Available online at www.sciencedirect.com
SCIENCE DIRECT®

Earth and Planetary Science Letters 243 (2006) 85–93

EPSL

www.elsevier.com/locate/epsl

Nanometric inclusions of carbonates in Kokchetav diamonds from Kazakhstan: A new constraint for the depth of metamorphic diamond crystallization

Larissa F. Dobrzhinetskaya [a,*], Richard Wirth [b], Harry W. Green II [a,c]

[a] Department of Earth Sciences, University of California at Riverside, Riverside, CA 92521, USA
[b] GeoForschungsZentrum, Telegrafenberg, Experimental Geochemistry and Mineral Physics, D-14473 Potsdam, Germany
[c] Institute of Geophysics and Planetary Physics, University California, Riverside, CA 92521, USA

Received 27 May 2005; received in revised form 2 September 2005; accepted 22 November 2005
Available online 13 February 2006
Editor: E. Boyle

Abstract

Previous studies have revealed that microdiamonds from the Kokchetav ultra-high pressure metamorphic terrane of Kazakhstan contain nanometric scale inclusions of Si-, Fe-, Ti-, and Cr-oxides. Because the structure of SiO_2 inclusions was not confirmed to be coesite or stishovite due to their very small size, such diamonds formerly served only as an indicator of a minimum pressure, ca. 4 GPa. Geothermobarometry applied to Kokchetav diamond-bearing rocks yielded a wide range of conditions: $T = 700$ °C–1250 °C, and $P = 4$–9 GPa. Our paper presents transmission electron microscopy studies with focused ion beam assistance that indicate that diamonds from marbles contain inclusions of aragonite ($CaCO_3$) and magnesite ($MgCO_3$), and that aragonite and nitrogen-bearing nanometric particles are associated with dislocations reflecting diamond growth at relatively high-temperature conditions. We determined the boundary of dolomite stability using the reaction $CaMg(CO_3)_2$ (dolomite) = $CaCO_3$ (aragonite) + $MgCO_3$. This allowed us to utilize available experimental data to evaluate the pressure at which diamond was crystallized. Taking into consideration uncertainties existing between experimental data produced in different laboratories, we propose the pressure for Kokchetav diamond crystallization to be ~6 to 9 GPa. This evaluation is based on the assumption that temperature was determined correctly as 980 °C (minimum) and 1250 °C (maximum) for diamond-grade dolomitic marbles. Our data provide strong evidence that the metasedimentary rocks of the Kokchetav massif containing diamonds were subducted to the depth of ~190–280 km.

Keywords: microinclusions in diamonds; dolomite; aragonite; magnesite; pressure

1. Introduction

The maximum depth from which ultra-high-pressure (UHP) metamorphic rocks of the Kokchetav massif, Kazakhstan return back to the Earth's surface remains uncertain due to the absence of confident mineralogical constraints. Diamond and coesite occurring in UHP metasedimentary rocks are the minerals best suited for determining a minimum pressure to which the rocks have been subjected during their subduction and, therefore, a minimum depth from which these rocks were exhumed during formation of collisional orogenic belts. A conventional geothermometry applied for diamondiferous rocks of Kokchetav massif, Kazakstan suggests the following temperature range, assuming a minimum

* Corresponding author. Tel.: +1 951 827 5516.
E-mail address: Larissa@ucr.edu (L.F. Dobrzhinetskaya).

0012-821X/$ - see front matter
doi:10.1016/j.epsl.2005.11.030

pressure of 4–4.6 GPa: 880–910 °C (garnet–biotite gneisses), 960 °C (dolomitic marbles), and 1035 °C (calc–silicate rocks) [1]. The lower temperature for diamond formation (700 °C) was proposed by Cartigny et al. [2] based on studies of nitrogen aggregation in diamond structure. Ogasawara et al. [3] calculated that the maximum temperature for the diamond-bearing dolomite marbles is 1250 °C, whereas 980 °C corresponds to the diamonds' crystallization. Okamoto et al. [4] suggested that diamondiferous rocks are metamorphosed at $T=950$–1200 °C. Later, the discovery of coesite exsolution lamellae in titanite from dolomitic marbles of the Kokchetav massif by Ogasawara et al. [5] led to the estimation of the pressures during metamorphism of the Kumdi-kol rocks to be 6–9 GPa.

