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Synchrotron infrared and Raman spectroscopy of microdiamonds from Erzgebirge, Germany

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Abstract

Metamorphic diamonds from the Erzgebirge, Germany have been investigated using synchrotron infrared absorption, Raman scattering, and fluorescence spectroscopy. Infrared absorption features associated with C–C, C–H bonds, molecular H_2O, OH^- and CO_3^{2-} radicals, and N-impurities were observed. The results suggest that a carbon–oxygen–hydrogen (COH) supercritical fluid is the most probable concept to explain the origin of diamonds from ultrahigh-pressure metamorphic terranes (UHPM). Investigation of the nitrogen impurities suggests that the Erzgebirge diamonds belong to the Type 1b-1aA, which is similar to metamorphic diamonds from the Kokchetav massif of Kazakhstan and the Western Gneiss Region of Norway, and differentiates them from other nitrogen-bearing diamonds from kimberlitic sources (Type 1aAB). The occurrence of nitrogen impurities as single atoms in the crystal lattice implies that the Erzgebirge diamonds had a short residence at high-pressure and high-temperature, which therefore suggests a possibility for very fast exhumation. Both infrared and previous studies of nanoinclusions using a transmission electron microscope support a concept of diamond crystallization from a COH rich supercritical fluid.

Keywords: synchrotron; infrared; Raman; microdiamond

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1. Introduction

Over the last decade, microdiamonds of 1- to 300-μm size have been found in ultrahigh-pressure metamorphic (UHPM) rocks with crustal affinities within the Paleozoic–Mesozoic collisional orogenic belts of Kazakhstan (Kokchetav massif), China (Dabie and Qiadam territories), Norway (Western Gneiss Region), Germany (Erzgebirge massif), Greece (Rhodope), and Russia (Ural Mountains) [1–12]. The microdiamonds in all of these areas, except for a pseudomorphic cubic graphite replacing diamond and microcrystalline diamonds in the Ural Mountains [12], have been repeatedly confirmed and unconditionally accepted.

The largest diamond deposits are located in the Kokchetav massif, with the average diamond containing ~20–30 carats/ton in felsic gneisses and up to

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~2700 carats/ton in marbles [13]. The Erzgebirge massif in Saxonia, Germany is another site with a high diamond concentration similar to that of Kazakhstan. In both localities, the diamonds are well preserved, although some of them are graphitized or completely transformed to graphite. In contrast, only a few diamond crystals have been found in other UHPM terranes. Geologists believe that the rarity of diamonds in some ultrahigh-pressure rocks is due to a complete diamond-to-graphite transformation accompanied by intensive recrystallization of rock-forming minerals at low temperatures and low pressures or a very low concentration of CO_2 ($X_{CO_2}<0.01$) that would not lead to a significant diamond crystallization, or both [14,15].

The size of microdiamonds is an important parameter because it may cast light on the history of the diamonds' formation. In the Kokchetav massif of Kazakhstan, the microdiamonds range in size from 1 to 300 μm; smaller diamonds of a size ~1–50 μm are abundant within Si-rich rocks (quartzo-feldspathic gneisses), whereas diamonds of larger size (~50–300 μm) occur mostly within garnet pyroxenites and marbles. The larger Kokchetav diamonds (100–300 μm) were intensively studied with conventional infrared (IR) spectroscopy [16–18], which revealed that the diamonds contain molecular H_2O, CO_3^{2-} and OH^- radicals, and nitrogen; the latter exists in a low aggregation state (Type 1b-1aA). The IR data are consistent with direct observations of nanometric fluid and carbonate and OH-bearing crystalline inclusions in these microdiamonds [19–22]. Two concepts of diamond origin are under discussion: (1) crystallization from a supercritical carbon–oxygen–hydrogen (COH) or COH-multicomponent fluid [13,17–23], or (2) from a silicate or carbonate melt [24,25]; it has also been proposed that diamonds from the Kumdikol area of the Kokchetav massif were crystallized during two episodes [13]. The uncertainties in interpretation of diamond origins and the evidence of two stages of diamond crystallization suggest that IR studies with a better resolution, including those utilizing advanced microspectroscopy techniques, are needed to investigate smaller diamonds and their zoning, because the smaller and larger crystals may be formed by different mechanisms. It is also possible that diamonds of different sizes may originate from different carbon sources [13].

In contrast to the Kokchetav massif, the Erzgebirge diamonds are hosted by quartzo-feldspathic gneisses, with no evidence of any carbonate rocks that would associate with the diamond-bearing lithologies. Moreover, the Erzgebirge diamonds are represented only by small crystals of ~1–50 μm in size. There is a need for characterizations of diamonds from UHPM terranes using state-of-the-art microspectroscopy techniques. This paper presents first IR absorption, Raman scattering and fluorescence spectroscopy studies of loose diamonds extracted from garnet–phengite–quartzo-feldspathic gneisses collected from the Erzgebirge massif in Germany.

2. Geological setting and sampling

The Late Paleozoic crystalline massif of the Erzgebirge is located in Saxony, Germany and continues to the northern part of the Czech Republic. The central part of the massif is composed by ortho- and paragneisses that contain numerous lenses of eclogite and a few lenses of garnet peridotite [25–27]. Diamonds occur in quartzo-feldspathic gneisses as inclusions in garnet, kyanite, and zircon [7,8]. Relics of TiO_2 with α-PbO_2 structure [28] and conventional geothermometry data suggest that felsic rocks were metamorphosed at $T=1200$ °C and $P\sim8$ GPa in a course of deep subduction [27]. During exhumation process, the diamond-bearing rocks were partly recrystallized at lower pressures and temperatures, although many diamond crystals still remain well-preserved in these rocks [14,25].

We collected diamond-bearing garnet–phengite–quatzo-feldspathic gneisses in small outcrops at the eastern shore of the Saidenbach Water Reservoir, about 1.5 km northwest of the village of Forchheim, Saxonian Erzgebirge, Germany. We found abundant microdiamonds of 3–20 μm size as inclusions in garnets, kyanites, and zircons during studies of the polished thin sections with the aid of an optic microscope. Several diamond grains were extracted from the rock specimens for synchrotron micro-IR studies, which require a single crystal sample.

3. Diamond extraction from the rock

The separation of diamonds from their host rocks by NaOH fusion is a well-established technique in the kimberlitic diamond exploration industry, but the procedure is not applicable to the extraction of microdiamonds from UHPM rocks due to their very small size and fragility. A special method of thermo-chemical digestion of diamond-bearing, ultrahigh-pressure rocks was developed in Russian institutions in the 1980s during the period of Kokchetav diamond prospecting and exploration [29]. This method combines elements of the traditional chemical digestion of rock-forming minerals such as quartz, feldspars, garnet