Available online at www.sciencedirect.com
ScienceDirect
Earth and Planetary Science Letters 259 (2007) 384–399
EPSL
www.elsevier.com/locate/epsl

Inclusions of nanocrystalline hydrous aluminium silicate "Phase Egg" in superdeep diamonds from Juina (Mato Grosso State, Brazil)

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Received 4 January 2007; received in revised form 5 April 2007; accepted 29 April 2007
Available online 8 May 2007
Editor: C.P. Jaupart

Abstract

Inclusions in alluvial diamond from Juina (Mato Grosso, Brazil) have been investigated by TEM methods (electron diffraction, HRTEM, AEM, HAADF, EELS) and Raman spectroscopy. The inclusion paragenesis of Juina diamonds is dominated by ultrahigh-pressure ("superdeep") phases. One of these diamonds, sample #1.1/4, contains several micrometer-sized (approximately 200 µm by 50–70 µm) inclusions, which have been studied. TEM foils prepared applying Focused Ion Beam (FIB) technique revealed that these inclusions consist of a porous, nanocrystalline groundmass, which is composed of nanometre-sized crystals of a hydrous aluminium silicate phase with Al:Si approximately 1:1 and chemical composition of phase "Egg" ($AlSiO_3(OH)$), a minor volume fraction of nanocrystalline stishovite and pore space, which was originally filled with a fluid or gas. The nanocrystalline hydrous aluminium silicate phase is idiomorphic, randomly oriented (approximately 20–30 nm in size) predominantly with tetragonal crystal structure (a_0 = 0.743 nm, c_0 = 0.706 nm). The monoclinic structure of synthetic phase "Egg" determined at ambient conditions [M.W. Schmidt, L.W. Finger, R.J. Ross, R.E. Dinnebier, Synthesis, crystal structure, and phase relations of $AlSiO_3OH$, a high-pressure hydrous phase, American Mineralogist 83 (1998) 881 – 888] is only occasionally observed. The fluid filling in the porosity has been released into the vacuum of the FIB during TEM specimen preparation. Quench products of the fluid containing minor concentrations of F- P- S- Cl- K- Ca and Ba were detected at the walls of the pores. In addition phase "Egg" is identified by µ-Raman spectroscopy within a second sample (RS 43a) from the same location. The presence of Phase "Egg" in the inclusions in diamond may suggest that crustal material has been subducted to a depth of the lower Transition Zone. Although, metastable growth of nanocrystalline high-pressure phases or extension of their respective stability fields to lower pressure can not ruled out completely.

Keywords: diamond; inclusion; TEM; mantle; subduction; crustal material

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0012-821X/$ - see front matter
doi:10.1016/j.epsl.2007.04.041

