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First findings of monocrystalline aragonite inclusions in garnet from diamond-grade UHPM rocks (Kokchetav Massif, Northern Kazakhstan)

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ABSTRACT

The presence of aragonite inclusions in garnet from diamond-grade metamorphic rocks from the Kokchetav Massif, Northern Kazakhstan was identified for the first time by means of Raman analyses and mapping. Aragonite appears within the inclusions up to 50 μm in size as a single crystal. These inclusions have rounded shape. The grain boundary between the host–garnet is smooth. No cracks occur around the aragonite inclusions. No significant shift in the main aragonite Raman band was measured. These observations indicate that residual pressure within the inclusion is minor. These findings imply either non-UHPM origin of the host garnet or significant plastic deformation of host minerals during retrograde stage. These features should be taken into account for recovery peak metamorphic conditions and modeling of exhumation processes of UHPM complexes.

1. Introduction

Aragonite, the high-pressure $CaCO_3$ polymorph, is expected to form from calcite during incipient subduction of carbonated sediments and, at much higher pressure ($P > 5$ GPa), through the breakdown of dolomite, $CaMg(CO_3)_2$, to $MgCO_3$ (magnesite) + $CaCO_3$ (e.g. 1,2). However, the presence of aragonite in subducted slab is generally restricted to low temperature high pressure (HP) or ultrahigh pressure (UHP) metamorphic rocks. The rapid kinetics of the back-transformation of aragonite to calcite makes the preservation of metamorphic aragonite to the surface an indicator of decompression under quite low temperatures [3,4]. Recently, relics of aragonite were identified as inclusions in garnet from high temperature diamond-grade metamorphic rocks from Erzgebirge [5] and as nanometer-sized inclusions in diamond from the Kokchetav massif [6].

Carbonates (e.g. calcite, dolomite, aragonite) are quite common in high pressure metamorphic rocks. Whereas $CaCO_3$ and (Mg, Ca)$[CO_3]_2$ can be easily distinguished by CL, EMP and SEM analyses, the identification of $CaCO_3$ polymorphs especially in very tiny inclusions is tricky. In these cases, Raman spectroscopy has been proven to be a useful tool. Recently aragonite inclusions were identified in diamond-grade UHPM localities [5,7], however, the origin of aragonite inclusions remains poorly understood [6,8,9].

The presence of aragonite inclusions in metamorphic diamonds by [6] indicates that diamond-bearing rocks were subducted to depth >280 km. The ultradeep subduction was deducted from the dolomite breakdown to form aragonite and magnesite at peak metamorphic conditions [6,8]. Complex aragonite–calcite inclusions occurring in the diamond-bearing metamorphic rocks were identified by Raman spectroscopy [7]. All mineralogical observations indicate that origin of aragonite is not related to dolomite breakdown. Here we present the results of Raman spectroscopic study of monocrystalline aragonite inclusions in garnet from diamond-bearing metamorphic rocks (Kokchetav massif, Northern Kazakhstan). Raman mapping was performed in aim to check the possible presence of any optical undetectable calcite and strain pattern inside inclusions and surrounding host garnet.

2. Analytical methods

Raman mapping was performed with a Sentera Raman system equipped with two lasers at 532 nm and 785 nm. The map size is 35 × 35 points with 1 μm step. The Raman signal was collected in

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the spectral interval 80–2660 cm^{-1} with a spectral resolution of 4 cm^{-1}. Further details of the calibration procedure can be found elsewhere [10].

Textural relations were examined in polished thin sections by transmitted and reflected light optical microscopy and back-scattered electron images on a JEOL 6380LA (Institute of Geology and Mineralogy SB RAS, Novosibirsk). The phase compositions were determined on a JEOL JXA-8100 using an acceleration voltage of 15 kV and a beam current of 1 nA and on a Camebax Electron Microprobe using an acceleration voltage of 15 kV and a beam current of 6 nA.

3. Petrography

The samples in this study belong to the carbonate-bearing garnet–pyroxene rocks of the diamondiferous Unit 1 of the Kokchetav Massif [11–15]. Some diamondiferous garnet–pyroxene rocks have been considered to be isolated bodies within pelitic gneisses [12,16]. This study has focused mainly on sample (GAK101), where aragonite was documented for first time [7].

Sample GAK101 consists of four different layers ranging from almost white (layer 1) over grey (layers 2 and 3) to green (layer 4) with variable amounts of carbonate minerals, garnet and clinopyroxene (Fig. 1a and Table 1).

Grey layers are rich in sulphides (e.g. pyrite and pyrhotite), Ti–clinohumite and serpentine pseudomorphs after forsterite. Dolomite was identified exclusively in layer 2 (Fig. 1). Only the light-colored, almost white, layer 1 contains accessory microdiamonds.

Polycrystalline and monocrystalline carbonate inclusions up to 400 μm in size appear predominantly within layer 3 (Fig. 1). They occur mainly in garnet and clinopyroxene porphyroblasts. All aragonite-bearing inclusions display rounded shapes and sharp carbonate–garnet interface. The lack of dense radial crack patterns around the aragonite-bearing inclusions is another typical feature of this type of inclusions. There is no systematic in spatial distribution of poly- and monocrystalline carbonate inclusions within the garnet and clinopyroxene host–porphyroblasts.

