Lithos 206–207 (2014) 201–213

Contents lists available at ScienceDirect

Lithos

journal homepage: www.elsevier.com/locate/lithos

Radiation damage to Kokchetav UHPM diamonds in zircon: Variations in Raman, photoluminescence, and cathodoluminescence spectra

Rentaro Shimizu *, Yoshihide Ogasawara

Department of Earth Sciences, Waseda University, 1-6-1 Nishiwaseda, Shinjuku-ku, Tokyo 169-8050, Japan

ARTICLE INFO

Article history:
Received 21 December 2013
Accepted 7 July 2014
Available online 12 July 2014

Keywords:
Microdiamond
Radiation damage
Raman spectroscopy
Luminescence
Crystal defect
Ultrahigh-pressure metamorphism

ABSTRACT

We conducted detailed in-situ Raman, photoluminescence (PL) and cathodoluminescence (CL) studies on microdiamonds in a tourmaline-rich quartzofeldspathic rock from the Kokchetav Massif, Kazakhstan. The microdiamonds occur as inclusions in the cores of K-tourmaline and in zoned zircons with varying U contents. The results of 2D Raman mapping of zircon showed that the U-rich parts were more metamictized than the U-poor parts. All the diamonds showed a strong Raman band at approximately 1332 cm^{-1}, however, the features of the Raman bands were distinctly different depending on the host minerals. On the one hand, diamonds in tourmaline had a sharp Raman band that is similar to that of kimberlite diamonds [full width at half maximum (FWHM): 2–3 cm^{-1}]. On the other hand, diamonds in zircon had a broad and downshifted band compared to those in tourmaline. In particular, diamonds in U-rich cores of zircons (up to 0.15 wt.% UO_2) showed broader and more downshifted Raman bands (FWHMs and peak positions varied up to 9.3 cm^{-1} and 1328 cm^{-1}, respectively), with additional small bands at approximately 1490 cm^{-1} and 1630 cm^{-1}. A negative correlation was observed between the peak position and the FWHM of the principal Raman band of microdiamonds. Furthermore, the PL and CL spectra showed systematic variations. Diamonds in zircons with low to moderate U-concentrations had very strong PL and CL compared to diamonds in U-rich zircons and in tourmalines. Several characteristic peaks appeared in the PL and CL spectra, indicating the presence of irradiation and/or nitrogen-related point defects in the diamonds. PL and CL of microdiamonds in high-U zircon were weak, but still showed irradiation-related peaks. The relationship between the occurrence of microdiamonds (i.e., corresponding to the estimated total α-dose since crystallization) and the Raman, PL, and CL spectral characteristics of microdiamonds strongly suggests that radiation damage predominantly caused by α-particle emission from radioactive decay of actinides (mainly U) in zircon is a principal factor for the spectral variations. Radiation damage (metamictization) is probably a common phenomenon among microdiamonds in zircons in various diamond-bearing rocks from the Kokchetav Massif. To discuss the genesis of diamonds based on their Raman, PL, or CL spectra, it is highly recommended that microdiamonds included in actinide-bearing minerals (e.g., zircon) should be treated with the most careful attention, because post-crystallization radiation damage significantly influences the spectra.

1. Introduction

Since diamonds of metamorphic origin were first reported from the Kumdy-Kol area of the Kokchetav Massif, northern Kazakhstan (Sobolev and Shatsky, 1990), the Kokchetav ultrahigh-pressure (UHP) metamorphic diamonds have attracted a high level of interest because of their outstanding abundance (e.g., Yoshioka et al., 2001) and diversity (e.g., Dobrzhinetskaya, 2012). Most of the diamonds occur as micrometer-scale inclusions (microdiamond) in UHP minerals such as garnet, zircon, clinopyroxene, K-rich tourmaline, and sometimes in low-P minerals such as quartz or micas or even in grain boundaries. They occur in various rocks such as gneisses (Korsakov et al., 2002, 2004; Ogasawara, 2005; Sobolev and Shatsky, 1990), marbles (Ogasawara, 2005; Ogasawara et al., 2000; Yoshioka et al., 2001), garnet–pyroxene rocks (Shatsky et al., 2005), and tourmaline-rich quartzofeldspathic rocks (Ota et al., 2008; Shimizu and Ogasawara, 2013). The occurrences of microdiamonds are diverse with regard not only to their host rocks and minerals but also to their morphology (e.g., Ishida et al., 2003; Korsakov et al., 2005; Ogasawara, 2005).

