

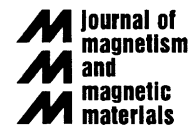


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Magnetic properties of carbonado diamonds

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Abstract

Carbonados are porous polycrystalline diamonds of uncertain origin, which are found at locations in Bahia (NE Brazil) and in the Central African Republic. Their combination of extreme hardness and toughness is ideal for drilling and cutting tools. A variety of elements including Fe, Ni, Cu and Ag are associated with the diamonds. Following a suggestion that Mn-doped diamond may be intrinsically ferromagnetic, we have analysed six samples from Brazil which show ferromagnetic moments of up to $3 \text{ A m}^2 \text{ kg}^{-1}$, which is reduced by acid leaching. X-ray diffraction on the crushed powder showed a cubic diamond structure, with no secondary phases visible. Scanning electron microscopy shows an inhomogeneous distribution of heavy metals and Mössbauer spectroscopy indicates that iron is present as native iron. We find no evidence from the carbonados for the existence of transition-metal doped ferromagnetic carbon. The intrinsic diamagnetic susceptibility of carbonados is $-4.5 \times 10^{-9} \text{ m}^3 \text{ kg}^{-1}$, similar to the accepted value for diamond, $-5 \times 10^{-9} \text{ m}^3 \text{ kg}^{-1}$.

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Carbonados are polycrystalline diamond aggregates, between 2.6 and 3.8 Ga old, found only in alluvial deposits in Brazil and the Central African Republic (CAR). Though they have no value as gems they are ideal industrial abrasives as their random crystallographic orientation makes them highly resistant to crack propagation. While theories surrounding their origin abound, the

Brazilian and CAR deposits may actually constitute a single source as the continents were then unseparated in the Precambrian. Their name is due to their grey-black colour, which develops when diamond crystallites are sintered in a region of temperature and pressure where there is a tendency for the diamond to transform to graphite [1]. Carbonados are irregularly shaped and porous (approximately 10% void space), with crystallite sizes ranging from 0.5 to 500 μm .

An extensive review discusses the possible origins of carbonados [2]. It has been suggested

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that they formed when crustal organic material subducted to the upper mantle and converted to diamond, consistent with their typically crustal selection of inclusion minerals (e.g. orthoclase, florencite, kaolinite) [3,4]. However, carbonados are absent from other well-known subduction zones. Although carbonados are similar in many ways to kimberlites, a mantle origin is considered to be unlikely given the significant amounts of helium within the samples and their high porosity, with trapped organic material inside, in addition to lacking significant mineral inclusions [5,6]. Kaminsky suggested that carbonado was formed by irradiation of carbonaceous materials by associated U or Th [7], while possible extraterrestrial origins include the idea that they originated outside the solar system as ejecta from a collapsing red giant star [8], or are the result of a meteoritic impact [9,10].

More than a dozen different mineral inclusions have been reported including haematite, magnetite, chromite, rutile, calcite and quartz [11–14]. In addition, a number of native metals and alloy inclusions have been documented including Fe, Fe–Mn, Fe–Ni, Ni, Cr, Ti and SiC [14,15]. Native iron occurs sparingly terrestrially, but is common in meteorites. In the native state, it is highly unstable in the oxidizing conditions in rocks of the upper crust and in the earth's atmosphere and so iron usually appears in oxides. Terrestrial native iron is either a primary magmatic constituent or a secondary product formed by reduction of iron compounds by assimilated carbonaceous material [16]. Whether the magnetic inclusions are within the carbonado matrix [17], or reside almost exclusively in open pores at the diamond surface [18], is disputed, but has implications for carbonado genesis.

Interest in the magnetic properties of doped diamond has been stimulated on the one hand by the prediction by Dietl et al. [19], based on mean field calculations of hole-mediated exchange, that diamond, a wide-gap semiconductor with $E_g = 5.4\text{eV}$, should become a ferromagnet with a high Curie temperature, $T_C \sim 480\text{K}$ when doped with 5at% Mn, and on the other hand by the observation of superconductivity in boron-doped bulk [20] and thin film [21] specimens. As it is difficult to obtain doped diamond films of good

