



## Hydrogen isotope compositions of hydrous components in carbonado diamond

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Among the most intriguing questions of geochemistry in the last decades is the origin of carbonado diamond, a special microcrystalline diamond variety that is found only placer deposits in Brazil and Central Africa. Carbonado has a number of unique features that distinguish it from other diamond types: restricted to single time and locality in earth's history, porphyroclastic and highly porous microstructure, in which the pores are filled with crustal minerals (like florencite, kaolinite, quartz, etc.), narrow stable carbon isotope composition range of about  $-27 \pm 3$  ‰ (relative to the V-PDB standard), high 4-He signal, to list only the most well known ones. Although the literature is extensive, there is no general consensus regarding the origin of carbonados.

Models for the origin of carbonados are extremely varied. Diamond formation from organic matter due to subduction-related metamorphism or extreme nuclear irradiation, precipitation from carbonic fluids in the mantle, or an impact origin either by transforming terrestrial organic matter into diamond due to the impact shock or transporting extraterrestrial diamondiferous material have been suggested. New evidence for the latter is the H-C bonds found in carbonados unprecedented in other terrestrial diamonds (Garai et al., 2006). If such H-C bonds serve as evidence for an extraterrestrial origin, D/H ratios may be used to infer the ultimate origin of the H component, as it should be strongly depleted in deuterium. Until now, the major obstacle of such study has been the low hydrogen content of the carbonado, which itself is usually available only in very small quantities. Recent technical developments now make it possible to analyse very small amounts of hydrogen extracted from minerals (Demény and Siklósy, 2008).

The main aim of this study was to determine the amount and hydrogen isotope composition of the H compounds contained in carbonados. For this purpose 5 carbonado samples (from Brazil and Central Africa) were studied by means of electron microprobe and stable isotope mass spectrometric analyses using different types of materials: 1) bulk, untreated carbonado chips of 1-2 mm size; 2) powdered samples treated with HCl and HF acids; 3) powdered, but chemically untreated sample stepwise heated to 500, 1000 and 1500 °C. H and C isotope data will be expressed as ‰ relative to V-PDB and V-SMOW, respectively, in the followings.

The carbonado samples had bulk  $\delta^{13}\text{C}$  values of  $-32.0$  to  $-24.3$  ‰. Carbonados may contain amorphous carbon with different C isotope values, which could be oxidized at lower temperature than diamond. In order to separate the carbon of two different origins, some of the samples were heated to 500 °C in oxygen atmosphere. The experiments yielded no detectable amounts of carbon dioxide. Thus the amount of amorphous carbon in the investigated samples is insignificant.

Untreated and HCl-dissolved samples were stepwise-heated that showed CO<sub>2</sub> and H release peaks at about 300, 600, 900 °C and a continuous release above 1000 °C. These peaks may be interpreted as fluid inclusion decrepitation, kaolinite and florencite decomposition. Long exposure Synchrotron Radiation XRD investigation has shown only diamond peaks after HCl-HF treatment of the samples. Even these samples with no florencite (that has decomposition T above 800 °C) released measurable amounts of H.

Hydrogen isotope compositions obtained in the bulk untreated samples range from  $-69$  to  $-85$  ‰ whereas HCl-HF treated samples tend to have lower  $\delta\text{D}$  values down to  $-140$  ‰. Stepwise heating of a bulk untreated carbonado

sample from which larger amounts of material was available for different types of analyses yielded  $-59\text{‰}$  at 550 °C,  $-204\text{‰}$  at 1000 °C and  $+38\text{‰}$  at 1500 °C ( $-194\text{‰}$  together for the 1000+1500 °C steps).

Bulk compositions around  $-80\text{‰}$  would be consistent with either crustal or mantle fluid origin. However, the negative  $\delta\text{D}$  shift in the acid-treated samples and the high-temperature component in the stepwise heating experiments indicate that there is a D-depleted hydrogen material in the carbonado. This compound can not be related to amorphous carbon as such material was not detected in our samples. The persistence of hydrogen in the florencite-free samples indicates that it is contained in the diamond.

Possible explanations may invoke hydrothermal influence, i.e. hydrogen diffusion into the diamond crystals at elevated temperature and pressure during florencite formation. As light isotopes diffuse much easier and faster than heavy ones, the diamond crystals may entrap hydrogen depleted in deuterium after cooling and structural closure for diffusion. However, the present dataset may equally be explained by an impact origin that assumes transportation of extraterrestrial diamond crystals that served as seeds for microcrystalline diamond and that partially preserved its strong D-depleted character.

Garai, J., Haggerty, S. E., Rekh, S., and Chance, M. (2006): Infrared Absorption Investigations Confirm the Extraterrestrial Origin of Carbonado-Diamonds *Astrophysical Journal Letters*, vol 653, L153-L156.

Demény, A., Siklósy, Z. (2008): Combination of off-line preparation and continuous flow mass spectrometry: D/H analyses of inclusion waters. *Rapid Communications in Mass Spectrometry*, 22, 1329-1334.