Theoretically, diamond has a simple crystal structure that consists of pure sp^3 carbon. However, in general, natural diamonds contain many types of crystal defects reflecting their genesis and changes of physico-chemical conditions after crystallization (such as thermal history). For example, nitrogen is a common impurity in natural and synthetic diamonds, and high-energy irradiation such as α-particles creates Frenkel defects (pairs of a vacancy and an interstitial carbon atom) in the diamond lattice structure. Such crystal imperfections can be detected by several techniques of optical spectroscopy (e.g., Zaitsev, 2001).

* Corresponding author. Tel.: +81 3 5286 1514; fax: +81 3 3207 4950.
E-mail address: ren@ruri.waseda.jp (R. Shimizu).

http://dx.doi.org/10.1016/j.lithos.2014.07.002
0024-4937/

A number of previous studies on the Kokchetav microdiamonds have shown their spectroscopic diversity. De Corte et al. (1998) obtained FTIR spectra of diamonds in garnet–pyroxene rocks and revealed the presence of type Ib–IaA diamonds with various nitrogen concentrations. Ishida et al. (2003) showed a slight difference in the shape of the Raman spectra of the core and the rim of "S-type" microdiamonds in dolomite marble and suggested two-stage growth of microdiamond. Yoshioka and Ogasawara (2005) demonstrated that the S-type microdiamonds are composed of two distinct generations using cathodoluminescence (CL) images. Imamura et al. (2013) showed carbon isotope heterogeneity of the microdiamonds in dolomite marble and validity of the two-stage growth theory. Furthermore, many other studies have demonstrated that the Kokchetav UHP diamonds are zoned in CL (Bruce et al., 2011; De Corte et al., 2002; Iancu et al., 2008; Korsakov et al., 2005; Schertl et al., 2004). Bruce et al. (2011) also conducted a photoluminescence (PL) study of various metamorphic diamonds, however, their Kokchetav UHP microdiamonds were too small for their PL measurements. The diversity of Raman spectra of microdiamonds has been discussed in a number of studies (e.g., Korsakov et al., 2005; Perraki et al., 2009; Shimizu and Ogasawara, 2006). These studies mainly focus on the peak position and the full width at half maximum (FWHM) of the principal band at approximately 1332 cm^{-1} (F_{2g} mode). However, the reasons for the variations in the Raman parameters appeared to remain ambiguous. In addition, Steger et al. (2013) compared the peak positions and the FWHMs of diamond abrasives with those of UHP microdiamonds and pointed out that simple position–FWHM relationships may be insufficient for diagnostic of any microdiamonds.

Recently Smith et al. (2011) reported that a diamond in zircon from garnet–biotite feldspathic gneiss showed a significantly downshifted Raman band at 1321 cm^{-1} and some extra Raman bands. They concluded that irradiation of α-particles from zircon generated the extra bands and caused the downshift based on the similarity with the experimental results of Orwa et al. (2000). Although Smith et al. (2011) carefully concluded that the downshifted Raman band at 1321 cm^{-1} accompanied by some extra bands was a result of radiation damage, they also mentioned that many other different interpretations were available. Considering the comments by Smith et al. (2011) together with the statements by Steger et al. (2013), we realized that researches on this issue have only just begun.

We have analyzed hundreds of in-situ microdiamonds from the Kokchetav Massif since the early 2000s (e.g., Ishida et al., 2003; Shimizu and Ogasawara, 2006, 2011; Yoshioka and Ogasawara, 2005; Yoshioka et al., 2001). Thus, we are aware of the significance of in-situ analyses of microdiamond. In this paper, we will demonstrate an example of systematic changes in the Raman, PL, and CL spectra of microdiamonds in a quartzofeldspathic rock with their occurrence in host minerals. In particular, we observed that the microdiamonds contained in zircon are spectroscopically unique, and therefore, we will discuss the effect of α-particle radiation from actinide elements in zircon on the crystal structure of diamond and the resulting spectral changes.