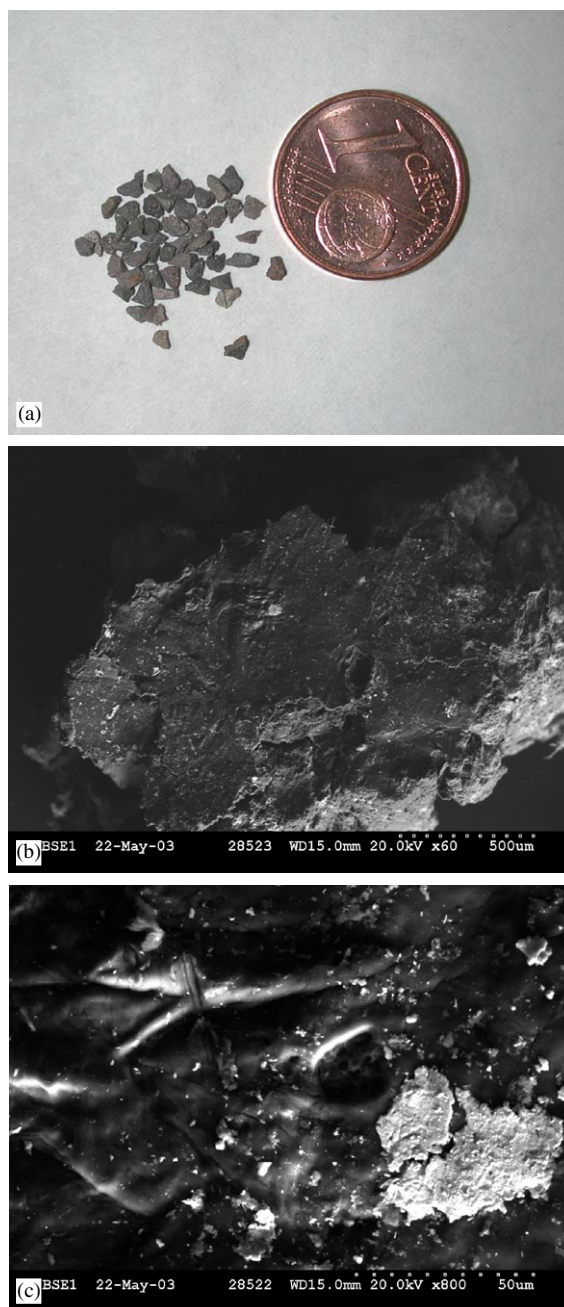
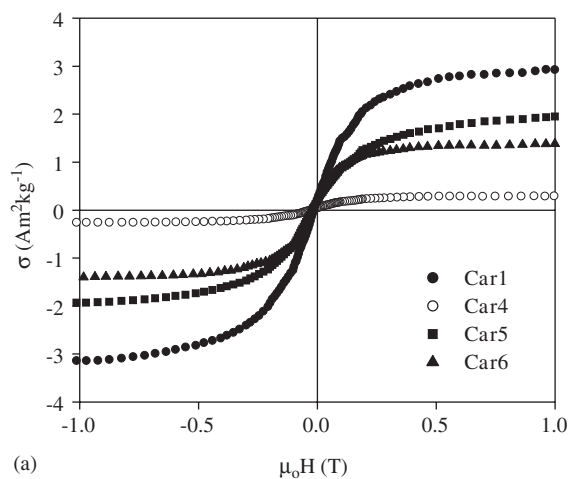
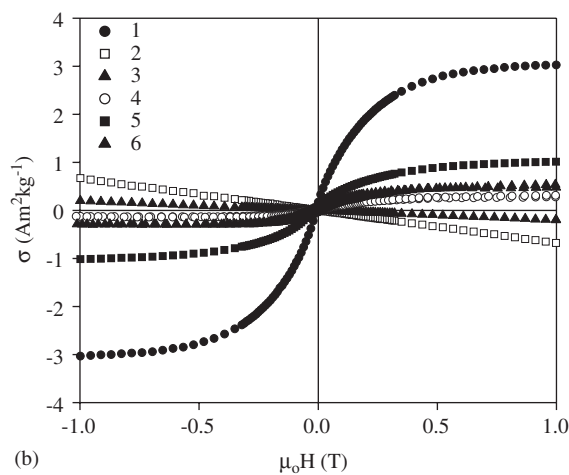


Fig. 1. Carbonado diamonds from Brazil: (a) many carbonados (b and c) scanning electron micrograph images showing metallic inclusions in the carbon matrix (bright spots).

crystalline quality, or to produce bulk doped synthetic diamond, we chose to examine the magnetic properties of natural carbonados in



(a)



(b)

Fig. 2. Magnetization curves for carbonados (a) before and (b) after acid treatment.