The most precise data related to the evaluation of the pressure and the temperature conditions for any diamond formation are those that are obtained from crystalline inclusions incorporated in diamonds. Such inclusions, due to the chemical inertness of diamonds, are pristine witnesses of the media and conditions from which the diamonds were crystallized. Studying mineral inclusions in kimberlitic diamonds by different analytical techniques has shown that some of them might originate from the Earth's mantle transition zone or the lower mantle (e.g., a depth >400–600 km) [6–10].

Only the small size (mostly <50 μm) of diamonds from UHP metamorphic terranes has prevented them for a long time from undergoing similar investigations. De Corte et al. [11] have polished some Kokchetav diamonds and have studied them by electron microprobe and laser ablation mass spectrometry to determine the composition of microinclusions. Because the size of the electron beam applied by De Corte et al. [11] was too large (12–15 μm deep and 5–6 μm across) with respect to the 10–100 nm size of the inclusions [12], their researches have provided only the "bulk chemistry" of some diamond inclusions. Therefore, no clear results on the chemical diversity of crystalline or fluid inclusions or their relationships were obtained. Dobrzhinetskaya et al. [12–15] and Wirth [16] have initiated studies of nanometric inclusions in such microdiamonds by applying an innovative focused ion beam technique. This technique allows an excavation of thin foils (10 × 5 × 0.15 μm) from microdiamonds in situ to be studied by transmission electron microscopy. Although many solid and fluid inclusions of nanometric size were observed in Kokchetav diamonds, and stoichiometries of some of them were determined [12,13,15], no electron diffraction patterns were obtained for SiO_2 (a pressure-indicator phase) to allow classification of it as either quartz, coesite, or stishovite, because of very small size of the inclusions. Therefore, because unit cell parameters of SiO_2 inclusions are not known, such diamond formerly served only as the indicator of a minimum pressure (ca. 4 GPa) appropriate for diamonds crystallization at high temperature. This paper discusses our further exploration of the use of the focused ion beam technique on diamonds from garnet–clinopyroxene dolomitic marbles of the Kokchetav massif that brought us a first successful result. Several solid inclusions of $CaCO_3$ were detected to be aragonite, a high-pressure polymorph of calcite. Re-investigation of our earlier prepared foils showed that $MgCO_3$ inclusions [12] are associated with $CaCO_3$ inclusions in the same diamond. Such an association allows us to use the breakdown reaction of dolomite = aragonite + magnesite to apply a better constraint to the determination of the pressure at which diamond crystallization occurred in metasedimentary rocks of the Kokchetav massif.

2. Geological setting and rock samples

The Kumdi-kol area of the Kokchetav massif, Kazakhstan is the first geological site where microdiamonds have been discovered within metamorphic rocks of continental affinities by efforts of Russian and Kazakh geologists from the local Kokchetav Geological Survey. Since 1990, this site has become a subject of intensive international research due to a recognition of the revolutionary significance of such diamond formation for understanding deep subduction of continental material to the Earth's mantle depths [17]. Diamonds are hosted by mineralogically diverse felsic gneisses, calc–silicate rocks, garnet–pyroxenites and marbles associated with eclogite pods and garnet peridotite lenses [1]. We have collected samples from the dolomite marble outcrop located close to the underground gallery in the vicinity of Kumdi-kol Lake, the main place of the diamond exploration. The rock consists (in vol.%) of dolomite

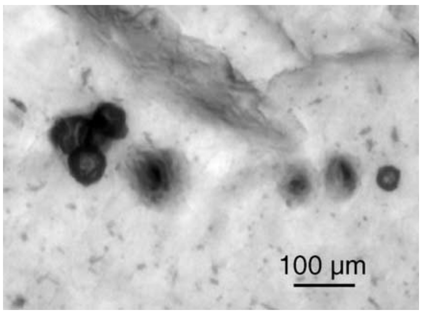

Fig. 1. Optical micrograph of diamonds included in garnet of dolomitic marble collected from the vicinity of the Kumdi-kol Lake at the Kokchetav massif, Kazakhstan.