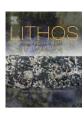
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Acid compositions in a veined-lower mantle, as indicated by inclusions of (K,Na)-Hollandite + SiO₂ in diamonds



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ABSTRACT

Diamonds from Juína area, Brazil, are known by their superdeep origin related to recycling of oceanic crust, basalts and pelagic sediments in the lower mantle. Chemical and structural data on mineral inclusions support this hypothesis. We have studied the inclusions of five diamonds from Juininha alluvial deposits, part of the Juína province, and we have found for the first time in terrestrial rocks, a paragenetic assemblage only observed in high-pressure experiments and/or extraterrestrial rocks. The results suggest the presence of a veined-type lower mantle, where an assemblage of hydrous basaltic origin (MgFeAl-perovskite) is crosscut by pockets and/or veins of intermediate to acid compositions, dominantly constituted by $SiO_2 + (K,Na)$ -Hollandite. The silicate paragenesis (KNa-Hollandite and SiO_2) can be produced by melting of a pelagic metasedimentary source subducted together with the oceanic slab down to the uppermost lower mantle. Such a veined-type lower mantle puts in evidence a derived source modified by melting/dehydration of multicomponent from a subducted slab

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1. Introduction

Mineral phases with compositions equivalent to feldspars, found as inclusions in diamonds, are described in the lower mantle. Among these polymorphs is (K,Na)-Hollandite – (KNa)hl, which forms solidsolution and is an important phase to host K and Na in the transition zone and in the lower mantle, according to experimental petrology and natural rock data (Ferroir et al., 2006; Gillet et al., 2000; Irifune et al., 1994; Liu, 1978, 2007; Ono, 1998; Ringwood et al., 1967), Experimental results suggest that Nahl cannot exist as an end-member phase and, a maximum of 53 mol% (Liu, 2006) can be dissolved in the structure of KAlSi₃O₈. Most experiments confirm that these two high-pressure phases can form extensive solid-solutions (Liu, 2006, 2007; Liu and El Goresy, 2007; Yagi et al., 1994). (KNa)hl was found in several meteorites (Liu, 2007) and, based on experimental studies, it is considered a stable phase up to 23 GPa (Gillet et al., 2000), which points out to its presence in the transition zone (up to 660 km). Between 21 and 23 GPa, Khl transforms to Khl II (Ferroir et al., 2006; Sueda et al., 2004), with a monoclinic structure, that is stable up to 95 GPa (Tutti et al., 2001). Liu (1978) argues that "calcium-ferrite-phase — CAF" (NaAlSiO₄) is the lower mantle precursor of Nahl. Until the present, Nahl is

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unknown in terrestrial rocks, while an inclusion with stoichiometry KAlSi₃O₈, derived from a Khl, and associated to MgSi-perovskite, was observed in African diamonds (Stachel et al., 2000).

The diamonds of Juína province are considered to be originated in the transition zone and uppermost lower mantle (Harte and Harris, 1994; Harte et al., 1999; Hutchinson, 1997; Kaminsky, 2012; Kaminsky et al., 2009; Walter et al., 2011; Wilding, 1990 and references therein), which is indicated by the following inclusions: Fe-periclase (Fper), MgSi- and CaSi-perovskites (MgSi-Prv and CaSi-Prv), tetragonal almandine-pyrope phase (TAPP), majoriticgarnet (Maj) and egg-phase (AlSiO₃OH). Furthermore, some studies (Hayman et al., 2005; Kaminsky and Wirth, 2011) have proposed that Juína diamonds can be originated at the D" region, the mantle-core interface, due to the presence of inclusions of wustite, iron carbides and nitrocarbides. According to Kaminsky (2012), Juína diamonds contain inclusions with different origins: (i) juvenile ultramafic associations, (ii) subducting lithosphere associations analogous to eclogite and, (iii) carbonatitic associations. Recently, a series of inclusions (CAF and Na-bearing hexagonal phase - NAL) in diamonds from Juína-5 kimberlite have been interpreted as originated from liquids produced by melting of basaltic oceanic crust under lower mantle conditions (Walter et al., 2011). In Juína, the occurrence of Khl was suggested in one diamond from pipe Collier 4 (Bulanova et al., 2010) based on one chemical analysis. Such phase is silica-deficient for feldspar stoichiometry and no structural identification was shown.

