Geochemical analysis of diamond: a reliable and direct method useful in geochemical survey for diamonds

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A geochemical method to identify presence of microdiamond in rock, soil or stream sediment sample, by analysing it directly, is discussed in this communication. Diamond being carbon in composition, C% of the diamond-bearing samples is estimated by analysing them in carbon analyser (Coulomat). Five stream sediment samples from Wajrakarur, an area known for diamond-bearing kimberlite pipes were tested using industrial diamond as reference standard. The 0.125–0.177 mm size samples were treated with a combination of acids, HCl, HNO_3, H_2O_2 and run in an isodynamic separator to separate non-magnetic components. The components were then analysed in X-ray diffractometer and Coulomat. The data shows anomalous values for carbon and indicate presence of diamond in the sample. The method allows detection of diamonds as low as 0.02 mg size reliably and is particularly useful to locate palaeo-placers and primary diamonds of microdiamond variety.

Keywords: Diamond, geochemical survey, microdiamonds, Wajrakarur.

DIAMOND, being the hardest and a weathering-resistant mineral, tends to withstand both chemical and mechanical breakdown in the secondary environment. It remains as a placer mineral in the stream channels and travels longer distances until it gets deposited into suitable traps, producing placer deposits. The geological, geochemical and geophysical methods used extensively in search of diamond are fraught with shortcomings. Geological methods are ineffective if the host rocks (kimberlite etc.) are not exposed or completely eroded. Geochemical methods which make use of the chemistry of the associated minerals like ilmenite, pyrope, diopside, etc. suffer from variation in the type and concentration of associated minerals and hence need modification in the method to locate diamonds in rock[1–4], stream sediment[5] or soil[6] using standard laboratory techniques[7] because of its occurrence in different types of pipe rocks[8] (kimberlite/lamproite) and geological environments[9]. Geophysical methods, though effective in locating (regional or local) potential areas for kimberlite or volcanic pipes[6], do not confirm the presence of diamonds. Both geochemical and geophysical methods

are totally ineffective in the case of recent or palaeo-placer (micro or macro) deposits[6].

Even the analytical methods such as XRD, optical, UV light (fluorescence), infrared, etc. which are used to identify diamonds, are effective only for crystalline and transparent variety but not for the amorphous and opaque. Besides, other sophisticated techniques like high energy X-ray diffraction has hitherto been merely at an experimental stage; and electron microprobe though effective, is expensive and not easily available. Further, these techniques will be effective during the exploitation stage rather than at the exploration stage.

In view of these shortcomings, I propose a new geochemical method particularly suited for prospecting for microdiamonds and providing an alternative for both primary[9] (kimberlite or lamproit pipes) and secondary as a placer (including palaeo-placer), in soils, stream sediments or metamorphosed sediments (Coanjula diamonds, Northern Territory, Australia[6]).

Diamond being carbon, at high temperatures (1200°C) in the presence of oxygen, gets converted to CO_2 gas. The amount of gas which is proportional to the carbon content present in the sample is used to estimate total carbon (%) present in the sample. The samples, prior to analysis, are treated with different acids and heavy liquid bromoform and run in an isodynamic separator (IS). As the procedure demands a particular size range of the sample (particularly IS), 0.125–0.177 mm size range is considered optimum in the present study.

Coulomat-702 is an equipment designed to analyse both carbon and sulphur. It comprises mainly three components, i.e. furnace, titration vessel and analyser. A sample of known weight (mg) is introduced in a specially prepared ceramic boat into the furnace and heated for 5 min at 1200°C in the presence of oxygen. The diamond is burnt and CO_2 is produced and flushed into a titration vessel containing absorbing solution (barium perchlorate). The gas changes the pH of the absorption solution which is pre-set at 10. The potentiometer connected to the vessel nullifies the shift in pH by back titration using electrolysis current. The amount of current consumed in the process is measured in terms of counts. Since the count is directly proportional to the carbon content present in the sample, it is converted to C% using the following standard formula (Coulomat-702 manual).

