First find of merrillite, Ca₇(PO₄)$_2$₄, in a terrestrial environment as an inclusion in lower-mantle diamond

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ABSTRACT

Merrillite, ideally Ca$_3$Na$_2$Mg$_4$(PO$_4$)$_6$ (Dana No: 38.03.04.04; Strunz No: 08.AC.45), an analog to synthetic tricalcium phosphate β-Ca$_3$(PO$_4$)$_2$, was identified as an inclusion in lower-mantle diamonds from the Rio Soriso area, Brazil. It was associated with former bridgmanite, CaSi$_3$- and CaTi-perovskites, and ferropericlase. This is the first report of merrillite in a terrestrial environment; previously, it was known only in meteorites and lunar rocks. The compositions of merrillite vary in different localities; the Rio Soriso sample was enriched in SO$_2$ (2.03 wt%). Merrillite from lower-mantle diamonds may be a retrograde phase of the tuite [γ-Ca$_7$(PO$_4$)$_2$]. Owing to their crystal structures, both merrillite and tuite may be important potential hosts for rare earth elements (REE) and large ion lithophile elements (LILE), including Sr and Ba, in the deep Earth. The find of merrillite suggests a larger variety of mineral species in the lower mantle than previously assumed.

Keywords: Merrillite, tuite, whitlockite, diamond, phosphates, lower mantle, Raman spectra

INTRODUCTION

Phosphorus is a minor element on Earth, particularly in its deep interior. The average concentration of phosphorus in the Earth’s mantle is 90 ppm, or 0.021 P$_2$O$_5$, which is almost eight times less than that in the bulk Earth (McDonough and Sun 1995; McDonough 2014). It has been suggested that most terrestrial phosphorus resides in the lower mantle (Nash 1984). Under normal oxidative conditions, phosphorus crystallizes as phosphate. However, phosphates are rare minerals in the mantle.

Previously, we reportedapatite and two unnamed orthorhombic phosphates, mixed-anion phosphate Na$_2$Mg$_6$(PO$_4$)$_3$(P$_2$O$_7$) and Fe-diphosphate Fe$_2$Fe$_3$(P$_2$O$_7$)$_2$, as members of the Earth’s lower-mantle natrocarbonatitic association and found as inclusions in diamonds from the Juina area, Brazil (Kaminsky et al. 2013, 2016). This association represents the near-solidus melt, which has a carbonate-phosphate composition, stimulating the formation of diamond in the deep Earth (Ryabchikov and Hamilton 1994).

During the study of possible lower-mantle diamonds from the Juina area (Mato Grosso State, Brazil) and their inclusions, we identified several grains of Ca-phosphate in association with enstatite, breyite, and ferropericlas (Fe-rich periclase, Per68Wüs32). We suggest that enstatite and breyite are retrograde transformation products of bridgmanite and CaSi-perovskite. Detailed examination of these phosphate grains with the use of Raman spectroscopy indicated that they were merrillite, an analog to synthetic tricalcium phosphate β-Ca$_3$(PO$_4$)$_2$, with an ideal formula Ca$_7$Na$_2$Mg$_4$(PO$_4$)$_6$ (Dana No: 38.03.04.04; Strunz No: 08.AC.45).

Merrillite, which we will describe below as [β-Ca$_7$(PO$_4$)$_2$], is a major accessory phosphate in meteorites and lunar rocks (Wherry 1917; Fuchs 1969; Hughes et al. 2006, 2008; Jolliff et al. 2006; https://www.mindat.org/min-6577.html), but virtually unknown in the Earth’s rocks, although minor admixture of merrillite component has been found in terrestrial whitlockite (Hughes et al. 2008). An Fe-dominant analog of merrillite, identified as a separate mineral species in several martian meteorites (shergottites), was named ferromerrillite (Britvin et al. 2016). Below, we present characteristics of the first terrestrial finding of merrillite in diamonds from the alluvial deposits of Juina area (Brazil).

SAMPLES AND METHODS

Alluvial diamonds from Rio Soriso in the Juina area (Mato Grosso State, Brazil) were previously studied by Hayman et al. (2005). A set of oxide minerals (ferropericlas, CaSi-perovskite, bridgmanite, unknown phase of SiO$_2$, and others) was identified as inclusions in diamonds; their origin was suggested as being at depths of the Earth’s lower mantle (Hayman et al. 2005). In addition to those earlier minerals found in the current study, we found more inclusions in the Rio Soriso diamonds, not only oxides but also magnesite and phosphate. Phosphates were identified in two samples, no. 3.6.2 and no. 3.10.2. In sample no. 3.6.2, it occurred as a single elongated inclusion, ~40 μm in size (Fig. 1a). In sample no. 3.10.2, phosphate formed a chain of five tubular, elongated inclusions, 15–50 μm in size (Fig. 1b), in association with ferropericlas with f = 0.32.

Prior to analyses, samples were polished to expose the inclusions. Exposed individual inclusions were identified in electron backscattering mode (BSE) using a focused electron beam (15 kV, 10 nA) and an acquisition time of 30–60 s. Mineral inclusions were analyzed using an Oxford energy-dispersive X-ray spectrometer (EDS XMax 80) attached to a Tescan MIRA 3 LMU scanning electron microscope (at IGM). Prior to analyses, samples were polished to expose the inclusions. Exposed individual inclusions were identified in electron backscattering mode (BSE) using a focused electron beam (15 kV, 10 nA) and an acquisition time of 30–60 s. Mineral inclusions were analyzed using an Oxford energy-dispersive X-ray spectrometer (EDS XMax 80) attached to a Tescan MIRA 3 LMU scanning electron microscope (at IGM). Chemical compositions (without P$_2$O$_5$ and SO$_2$ concentrations) were also determined using a JEOL JXA-8100 EMPA, equipped with five wavelength-dispersive spectrometers and an energy-dispersive (EDX) spectrometer at an accelerating voltage of 20 kV, beam current of 20 nA, and beam diameter of 1 μm. The full protocol of the EMPA was described by Lavrent’ev et al. (2015).

Raman spectra were collected using a Horiba Jobin Yvon LabRAM HR800 Raman microspectrometer equipped with a 532 nm Nd:YAG laser and an Olympus BX41 microscope at 50× magnification. Spectra were recorded at room temperature in a backscattering geometry in the range 100 to 1200 cm$^{-1}$ with a spectral resolution of 1 cm$^{-1}$. The spectra were calibrated using the 520.6 cm$^{-1}$ line of a silicon wafer. The wavelengths were accurate to ±1 cm$^{-1}$.

Carbon isotopic ratios were measured using a Flash EA 1112 (Thermo-Fisher Scientific) coupled to a Finnigan Delta Plus XP isotope-ratio mass spectrometer. The diamonds were crushed in an agate mortar, and diamond fragments of ~50–100 μm were inserted into Sn capsules and dropped into the combustion reactor (1020 °C). The temperature of the reduction reactor was maintained at 650 °C. All carbon isotopic compositions of the samples are reported in standard δ notation on the VPDB scale ($^13$C$_{VPDB}$). Two to five fragments of each sample were analyzed to calculate the average and standard deviation (1σ) values.