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Petrography of the carbonaceous, diamond-bearing stone "Hypatia" from southwest Egypt: A contribution to the debate on its origin

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Abstract

The stone named "Hypatia" found in the Libyan Desert Glass area of southwest Egypt is carbon-dominated and rich in microdiamonds. Previous noble gas and nitrogen isotope studies suggest an extraterrestrial origin. We report on a reconnaissance study of the carbonaceous matrix of this stone and the phases enclosed in it. This focused on areas not affected by numerous transecting fractures mostly filled with secondary minerals. The work employed scanning electron microscopy (SEM) with energy-dispersive (EDS) and wavelength-dispersive (WDS) electron microprobe (EMPA) analysis, Proton Induced X-ray Emission (PIXE) spectrometry and micro-Raman spectroscopy. We found that carbonaceous matrices of two types occur irregularly intermingled on the 50–500 μm scale: Matrix-1, consisting of almost pure carbonaceous matter, and Matrix-2, containing Fe, Ni, P and S at abundances analyzable by microprobe. Matrix-2 contains the following phases as inclusions: (i) (Fe,Ni) sulphide occurring in cloud-like concentrations of sub-μm grains, in domains of the matrix that are enriched in Fe and S. These domains have $(Fe + Ni)/S$ (atomic) $= 1.51 \pm 0.24$ and $Ni/Fe = 0.086 \pm 0.061$ (both 1SD); (ii) grains up to ∼5 μm in size of moissanite (SiC); (iii) Ni-phosphide compound grains up to 60 μm across that appear cryptocrystalline or amorphous and have $(Ni + Fe)/P$ (atomic) $= 5.6. \pm 1.7$ and $Ni/Fe = 74 \pm 29$ (both 1SD), where both these ratios are much higher than any known Ni-phosphide minerals; (iv) rare grains (observed only once) of graphite, metallic Al, Fe and Ag, and a phase consisting of Ag, P and I. In Matrix-2, Raman spectroscopy shows a prominent narrow diamond band at $1340\ cm^{-1}$. In Matrix-1 the D and G bands of disordered carbon are dominant, but a minor diamond band is ubiquitous, accounting for the uniform hardness of the material. The D and G bands have average full width at half maximum (FWHM) values of 295 ± 19 and $115 \pm 19\ cm^{-1}$, respectively, and the D/G intensity ratio is 0.75 ± 0.09 (both 1SD). These values are similar to those of the most primitive solar system carbonaceous matter. The diamond phase is considered to be a product of shock. The (Fe, Ni) sulphide phase is probably pyrrhotite and a shock origin is likewise proposed for it. Moissanite is

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frequently associated with the Ni-phosphide phase, and a presolar origin for both is suggested. The lack of recrystallization of the Ni-phosphide phase suggests that the Hypatia stone did not experience long-lasting thermal metamorphism, in accord with the Raman D-G band characteristics.

A lack of silicate matter sets the stone apart from interplanetary dust particles and known cometary material. This, along with the dual intermingled matrices internal to it, could indicate a high degree of heterogeneity in the early solar nebula.

Keywords: Extraterrestrial carbonaceous matter; Silicon carbide; Nickel phosphide; Shock metamorphism; Early solar nebula heterogeneity

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1. INTRODUCTION

A carbon-rich, microdiamond-bearing stone 30 grams in mass and of dimensions 3.5 × 3.2 × 2.1 cm was found in 1996 by Aly A. Barakat in the Libyan Desert Glass (LDG) area in southwestern Egypt. Barakat (2012) describes it as extremely hard yet very brittle and heavily fractured, and showing a curious pitch-like lustre beneath the coating of desert varnish. Its enigmatic appearance and physical properties motivated recent multidisciplinary studies (Kramers et al., 2013, who named it "Hypatia"; Andreoli et al., 2015; Avice et al., 2015).