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This Khl was found associated with a CaAl silicate phase, identified as CAS-phase (Irifune et al., 1994). Such paragenetic association is considered to represent pelagic sediment re-equilibrated under lower mantle conditions (Bulanova et al., 2010).

In the present study, Scanning Electron Microscope (SEM) images, Electron Probe Microanalysis (EPMA) data and spectra obtained by Raman microspectroscopy demonstrated that minerals, with compositions equivalent to alkali feldspars, originated from natural (KNa)hl and formed extensive solid-solution in the lower mantle. Khl and Nahl are structurally reported for the first time in terrestrial materials and its identification shed new light on the lower mantle heterogeneity, pointing to the presence of pockets/veins with acid compositions crystallized under high-volatile influx and highly oxidized conditions.

2. Situation and geology

The Juína diamondiferous district is located in the western portion of the Mato Grosso state, Brazil (Fig. 1), near to the limit with Rondônia state. It is situated close to the border of the Archean (>2.5 Ga) Amazonian Craton, more specifically in one of the younger accretion foldbelts, the Rio Negro-Juruena (1.55 to 1.8 Ga) province (Tassinari and Macambira, 1999). The Rio Negro-Juruena geochronological province is dominantly composed by gneisses, tonalites and granodiorites (Tassinari and Macambira, 1999). Diamonds are found in kimberlites (92–95 Ma; Heaman et al., 1998) in the southwestern margin of the Amazonian Craton, in Quaternary alluvial deposits and, in Tertiary–Quaternary conglomerates (Abdallah and Martins, 2008). These secondary deposits occupy channels, paleo-channels, flats and terraces of several drainages, such as the Cinta Larga, Vinte e Um, Mutum, Igarapé Porcão, Sorriso, Juininha, São Luiz and Juína-Mirim, most of them tributary of the Aripuanã river.

3. Material and methods

The inclusions of five alluvial diamonds from Rio Juininha, some with unusual compositions, were chemically and structurally characterized. Inclusions were obtained by mechanical crushing in an enclosed steel cracker. The inclusions were separated using a Leica Zoom 2000 binocular microscope and mounted in resin stubs with a 1 cm diameter.

The studied diamonds have irregular and rounded octahedral shape, with colors varying from colorless (samples JU-03, JUSC-10 and JUSC-11) to yellowish (sample JU-02) and brown (sample JUSC-05) varieties, and size ranging from (6 mm \times 4 mm; JUSC-10) to (8 mm \times 6 mm; JU-02). The studied inclusions were considered syngenetic based on two distinct evidences: (i) the morphology imposed by the diamond-host and (ii) similar chemistry with other syngenetic inclusions described in Juína diamonds.

Chemical compositions were obtained using a CAMECA SX-50 Electron Microprobe at the Serveis Cientificotècnics of the Universitat de Barcelona, Spain. The analytical conditions were a beam current of 10 nA, a beam energy of 15 keV and a spot size of 5 μ m. The acquisition time was 20 s on the peak and 10 s on the background for all elements. Each element was standardized on either synthetic or natural minerals.

BSE (Backscattered Electron) images and EDS (Energy Dispersive X-ray Spectrometry) data were obtained on a JEOL SM-5800 and a JEOL SM-6390LV Scanning Electron Microscopes at the Electronic Microscopy Centers of the Universidade Federal do Rio Grande do Sul and Universidade Federal de Santa Catarina, Brazil, respectively. BSE images were obtained using an accelerating voltage of 15 keV and for the EDS data of 20 keV.

Raman Microspectroscopy (wavelength = 632.8 nm): Raman spectra were measured at room temperature using a microspectrometer at the High-Pressure Laboratory of the Physics Institute, Universidade Federal do Rio Grande do Sul, Brazil. The equipment consists of an Olympus (BH-2 model) microscope, with a simple monochromator (Jobin Yvon;



Fig. 1. Localization map of Mato Grosso State in Brazil (A) and Juína district in the western Mato Grosso, nearby Rondônia State (B).

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