Shocked Diamonds in agglutinated foraminifera from the Cretaceous/Paleogene Boundary, Italy – a preliminary report

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ABSTRACT

Washed acid residues from rock samples taken at measured intervals across the Cretaceous/Paleogene boundary (KPB) section at Monte Cònero, Italy, were examined for agglutinated foraminifera to assess their ability to select heavy mineral phases. Examination with scanning electron microscopy (SEM) and electron microprobe has enabled us to identify minerals comprising the outer walls of several agglutinated foraminiferal species, including *Psammosphaera fusca*, and *Reophax* cf. *parvulus*. Modern representatives of these genera are known to preferentially agglutinate heavy minerals. Because of this curious behaviour, we postulated that heavy detrital minerals, including impact ejecta, would have been scavenged by these organisms and incorporated into their tests. We have identified microdiamond likely formed by impact, together with distinctive Ni-Co-rich mineral residues in agglutinated foraminifera from the KPB clay, and also from specimens sampled both above and below the boundary clay. This is the first reported occurrence of impact-related microdiamond associated with the KPB discovered outside North America. We conclude that scavenging of ejecta grains by agglutinated foraminifera is an important process for subsequent bioturbation and redistribution of the ejecta material. The grain-size distribution of the microdiamond is consistent with impact diamond formed uniquely as ejecta from the Chicxulub Crater, but further work is needed.

INTRODUCTION

Shocked diamonds are a product of the physical modifications induced when graphite (pure carbon) is subject to shock metamorphism at the highest pressures. The conversion is direct and simple, requiring only an increase in the interatomic distance within the individual carbon planes of the graphite of 0.12 Å and an increase in the interplanar spacing of 1.86 Å (Lipschultz, 1964). Diamonds are also known to occur as inclusions in iron meteorites (the first reported findings were by Jerofejev & Lachinov, 1888). Impact-derived microdiamonds associated with the Chicxulub impact structure have been reported from the Western Interior of North America, first in Alberta, Canada (Carlisle & Braman, 1991) and then in Montana and Colorado (Gilmour *et al.*, 1992). Subsequently, impact diamonds up to 30 μm in size have been reported from proximal KPB sequences at El Mimbral in NE Mexico (Hough *et al.*, 1997). The carbon isotope composition of the impact diamonds from these localities points to a heterogeneous origin, with most specimens derived from the target rock (Hough *et al.*, 1999), and a minor meteoritic component. Searches for impact diamonds from the KPB have been carried out in Italy (e.g., Gilmour *et al.*, 1992), but thus far diamonds have not been documented from localities outside North America.

Agglutinated foraminifera are ubiquitous inhabitants of the deep ocean, building their tests out of sedimentary particles collected from the sea floor. Numerous species of agglutinated foraminifera exhibit clear affinities towards individual mineral phases, involving a curious ability to distinguish between individual minerals (Heron-Allen & Earland, 1909, 1912; Heron-Allen, 1915; Murray, 1971; Jorgensen, 1977). Certain species of agglutinated foraminifera often preferentially choose relatively dense phase minerals (Heron-Allen & Earland, 1920; Allen *et al.*, 1999), a behaviour that may be related to the species microhabitat. For example, species of *Reophax* have been found to

In: Kaminski, M.A. & Coccioni, R., (eds), 2008. Proceedings of the Seventh International Workshop on Agglutinated Foraminifera. *Grzybowski Foundation Special Publication*, **13**, 57-61.

agglutinate heavy minerals such as topaz, which is normally a very minor component of shallow marine sands in which they live (Heron-Allen, 1915).

In the northern Appenines of Italy, the KPB interval lies within Scaglia Rossa Formation, a nearly pure pelagic limestone. Because the Upper Maastrichtian part of the Scaglia Rossa has an insignificant detrital component, we hypothesised that heavy mineral grains from the impact ejecta settling to the sea floor would have been rapidly scavenged by the agglutinated foraminifera. The purpose of this study was to examine agglutinated foraminifera from the KPB interval to determine whether or not impact-derived minerals are found within their walls, and whether or not minerals scavenged by the foraminifera could have been carried away from the boundary clay layer.

STUDY AREA

Ever since the discovery of iridium by Alvarez *et al.* (1980) in the KPB clay layer near Gubbio, Italy, this layer is widely regarded to be evidence of an extraterrestrial impact event. Subsequent decades of intensive research have amassed a large array of geochemical and mineralogical evidence, including the siderophile elements iridium, nickel, glass spherules, and shocked quartz from localities around the world and impact diamonds from North America (see Carlisle, 1995).

In the Umbria-Marche Basin of NE Italy the KPB clay layer is contained within red or white pelagic limestones of the Scaglia Rossa Formation. At the classic localities near Gubbio, the exposure is often incomplete and the clay layer has been almost totally removed by decades of sampling. The Monte Cònero section (Fig. 1) was selected for its more complete exposure including the 3 cm-thick boundary clay itself. The section contains only a minute amount of detrital material (less than 1% sand fraction). The Monte Cònero promontory constitutes the easternmost anticline of the northern Appenine thrust and fold belt of Italy. The Umbria-Marche carbonate succession is exposed here from the middle part of the Maiolica Formation up to the Schlier Formation of late Miocene (Tortonian) age. The Maastrichtian to Paleocene interval exposed in Fonte d'Olio Quarry consists of pelagic limestones, that are interbedded with coarse calcarenite turbidites of various thickness. The Maastrichtian part is whitish all the way up to the KPB, whereas the basal Paleocene limestones are more yellowish in colour (Montanari & Koeberl, 2000).