In order to measure the diamagnetic susceptibility accurately, we took an acid-treated sample with very little ferromagnetic signal, and placed it symmetrically between two gel caps in a straw for the SQUID measurement. A background measurement with no sample was made for comparison. Data are shown in Fig. 3. The smaller (in magnitude) susceptibility at 2 K compared with 300 K is attributed to the presence of some paramagnetic impurities in the diamond. Assuming a Curie law, with an effective moment of $\sqrt{3}\mu_B$, the concentration is <5 ppm. The main contribution to the susceptibility is therefore deduced from the 300 K data. The room-temperature susceptibility

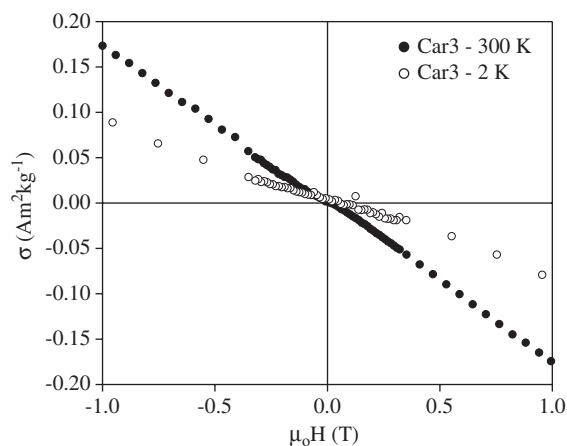


Fig. 3. Carbonado 3 measured at 300 and 2 K.

of carbonado is deduced as $-4.5(1) \times 10^{-9} \text{ m}^3 \text{ kg}^{-1}$. This is similar to the accepted value for diamond, $-5 \times 10^{-9} \text{ m}^3 \text{ kg}^{-1}$. We find no evidence for superconductivity.

The magnetization of sample 1 is almost unaffected by the acid treatment and so it was chosen for Curie temperature measurements. The magnetization was measured as a function of temperature, data below 300 K being taken in the SQUID magnetometer, and a high-temperature furnace attachment used to measure up to 800 K. Data indicate that the Curie temperature, T_C , exceeds 800 K. They are consistent with metallic iron, for which T_C is 1043 K.

Definite confirmation that the ferromagnetism of the carbonados is really due to the inclusions of ferromagnetic iron is provided by the Mössbauer spectrum of carbonado 6, shown in Fig. 4. The spectrum is poorly defined because of the small size of the absorber, and the small iron content. Nevertheless, a least-squares fit to a lorentzian sextet with the linewidth constrained as 0.3 mm s^{-1} gives a hyperfine field $B_{\text{hf}} = 32(1) \text{ T}$, an isomer shift $= 0.00(5) \text{ mm s}^{-1}$ relative to iron metal, and a quadrupole shift $\Delta = 0.0(1) \text{ mm s}^{-1}$. Their parameters are those of metallic iron.

Our results are largely consistent with the recent work of Kletetschka et al. [18] who examined the magnetic properties of a series of 20 samples from the CAR. They found evidence of ferromagnetism in room-temperature measurements, with a

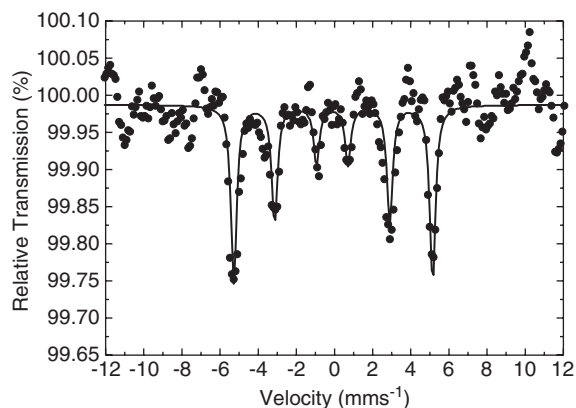


Fig. 4. Mössbauer spectrum at room temperature for sample car1.

saturation magnetization in the range 10^{-4} – 10^{-2} $\text{A m}^2 \text{kg}^{-1}$. From the variation of the ferromagnetic signal on acid leaching, they concluded that the ferromagnetism was mostly associated with magnetic carriers at the surface and in open pores, rather than in the bulk of the material.

In conclusion, we find no evidence from the carbonados for the existence of transition-metal-doped ferromagnetic carbon. Instead, the ferromagnetism is associated with inclusions of metallic iron, iron-based alloys or cobalt.

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