SUBMICROSCOPIC DIAMOND WITHIN CARBONATE MELT GLOBULES IN IMPACT MELT BRECCIA FROM DHALA (MOHAR), SHIVPURI DISTRICT, M.P, INDIA. Madhuparna Roy [1], Pranesh Sengupta[2], Pooja Mahadik[2] and Pradeep Pandey[1], [1]Atomic Minerals Directorate for Exploration and Research, New Delhi, Hyderabad, [2]Bhabha Atomic Research Centre, Mumbai, email: madhuparnaroy.amd@gov.in.

Introduction: Diamond is reported for the first time within carbonate melt globules from the Dhala (Mohar) impact structure, Shivpuri district, M.P, India. These carbonate melt globules were petrologically observed in subsurface melt breccia, thereby indicating evidence of rare carbonate-silicate melt immiscibility. Similar immiscible textures are reported from natural carbonatites and in experiments [1]. Laser Micro Raman spectroscopic data of selected spots within the melt globules give characteristic peaks of diamond. The finding of near-surface carbonate melt globules with submicroscopic diamonds re-iterates hypervelocity impact triggering concomitant melting of a largely granitoid target containing minor carbonate supracrustal relicts, evidence of which is observed in drill cores.

Background : The Dhala structure is defined by an oblate central mesa of Kaimur Group of sediments underlain and surrounded by concentric annular rings of Pre-Kaimur Dhala (Sumen Group) and hummocky brecciated Bundelkhand granite outcrop. Previous studies of the structure brought out a spectrum of shock metamorphic features preserved in subsurface samples of voluminous melt breccia and granite bedrock [2]. The shock imprints include planar deformation features (PDFs) in quartz and feldspar, ballen quartz, ladder- and mosaic texture in feldspar, shock melting in feldspar/quartz and diaplectic quartz/feldspar.

Analytical methods : Optical study of thin polished section of melt breccia was carried out under Nikon microscope. Micro Raman spectroscopy, using Horiba JY HR Lab Ram laser micro Raman spectrometer, was performed repeatedly on few dark spots (measuring upto 30µ) within carbonate globules in the same sample of melt breccia. The 514.4 nm exciting line of Spectra Physics Ar^+ laser was used and the size of the laser beam was <2 µm at 100x objective. Micro Raman spectroscopy on additional spots was carried out with STR-300 micro-Raman spectrometer (SEKI Technotron, Japan) and the sample was excited at 532 nm (power ∼20 mW at sample position, continuous wave (CW) YAG laser.

Results:

Petrological study: Thin-polished section study indicates that the minor carbonate in the melt breccia occurs as train of bulbous globules often showing budding-out texture and strongly curved outline with sharp meniscus (Fig.1a) against the surrounding quenched feldspathic glass. These carbonate globules are dotted with fine dark specs (Fig.1b), indeterminable under transmitted and incident light optical microscope. Rarely, the globules show vesiculation and flowage (Fig.1c).

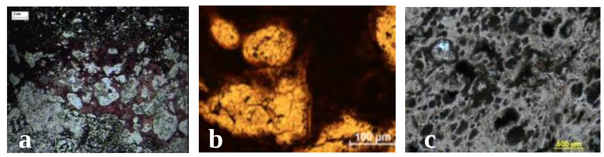

Fig.1a) Carbonate melt globules in felsic glass b) magnified view of globules with dark spots c) transient melt in carbonate showing vesiculation and flow

Micro Raman Spectrometry: Three dark spots (10-20µ across) within the above mentioned carbonate globules were analysed using Horiba JY HR Lab Ram laser micro Raman spectrometer and consistent Raman band positions were obtained at each spot (varying from 1.08 to 3.37 cm^{-1}). The representative Raman spectra, with prominent sharp peaks and narrow FWHM (full width at half band-maximum), show band positions at 1333.29 cm^{-1} (Fig.2a), 1334.47 cm^{-1} and 1334.37 cm^{-1} (standard diamond peak at about 1332 cm^{-1}). An upward shift was noted in the Raman band positions varying from 1.8 to 5.2 $cm-^{1}$ and the variation in the FWHM ranges 3.42 and 7.02 $cm-^{1}$. Four more similar dark spots were analysed using STR-300 micro Raman spectrometer and the corresponding spectra show sharp peaks at 1322.35 cm^{-1}, 1331.78 cm^{-1} (Fig.2b), 1331.98cm^{-1} and 1332cm^{-1}. Laser Micro Raman spectrometry was carried out on all minerals proximal to the diamonds and also on fifty random points in several other samples, but no characteristic peak of diamond was noted at any other point.

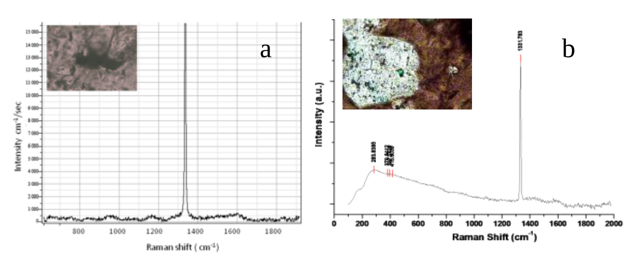

Fig.2a) Raman spectra of a dark spot in carbonate globule using Horiba JY HR Lab Ram laser micro Raman spectrometer (peak at 1333.29 cm^{-1}) and b) Spectra of another similar spos obtained using STR-300 micro-Raman spectrometer (peak at 1331.783cm^{-1}).