Identification of aragonite in diamond-grade metamorphic rocks is very challenging because of the size of the carbonate inclusions, and of the very low response to cathodoluminescence [7]. In general, aragonite is very pure end-member and finding of pure $CaCO_3$ inclusions with concentration of Mg below detection limit can be an indirect evidence for presence of aragonite in the samples (Table 3).

Diamond and graphite occur exclusively in diamond-bearing marbles, mainly as inclusions in K-bearing clinopyroxene and garnet porphyroblasts. Graphite was found (i) as inclusion in garnet and clinopyroxene (often together with diamond) and (ii) in the sample matrix. No graphite/diamond was found in the aragonite or aragonite-bearing inclusions.

4. Results

4.1. Raman spectroscopical analysis

Carbonates are distinguishable by their diagnostic Raman spectra (17–24 and references therein). However, only in the case of particular carbonates the pressure dependence of the vibrational frequencies is well known [22]. Because of the small sample volumes and the possibility to analyse unexposed inclusions, non-destructive Raman mapping is a very promising tool for the identification and study of the spatial distribution of carbonates (e.g. calcite, aragonite, dolomite, and magnesite) within inclusions.

The two polymorphs of $CaCO_3$, calcite and aragonite, were distinguished in the samples studied by their diagnostic Raman spectra (Fig. 2c and Table 2). Calcite is characterized by a strong band at *1086* cm^{-1}, along with other weaker bands at *156, 283*, and *713* cm^{-1} [25]. The main band of aragonite is also located at *1086* cm^{-1} with subsidiary bands at *154, 181, 191, 208, 249, 261*, 273, 283, and *704* cm^{-1} [25]. Only the bands marked in italics were documented in this study. The host garnet is characterized by a strong band at 896 cm^{-1}, along with other weaker bands at 367, 547, 835 and 1022 cm^{-1} (Fig. 2c). A slight downshift of roughly 1 cm^{-1} in the 283 cm^{-1} calcite band was observed. A weak band at 282 cm^{-1} in the aragonite spectrum appears. Most likely this band is attributed to very fine-grained calcite–aragonite intergrowth, since the band at around 283 cm^{-1} in the Raman spectrum of aragonite is very weak [25]. Several additional, very intense and rather narrow bands appear at around 1325, 1347, and 1452 cm^{-1} in the aragonite spectrum (Fig. 2c). When excited with a different laser source (Ar^+, 514.5 nm) the aragonite exhibited no band at these positions. Thus, these bands are considered to be luminescent bands.

Raman mapping of a monocrystalline carbonate inclusion revealed mainly calcite and only exceptionally rare monocrystalline inclusions with bands, typically assigned to aragonite, were found (Fig. 3). The band position of aragonite and calcite from monocrystalline inclusions corresponds to literature spectra obtained at ambient conditions (Fig. 2 and Table 2). The measured Raman band positions might also be slightly affected by the analytical conditions thus exhibit slight differences compared to the literature ones (different calibration standards, slit width, gratings, etc.) (Table 2).

4.2. Cathodoluminescence and SEM-EDS studies

Over 100 monocrystalline carbonate inclusions were analyzed by CL and SEM. Monocrystalline calcite or dolomite inclusions exhibit strong orange and dark red cathodoluminescence, respectively (Fig. 1b and c). On the contrary, monocrystalline aragonite inclusions exhibit extremely weak CL pattern and can be easily overlooked. SEM study of the monocrystalline carbonate inclusions revealed that they are rather homogeneous. Microprobe analyses proved that the aragonite inclusions are Mg-free $CaCO_3$ ($Ca_{0.99}CO_3$), whereas (i) the Mg-bearing calcite (orange luminescent) is $Ca_{0.95}Mg_{0.04}Fe_{0.01}CO_3$ and (ii) dolomite (dark red luminescent) is $Ca_{0.50}Mg_{0.49}Fe_{0.01}CO_3$.

5. Discussion and concluding remarks

5.1. The origin of aragonite in UHPM rocks

Aragonite-bearing assemblages (e.g. aragonite + Mg–calcite or aragonite + dolomite) should be stable at UHP or HP conditions; however, in very rare cases these assemblages occur in diamond-grade metamorphic rocks [5,7]. In the case of an UHPM origin of aragonite (~1000 °C and 5–6 GPa) the residual pressure should be as high as 1.7 GPa [7] and comparable with values of residual pressure measured for coesite inclusion in garnet (26 and references therein). Raman spectra of aragonite correspond well with Raman spectra obtained at ambient conditions. This indicates that there is no overpressure inside the inclusions. Pressure and temperature dependence of the main calcite and aragonite bands is rather well established [22] and can be used for the estimation of the residual pressure in the carbonate inclusions in the garnet porphyroblast. The lack of significant shifts and/or broadening in the main bands of aragonite (Fig. 3) indicates very low residual pressure in the aragonite inclusions in garnet. The different elastic properties of the aragonite inclusion and the host mineral result in