 0.4704	a₀ = 0.50807
b₀ = 0.4052 / 0.6697	b₀ = 0.4318	b₀ = 0.6753
c₀ = 0.2910 / 0.4458	c₀ = 0.2830	c₀ = 0.45152
<i>d-spacings d_{hkl}, nm</i>		
0.23636	0.23669 (011)	0.23883 (12-1)
0.20366	0.20655 (2-10)	0.20667 (102)
0.18310	0.18088 (201)	0.18534 (221)
0.13555	0.13865 (2-2-1)	0.13765 (0-23)
0.11899	0.11673 (212)	0.11963 (340)
<i>Angles between planes**</i>		
48.32°	(201)/(2-10) 47.52° (Δ = 0.80)	(221)/(102) 47.92° (Δ = 0.40)
59.56°	(201)/(011) 57.68° (Δ = 1.88)	(221)/(12-1) 59.06° (Δ = 0.50)
33.54°	(212)/((011) 33.05° (Δ = 0.49)	(340)/(12-1) 33.62° (Δ = 0.08)
25.42°	(212)/(201) 24.63° (Δ = 0.79)	(340)/(221) 25.44° (Δ = 0.02)
39.62°	(2-2-1)/(0-1-1) 40.38° (Δ = 0.76)	(0-23)/(-1-21) 39.57° (Δ = 0.05)
33.17°	(2-2-1)/(2-10) 34.42° (Δ = 0.25)	(0-23)/(102) 33.45° (Δ = 0.28)

Note:*Calculated lattice parameters from observed *d*-spacing for Fe₂C / Fe₃C structures.

** Differences between angles in standards and studied mineral are shown in brackets as Δ.

*** The indicative parameters are shown in bold.

Fe-N-Si-C, foil #3620 This work, observed data	Fe ₅ SiC Orthorhombic (Lomaeva et al., 2005)	Fe ₇ C ₃ Hexagonal (Herbstein and Snyman, 1964)	Fe ₃ (N _{0.8} C _{0.2}) ₁₃₉₅ Trigonal (Leinenweber et al., 2001)
<i>Lattice parameters, nm</i>			
a₀ = 1.1094	a₀ = 1.0043	a ₀ = 0.6882	a ₀ = 0.47644
b₀ = 0.7656	b₀ = 0.7944	b ₀ = 0.6882	b ₀ = 0.47644
c₀ = 0.7423	c₀ = 0.7469	c ₀ = 0.4549	c ₀ = 0.43906
<i>d-spacings d_{hkl}, nm</i>			
0.3198	0.32032 (112)	0.31973 (112)	
0.2290	0.22798 (41-1)	0.22533 (024)	0.2203 (002)
0.200	0.19978 (-303)	0.19380 (132)	0.20672 (020)
0.1724	0.17430 (521)	0.17587 (116)	
<i>Angles between planes</i>			
32.7°	(521)/(41-1) 32.58°	(116)/(024) 33.17°	
48.8°	(521)/(112) 49.17°	(116)/(1-12) 50.93°	
60.0°	(-303)/(112) 60.14°	(1-12)/(1-3-2) 58.82°	
38.7°	(-303)/(-4-11) 38.11°	(1-3-2)/(0-2-4) 37.08°	

Note: The indicative parameters are shown in bold.

a)

1 mm

b)

#3601

#3713

#3709

#3711

0.25 mm

c)

0.5 μm

d)

50 nm

a)

Polishing debris

Diamond

Mg-Cr-Fe oxide

Iron carbide

Ferropericlase +
Magnesioferrite

Ca-Cr oxide

Graphite

800 nm

This scanning electron micrograph (SEM) shows a cross-section of a polished surface. The image is characterized by several distinct phases: a bright, angular region on the left labeled 'Diamond'; a dark, irregular region at the top right labeled 'Polishing debris'; a large, light-gray central region labeled 'Ferropericlase + Magnesioferrite'; a darker gray region below it labeled 'Ca-Cr oxide'; a bright, irregular region on the left labeled 'Iron carbide'; and a dark, irregular region at the bottom labeled 'Graphite'. A scale bar at the bottom indicates 800 nm.

b)

Magnesioferrite

Ferropericlasite

50 nm

a)

diamond

graphite

MgO

diamond

KMgF₃

KMgF₃

hercynite

polishing debris

diamond

1 μ m

b)

a)

341_H

211_H

$1-21_H$

130_H

$0-51_H$

$-31-5_H$

$-1-30_H$

b)

431_{CT}

121_{CT}

-211_{CT}

310_{CT}

-501_{CT}

-13-5

-3-10_{CT}

a)

b)