$$C\% = (Count \times 0.02)/Sample\ weight\ in\ mg.$$

Different quantities of industrial diamond and calcium carbonate (analytical grade) (C = 12%) used as reference standards were analysed repeatedly by using different weights to check the reliability, reproducibility and detection limits of the Coulomat. The values obtained for known weights of industrial diamond are shown in Figure 1. One milligram of diamond in Coulomat gives a count of 5000 [(C% × mg)/0.02]. As the lower limit of detec-

tion in Coulomat in terms of count is reliable up to 100, a grain of 0.02 mg, which gives about 100 counts is detected reliably. The size of the stream sediment sample being used in the analysis ranges from 0.125 to 0.177 mm, a grain of diamond (3.5 density) of 0.177 mm size will approximately weigh $(4/3\pi r^3 \times density)$ about 0.081 mg, and a grain of 0.125 mm size about 0.029 mg. These grains ranging in weight from 0.029 to 0.081 mg will produce the count ranging from 145 to 405. Hence, one grain of diamond in about 500 mg sample (maximum weight used in the boat) will yield C% value ranging from 0.0058 to 0.016.

Prior to Coulomat analysis, industrial diamond was also run in XRD from 5° to 80° (2θ). Interestingly, the diffractogram indicates the presence of two types of diamonds, i.e. transparent variety which shows peaks as expected at 44° and 77° 2θ (Figure 2 a) and opaque variety which does not show any peak at all (Figure 2 b). When analysed in Coulomat, both the types have however, yielded C% as expected because they are essentially carbon in composition.

The proposed method was tested on stream sediment samples collected from Wajrakarur, Anantapur District,

Figure 1. Standard linear curve obtained for industrial diamond (weight vs count).

Figure 2. X-ray diffractogram of *a*, Diamond (transparent variety), *b*, Diamond (opaque variety), and *c*, Non-magnetic component of sample W-3.

Andhra Pradesh, one of the important diamond-bearing areas in India[10] and spread over nearly 200 sq km around Wajrakarur, Lattavaram, Venkatampalle, etc.[11] (Figure 3). Only five samples were chosen for testing out of 23 collected, keeping in view the limitation of facilities and funds (Figure 3).

100 g of 0.125–0.177 mm size fraction was transferred into a glass beaker and heated on hot plate initially with 20 ml concentrated H_2O_2 and then 20 ml concentrated HCl to remove organic carbon, inorganic carbon (including calcite-bearing rock) and also secondary iron oxides/hydroxides[12,13]. The samples were dried after a thorough wash and subjected to heavy liquid (bromoform) separation. The heavies thus collected were washed, dried and run in an isodynamic separator to separate non-magnetic (NM) components at 1.2 ampere (A) at 25°/15° slope settings[12]. Their proportions are given in Table 1. The NM components were scanned under stereo-zoom microscope for artifacts and anthropogenic material if any, and then, run first in XRD to record diamond-related peaks if any, and next in Coulomat. The NM components were analysed together with blank, and blank + standard (spiked) samples which were also processed in the same fashion as stream sediment samples, such as acid treatment, heavy liquid and IS separation to check the reliability of the method and reproducibility of the data (Table 2). All the analytical work was carried out in the Ore Geology Laboratory, Geology Department, Delhi University.

Possible limitations of the method could be (i) its ineffectiveness to separate minerals like silicon carbide (SiC) and other carbon alloys if present in the sample, and (ii) the grain size (0.177 and 0.125 mm) used is close to microdiamond. These limitations are not so serious because (i) melting point of SiC being very high (2730°C) compared to diamond and the temperature used in the method (1200°C), it is not expected to influence carbon data, and (ii) the grain size can be increased provided appropriate analytical instrument is available.

Five samples after the said treatment have yielded different proportions of heavy and light fractions (Table 1). The heavy fraction varies from 5.5 to 38.9 g and the NM component collected at 1.2 A from 0.14 to 0.24 g except for W-5 (5.3). In the heavy mineral fraction, magnetite is a fairly dominant mineral (2–24%) and others like ilmenite, garnet, mica, etc. (recovered between 0.2 and 0.6 A) account for about 48–84%.