2. Materials and methods

2.1. Geological background and sample description

We investigated the properties of microdiamonds in a tourmaline-rich quartzofeldspathic rock (sample A6) occurring as thin layers in diamond-bearing pelitic gneiss (Ota et al., 2008; Shimizu and Ogasawara, 2013) from the Kumdy-Kol area of the Kokchetav Massif, northern Kazakhstan. A detailed geological description of the Kumdy-Kol area is available in Kaneko et al. (2000). The area is characterized by abundant occurrence of microdiamonds and some very high pressure minerals such as coesite, potassium-rich clinopyroxene, and supersilicic titanite. The highest concentration of microdiamonds reaches 2700 ct/ton (Yoshioka et al., 2001) in dolomite marble; in addition, some pelitic gneisses have abundant microdiamonds (e.g., Ogasawara, 2005). The peak metamorphic conditions are estimated at >6 GPa and >1000 °C (Katayama et al., 2001; Ogasawara et al., 2000, 2002; Okamoto et al., 2000).

The investigated tourmaline-rich rock (three polished thin sections of sample A6) shows a granoblastic texture with variable grain sizes (Fig. 1A) and consists mainly of quartz, K-feldspar, and zoned K-rich tourmaline, with small amounts of goethite, titanite, zircon, phengite, phlogopite, apatite, chlorite, zoisite, pumpellyite, graphite, and diamond. The abbreviations for minerals used in the figures are after Whitney and Evans (2010). Diamonds occur only as inclusions in K-dominant cores of tourmaline (Fig. 1A and B; also see Shimizu and Ogasawara, 2013) and in zircon (Fig. 1C). Zircon occurs as euhedral grains approximately 100 μm in the long dimension. In a polished thin section (A6-a1) 22 grains of zircon were observed. The abundance of diamond-bearing zircons in the tourmaline-rich rock overwhelms that in other gneisses in which normally only a few grains of diamond-bearing zircons are observed in a thin section, and this enabled systematic in-situ analyses of microdiamonds in different kinds of host mineral. In total, 115 grains of microdiamond inclusions were confirmed in the three polished thin sections (88 grains in zircon and 27 grains in the K-dominant core of tourmaline). The analyzed microdiamonds are completely or at least partially enclosed in their host minerals. The microdiamonds used in the CL analysis exhibit clear growth-incorporated contacts with their host minerals in SEM images and microscope observation; the microdiamonds do not occur in a pocket on the surface of the thin sections (cf. Dobrzhinetskaya et al., 2014). Therefore, there is no possibility of contamination by diamond abrasives. Polycrystalline diamond like the S-type microdiamond in the dolomite marble was not observed.

2.2. Analytical methods

2.2.1. Electron microprobe analyses of zircons

Electron microprobe (EMP) analyses of zircons were performed by wavelength dispersive (WDS) methods using a JEOL JXA-8900 Super Probe at Waseda University, Japan. For spot analyses, the conditions were an accelerating voltage of 20 kV, a beam current of 50 nA, and a beam spot diameter of 2 μm. First, qualitative analyses were conducted to ensure that the LDEH, TAP, PETH, and LIFH crystals were completely scanned, with 25 μm steps and an acquisition time of 2000 ms for each step. In the results, the following elements were detected: O, Si, Zr, Hf, U, P, Fe, and Ti. Th and all REEs were not detectable under these conditions. The counting intervals for the quantitative analysis were: 20 s (for peak and background; hereinafter the same) for Si-Kα and Fe-Kα; 40 s for Zr-Lα, Hf-Lα, P-Kα, and Ti-Kα; and 300 s for U-Mα. A Φ(ρz) correction was applied to all analyses. The following standards were used: fayalite (Si), ZrO_2 (Zr), Hf (Hf), UO_2 (U), $KTiOPO_4$ (P and Ti), and Fe_2O_3 (Fe). The detection limit for U was approximately 0.007 wt.% UO_2 (i.e., ~60 ppm U). The conditions for characteristic X-ray mapping were an accelerating voltage of 20 kV, a beam current of 50 nA, a beam spot diameter of 1 μm, and a counting interval of 500 ms for each pixel.

2.2.2. Raman spectroscopy

Raman spectra were obtained by a Jobin Yvon LabRam300 Raman micro-spectrometer (HORIBA) equipped with confocal optics and Peltier-cooled CCD detector at Waseda University, Japan. In all measurements, the excitation line of a 514.5 nm Ar^+ laser with a power of approximately 10 mW was employed. The laser spot size was approximately 1 μm. A grating with 1800 grooves/mm was used for all analyses. The intensity, peak position, and FWHM of Raman bands were measured using the Lorentzian–Gaussian fitting (pseudo-Voigt function) after baseline correction.