Original suspicions that the stone might be an unusual variety of carbonado diamond, a type of polycrystalline diamond found in Brazil and the Central African Republic (e.g. Trueb and de Wys, 1969; De et al., 1998; Haggerty, 2014) were set aside by $\delta^{13}C$ values of $-0.2‰$ and $-1.1‰$ (Kramers et al., 2013) in contrast to the values between $-30‰$ and $-12‰$ obtained on carbonados (Shelkov et al., 1997; De et al., 2001). Further, Kramers et al. (2013) and Avice et al. (2015) reported $^{40}Ar/^{36}Ar$ ratios (∼39 and ∼0.5, respectively) far lower than the lowest present-day terrestrial value, which is the atmospheric ratio, 298.56 ± 0.31 (Lee et al., 2006). Avice et al. (2015) also found He, Ne and Xe with isotopic compositions distinctly different from terrestrial values, but very similar to those of the "Q" noble gas component, which is dominant in chondritic meteorites, where it is hosted in insoluble organic matter (IOM; Lewis et al., 1975; Ozima et al., 1998; Busemann et al., 2000; Ott, 2002). From cosmogenic ^{21}Ne data, Avice et al. (2015) further find that Hypatia must have been part of a bolide at least several m in diameter and if the body was much larger, the stone must have come from the outermost few m.

Nitrogen isotope data from Hypatia (Avice et al., 2015) present a bimodal picture, with low temperature releases yielding $^{15}N/^{14}N$ ratios of ∼0.00376 ($\delta^{15}N \sim +20‰$) and the dominant release at high temperatures ∼0.00327 ($\delta^{15}N \sim -110‰$). While $\delta^{15}N$ values up to $+20‰$ and $+50‰$ have been measured in Phanerozoic and Archean shales, respectively (Thomazo and Papineau, 2013), values below $-10‰$ are very rare, and values below $-40‰$ have never been found in any terrestrial (crustal or mantle-derived) material (Cartigny and Marty, 2013). These nitrogen isotope data allow comparisons with various types of extraterrestrial objects. Primitive carbonaceous chondrites have $^{15}N/^{14}N$ ratios higher than 0.0036 ($\delta^{15}N > -20$) (Füri and Marty, 2015). Avice et al. (2015) noted similarities of the light Hypatia values with diamonds in ureilites (Rai et al., 2003a) and graphite nodules in iron meteorites (Grady and Wright, 2003). Among primitive, carbon-rich objects, a very wide range of $^{15}N/^{14}N$ ratios has been found: from 0.0031 to 0.0072 ($\delta^{15}N$: $-150‰$ to $+970‰$), by high resolution spectrometry, for comets (Jewitt et al., 1997; Arpigny et al., 2003; Bockelée-Morvan et al., 2008) and from 0.0033 to 0.0055 ($\delta^{15}N$: $-97‰$ to $+505‰$), by mass spectrometry, in bulk primitive interplanetary dust particles (IDP's) and in comet 81P/Wild dust (Floss et al., 2006; McKeegan et al., 2006). The Hypatia data fall in the lightest part of this range, which as a whole is strongly fractionated towards ^{15}N relative to the best estimate for the bulk solar nebula (0.00227; $\delta^{15}N$: $-379‰$, Marty et al., 2010, 2011; Füri and Marty, 2015).

In Hypatia's carbonaceous matrix, X-ray diffraction (XRD), Raman spectroscopy and transmission electron microscopy (TEM) have revealed the presence of diamond (Kramers et al., 2013; Avice et al., 2015). TEM has shown that this diamond occurs as grains between 50 nm and 2 μm in size (Kramers et al., 2013; Avice et al., 2015). A comparison of TEM images with those of diamonds from the Popigai impact structure (Koeberl et al., 1997) suggests that the diamond was probably formed as a result of shock (Kramers et al., 2013). A widening of the X-ray diffraction patterns, the presence of the hexagonal diamond polymorph lonsdaleite, and distinct deformation bands visible by TEM also point to a shock-related origin (Avice et al., 2015). In Raman spectroscopy, the presence of disordered carbonaceous matter is revealed by both D and G bands as well as a high fluorescence background (Kramers et al., 2013).

In a microchemical study using Proton Induced X-ray Emission (PIXE) analysis, Andreoli et al. (2015) found extraordinary heterogeneity on the 100 μm-scale, with, for instance, regions showing up to 4‰ Ir and up to 0.6‰ Os and variable element distributions that do not show any relationship to established cosmochemical groupings.

The stone, when discovered, was larger by orders of magnitude than any carbon-dominated object of extraterrestrial origin found on Earth, with the exception of graphite-rich nodules in the Canyon Diablo meteorite (Vdovykin, 1973). Kramers et al. (2013) suggested that it is a remnant of a cometary nucleus fragment and suggested that it may have originated from a bolide which broke up and exploded in the atmosphere causing the formation of the LDG. This suggestion was dismissed by Reimold and Koeberl (2014), who state categorically: "There is no connection between the diamond-bearing rock fragment and the LDG except that they occur in the same region".