Non-magnetic components, when run in Coulomat, have yielded a range of C% values from 0.04 to 0.26. Together with NM components, blank and spiked samples were also analysed in Coulomat for comparison (Table 2). The data of these different types clearly suggest that (i) there is no contribution of carbon from acids/reagents (blank data), (ii) the processing procedure seems to be reliable as the carbon data are quite close to the expected values, i.e. 3000–17,000 count as against 5000–20,000 (blank + standard), and (iii) the C% values recor-
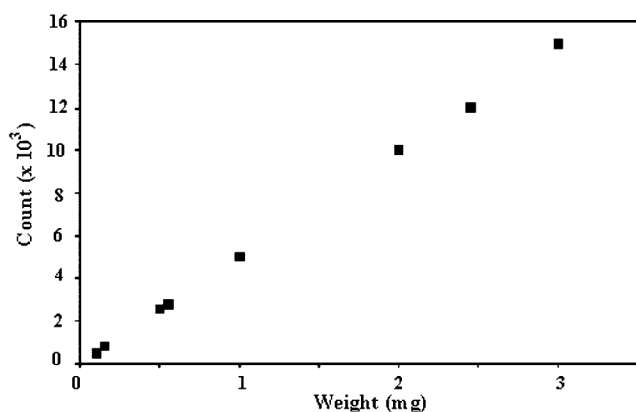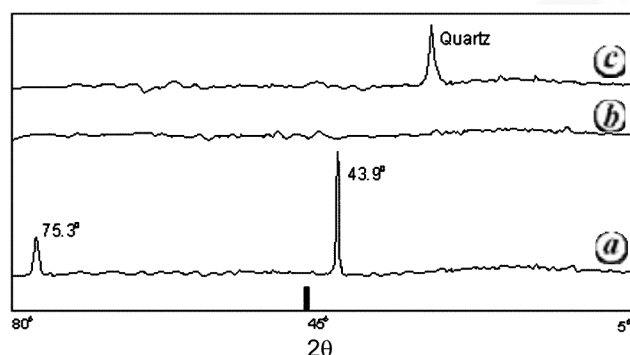
Table 1. Proportion of different weights (g) of heavy, light fractions in the sample and magnetic and NM components recovered at different amperage

		Fraction		Magnetic component						NM at 1.2
Sl no.	Weight used (g)	Light	Heavy	0	0–0.2	0.2–0.4	0.4–0.6	0.6–0.8	0.8–1.2	
				Ampere						
W-1	100 [4]	90.5	5.5	0.4 (7)	0.6 (11)	0.4 (7)	3.26 (60)	0.5 (9)	0.1 (2)	0.24 (4)
W-2	100 [8]	75.7	16.29	0.4 (2)	0.8 (5)	–	11.34 (70)	0.43 (3)	3.11 (19)	0.22 (1)
W-3	50 [10]	22.1	17.89	0.62 (4)	0.3 (2)	1.13 (6)	13.9 (77)	1.8 (10)	–	0.15 (1)
W-4	50 [10]	31.4	8.57	1.12 (13)	–	2.4 (28)	4.85 (56)	0.09 (1)	–	0.14 (2)
W-5	100 [5]	55.1	38.9	9.5 (24)	5.0 (13)	11.0 (28)	7.9 (20)	–	0.2 (1)	5.3 (14)

Values in [ ] indicate the loss due to acid treatment; values in ( ) are percentages.