Moreover, Raman spectra of the polishing diamond pastes (Fig.3a,b,c) obtained using STR-300 micro-Raman spectrometer, do not match those obtained from the carbonate globules.

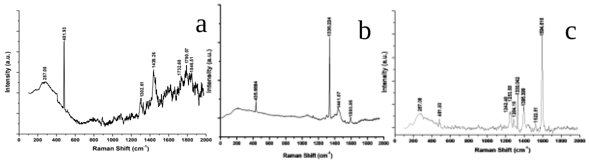

Fig.3.Raman spectra of a) diamond paste (1/4µ) with 1302.69 cm^{-1} peak, b) diamond paste 1µ with 1336.22 cm^{-1} peak and c) diamond paste 6µ with 1330.04 cm^{-1} peak obtained using STR-300 micro-Raman spectrometer.

SEM data: Scanning Electron Microscopy (Zeiss Auriga FE SEM) and X-ray imaging (EDS-Oxford Instrument X-Max^N) were carried out on gold coated (~10 nm) thin sections using a steady beam current of 4 -20 nA accelerated under 20 keV voltage. This documents the primary immiscible texture of the once dynamic melt droplets within a glassy groundmass (Fig.4a). The characteristic micro-Raman diamond peak mentioned above was obtained from one of the globules containing the dark spec (yellow box in Fig 4b). However, the various attributes of the submicroscopic diamond could not be ascertained at this stage.

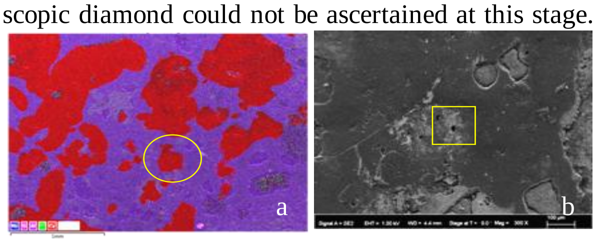

Fig.4.a. EDS Layered image of carbonate globules, bar=1mm b) SE image of white circle of (a); bar=100µm. Spot within yellow box shows characteristic diamond peak by micro Raman spectroscopy.

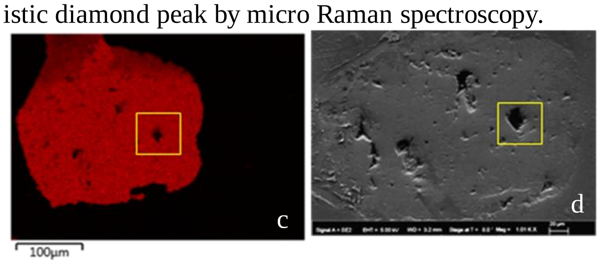

Fig.4c. X-ray image (Ca K∞1 of the same globule; bar = 100µm d) d. Back Scattered Electron image of the same globule (bar = 20µm)

Discussion and conclusion : Micro Raman data of eight different points of dark spots within carbonate melt globules show characteristic diamond peaks with upshift in the band positions and an increase in the FWHM. Such upward variation has earlier been attributed to compressive stress [3,4,5]. X-ray image (Fig.4c) and BSE image (Fig.4d) of one of the several dark spots with characteristic diamond micro Raman peak, shows a square pit-like feature. Since the thin sections were polished with diamond paste of size 6 µm, 1µm and 1/4 µm, micro-Raman spectra of the three diamond pastes were obtained, which show very different spectral patterns with peaks at different points. This, along with the fact that micro Raman spectrometry data of several points in the vicinity and also many other points in several other samples polished similarly, have not revealed any characteristic peaks or pattern of diamond, tends to eliminate the possibility of extraneous diamonds trapped by chance in crevices of carbonate globules. Under impact environment (high T and high shock P) carbonate largely melts at >10 GPa and >2000 K [6]. During post impact stage (high T and lesser shock pressure) this carbonate may undergo decarbonation [1] and the CO_2 thus produced, may reduce to carbon. The thermodynamic possibility of such a reaction {CO_2 (g)$\rightarrow$C (s, diamond) + O_2 (g)} is that ΔH^0 for diamond is +35.4kJ/mole and ΔS^0 is +1.9kJ/mole (at 25°C and 1atm) and hence >0. Thus, ΔG^0 in the reaction $\Delta G^0 = \Delta H^0 - T\,\Delta S^0$ will be <0 at very high temperature, triggering spontaneous recrystallisation of product, making the formation of submicroscopic diamond within carbonate melt globules a thermodynamic possibility under impact environment. The present study, thus, documents carbonate melting (from pre-existing carbonate supracrustal enclaves within the granitoid target) and submicroscopic diamond formation in a near-surface environment due to impact. The exact nature of the submicroscopic diamonds remains a future area of study.

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