1. Introduction

Slab subduction transports crustal components such as sediments and basalts into the Earth's interior. A still debated question is how deep crustal material can be subducted. Subduction depths of more than 130 km are documented in ultrahigh-pressure rocks from Dabie Shan (Okay, 1993). Various hydrous minerals in the descending slabs can transport water into the Earth's mantle. Phase "Egg", $AlSiO_3OH$ is a potential candidate for a water-bearing mineral in Al-rich sediments or hydrous basalts, which is stable even at the depth of the Transition Zone. Experiments in the system Al_2O_3–SiO_2–H_2O have shown that hydrous aluminium silicates are stable at very high-pressures and temperatures. Depending on the P–T conditions, different hydrous aluminium silicates exist. In the pressure range from 2 GPa to 6 GPa, phase Pi $Al_3Si_2O_7(OH_3)$ is stable (Wunder et al., 1993a). Above 5 GPa, topaz-OH $Al_2SiO_4(OH)_2$ was reported (Wunder et al., 1993b). Phase "Egg" $AlSiO_3(OH)$ with an Al:Si ratio 1:1 was observed at pressures exceeding 10 GPa and at about 1000 °C (Eggleton et al., 1978). The crystal structure of phase "Egg", including the position of the hydrogen, has been solved from high-resolution X-ray powder diffraction at ambient conditions. The resulting monoclinic cell is based on lattice parameters: a_0=0.7144 nm, b_0=0.4335 nm, c_0=0.6952 nm and the monoclinic angle β=98.396°; space group is $P2_1/n$ (Schmidt et al., 1998). The high temperature stability limit of phase "Egg" $AlSiO_3OH$ was determined in a pressure range from 7 to 20 GPa and at a temperature range from 900 to 1700 °C (Ono, 1999). A more recent investigation of the stability conditions of Phase "Egg" and aluminium oxide hydroxide δ-AlOOH finally clarified that Phase "Egg" is stable at least up to 1625 °C at 17 GPa (Sano et al., 2004). The upper temperature limit of phase "Egg" is controlled by the reaction: Phase "Egg"=stishovite+corundum+fluid. Decomposition of Phase "Egg" into δ-AlOOH and stishovite occurs at pressures greater than 23 GPa below the Transition Zone without any water release. At temperatures above 1200 °C at 23 GPa phase "Egg" decomposed into corundum+stishovite+fluid (Sano et al., 2004). The compressibility of phase "Egg", its equation of state up to 40 GPa, and the role of water at high pressure were reported in a recent paper (Vanpeteghem et al., 2003). NMR measurements of Phase "Egg" revealed that the Si–Al distribution in phase "Egg" is partially disordered. The observed structural disorder and hydrogen bonding is suggested to be responsible for the high upper temperature limits (1500–1700 °C) of phase "Egg" (Xue et al., 2006).

In recent decades, superdeep diamonds originating within the lower mantle and Transition Zone have been reported from South Africa, Australia, USA, Canada, Guinea, Venezuela and Brazil (Scott-Smith et al., 1984; Otter and Gurney, 1989; Davies et al., 1999; Stachel et al., 2000; Kaminsky et al., 2000; Brenker et al., 2002; Brenker et al., 2005; Kaminsky et al., 2006). Of particular interest are superdeep diamonds from the Juina area in Mato Grosso State, Brazil, which mostly comprise alluvial diamond crystals. These diamond crystals contain a large number of syngenetic, superdeep mineral inclusions that include some new mineral phases not previously observed in crustal and upper mantle associations (Wilding et al., 1991; Harte and Harris, 1994; Harris et al., 1997; Harte et al., 1999; Hutchison et al., 2001; Kaminsky et al., 2001; Hayman et al., 2005). Among those mineral inclusions are: Fe-periclase, CaSi-walstromite (former CaSi-perovskite), low Ni enstatite (former MgSi-perovskite), majoritic garnet, TAPP (tetragonal almandine pyrope phase), and a SiO_2 phase with unknown structure.

The objective of this study was to investigate a new collection of diamond crystals from the Juina area, in order to find new superdeep mineral inclusions and to determine their crystal structure.

As a result of this work, we herein document the first natural occurrence of phase "Egg"+stishovite as nanometre-sized, porous inclusions in diamond. The presence of OH-groups in the $AlSiO_3OH$ was also established.

2. Sample description and analytical techniques

The inclusion paragenesis of Juina diamonds is dominated by ultrahigh-pressure ('superdeep') phases (Kaminsky et al., 2001; Hayman et al., 2005). Ten new diamond crystals from alluvial sediments in the Juina area were selected for analysis; one of these contained a visible ilmenite inclusion (sample #1.1). The investigated diamond sample labelled sample #1.1/4 is part of a crushed diamond containing an ilmenite inclusion that has already been described (Kaminsky et al., 2001).

All inclusions in diamond reported in the present study have been investigated by transmission electron microscopy (TEM) techniques such as electron diffraction, analytical electron microscopy (AEM), electron energy-loss spectroscopy (EELS) and high-resolution electron microscopy (HREM). In addition, several diamonds were studied by confocal μ-Raman spectroscopy before the release of the inclusion.

In order to compare crystallographic and chemical parameters of the newly discovered natural Phase "Egg" with synthetic Phase "Egg" $AlSiO_3$ (OH) we used powder material that was synthesized using high-pressure techniques. Bernd Wunder performed the synthesis in a split-sphere multi-anvil press at the Bayerisches Geoinstitut,