Table 2. Carbon data (%) for blank, spiked and stream sediment samples

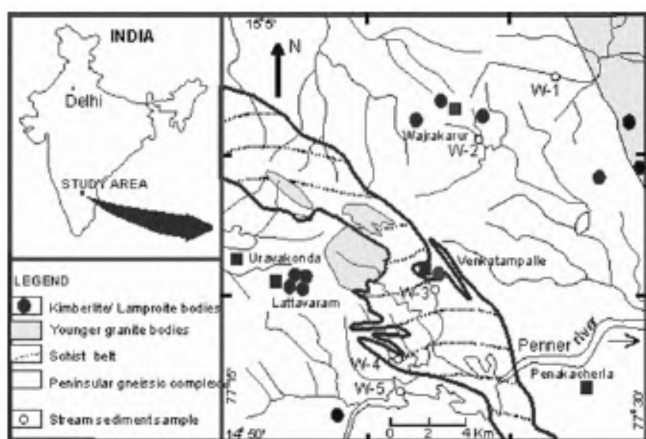| Sample type	Standard addition (mg)	Weight (mg)	Count	C%
Blank	–	110	0	0
Blank	–	120	0	0
Blank	–	135	0	0
Blank + standard	1	140	3000	0.42
Blank + standard	2	135	9000	1.33
Blank + standard	3	155	14800	1.91
Blank + standard	4	120	17000	2.83
W-1	–	240	1794	0.15
W-2	–	220	1410	0.13
W-3	–	150	1223	0.16
W-4	–	140	1829	0.26
W-5	–	128	254	0.04

Figure 3. Geological (after ref. 11) and stream sediment sample location map, Wajrakarur, Anantapur District, Andhra Pradesh.

ded for NM components are related to diamond grains present in the stream sediment sample (unknown).

The C% values in terms of count in case of stream sediment samples (Table 2) range from 254 to 1829. The highest being 1829, the expected weight of the diamond in the sample may be close to 0.4 mg (i.e. 1829/5000). As the weight of the grains in the sample range from 0.029 to 0.081 with an average weight of about 0.055 mg, the number of grains expected to be present is about 6–7

(0.4/0.055). Accordingly, their number is going to be 6 in W-1, 5 in W-2, 4 in W-3, 6 in W-4, and 1 in W-5. Their percentages in the samples analysed are about 0.15, 0.14, 0.16, 0.26 and 0.05 respectively. XRD analysis of the same could not indicate the presence of diamond (Figure 2 c) but showed minor peaks related to quartz. Diamond percentage in the sample being less than 1 is not detectable in XRD analysis even if all the diamonds present are of transparent variety. XRD detects the minerals if they are at minimum 5% in volume in the sample. So, XRD analysis is ineffective in this case.

Among different case studies available in the literature on microdiamonds, the study of Coanjula diamonds from Northern Territory, Australia[6] seems to explain better the need and relevance of the proposed method. In Coanjula area, the diamonds are mostly microdiamonds (<0.4 mm) present in soils and stream sediments, and constitute about 99% of the available diamonds. Interestingly, the aeromagnetic survey[6] carried out in the area was helpful in locating about 20 volcanic pipes within the metamorphosed sediments (murphy metamorphics), but was unable to locate the diamond-bearing metasediments. The Coanjula study, thus, not only demonstrates the shortcomings in the application of geophysical methods but also the ineffectiveness of the associated/indicator minerals in such cases.

In conclusion, the proposed method of analysing diamond directly can yield positive results. It has yielded anomalous values for diamonds in stream sediment samples from Wajrakarur area. SiC or related carbon alloys, if present, do not influence the carbon data due to their high melting points. Diamonds up to 0.02 mg size whether opaque or non-opaque are reliably detected. The proposed method is best suited in locating microdiamonds related to palaeo-placers, kimberlitic, lamproits, non-kimberlitic diamondiferous rocks. This can be effectively used in both soil and stream sediment survey for diamond. The method, though presently supported by limited data, stands on a well-tested technique. Being direct, simple, comparatively cheaper, reliable and effective to all types of naturally occurring diamonds, it has the potential to be a part of exploration programmes.

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Erratum

Biotechnology sector in India: strengths, limitations, remedies and outlook

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The caption for Figure 3 should read: 'Number of biotech trainees selected and absorbed in industry finishing schools'.

We regret the error.

–Editors