MATERIAL & METHODS

For the purpose of this study, the KPB at Monte Cònero was sampled at regular 5-cm intervals from 15 cm below the clay layer (taken as 0 cm) to 80 cm

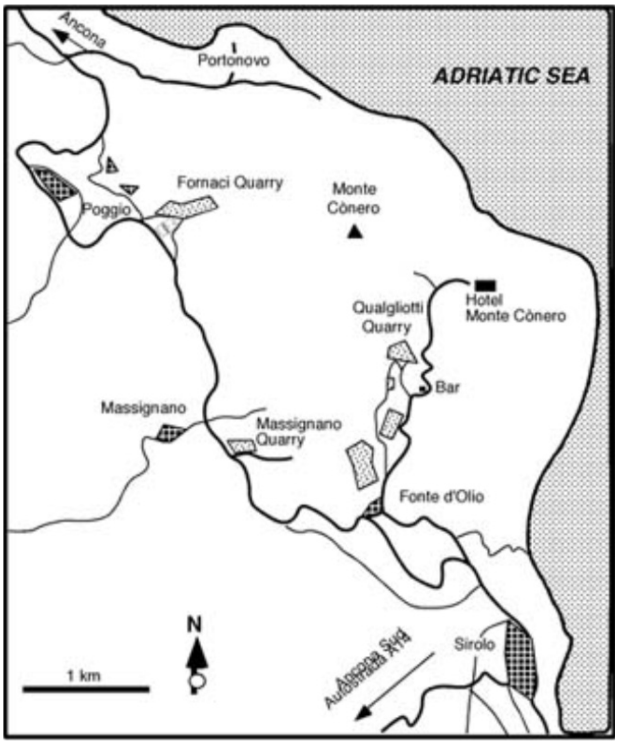

Figure 1. Location of the Fonte d'Olio section at Monte Cònero (from Montanari & Koeberl, 2000).

above. Samples of 100 grams of limestone were used from each interval, crushed by hand with a pestle and mortar and were left for 48 hours in a solution of dilute hydrochloric acid (one part HCl to 5 parts water) to dissolve the carbonate. A total of 60 grams of clay was washed from the KPB clay layer. This sample was left for 48 hours in a peroxide solution to disaggregate. All samples were washed over a 63 μm sieve and the residue left to dry overnight in a 70°C oven. Approximately 200 agglutinated foraminifera were picked from each sample and mounted on reference slides.

From each slide, five or six specimens (the largest and most complete infaunal forms) were mounted on aluminium stubs to be introduced into the microprobe/SEM. The infaunal forms (largely belonging to the genera *Reophax* and *Subreophax*) were selected because modern representatives are known to be motile, and we suspected that these organisms actively scavenged ejecta-derived minerals from the sediment.

For scanning electron microscopy (SEM) analysis, specimens were mounted on aluminium stubs and coated with carbon before being introduced into the vacuum chamber of the JEOL Superprobe 733 fitted with an energy dispersive system (EDS). Images were obtained using the secondary electron, backscattered electron, and cathodolumescence detectors. Photographs were taken so that a point correlation with EDS could be made. Semi-quantative point analysis was performed on individual mineral grains.

RESULTS

Complimentary spectroscopic techniques identified the predominant minerals in the tests of the studied foraminifera to be primarily quartz and feldspar, with a number of unusual minerals present as trace constituents. These comprise a minor proportion of the test, and are believed to be extraterrestrial in origin and associated with the Chicxulub impact ejecta. From the KPB layer itself several specimens, including *Reophax* cf. *parvulus* (Pl. 1, Fig. 1A) and *Psammosphaera fusca* (Pl. 1, Fig. 2A), revealed grains of microscopic (~2 μm) carbon. Photomicrographs were taken with electron backscatter (Pl. 1, Fig. 1B) and secondary electron imaging (Pl. 1, Fig. 1C). Additionally the carbon phase did not produce cathodoluminescence which is distinctive of graphite (Pl. 1, Fig. 1D; also EDS spectrum of carbon phase (Pl. 1, Figs 1E and 3E). In view of the significance of this carbon mineral, we further analysed two specimens using micro Raman, but we were unable to confirm the diagnostic diamond peak at 1332Å, probably due to the very small size of the grains, which are at the limit of resolution of the instrument used.

Additional non-silicate minerals identified in the test of a specimen of *Psammosphaera fusca* included tiny grains of a metallic phase with distinctive, cobalt and nickel (total contribution several percent). Electron microprobe EDS analysis (Pl. 1, Fig. 2B) indicated a complex composition with Mn, Cu, minor sulphur, and an alumino-silicate component probably derived from beam overlap onto surrounding clay minerals. The Ni and Co are not in proportions similar to meteorites, but the high Co/Ni ratio suggests these elements have been highly fractionated. Such fractionated siderophile element residues (especially Ni and Co) are important fingerprints of meteoritic impact events (Kearsley *et al.*, 2004). Additional suspected microdiamonds, with comparable diagnostic features to those found at the KPB, were also observed in specimens of Reophax cf. parvulus from samples collected 6 cm above the boundary (Pl. 1, Figs 3A, 3B, 3C and 3D) and 5 cm below. However, they were not found in our samples collected at other stratigraphic levels and appear to be restricted to samples collected within 5-6 cm above or below the KPB layer.

DISCUSSION

Because of the tendency of some species of agglutinated foraminifera to select and concentrate certain mineral grains into their test wall, these organisms constitute an important signal enhancer for otherwise widely dispersed grains. In deep-sea pelagic environments, the normal choice of agglutinated materials used by the agglutinated foraminifera is aeolian quartz, but when presented with a choice the infaunal species in particular tend to select heavy (dense) mineral phases, a behaviour already noted a century ago by Heron-Allen & Earland (1909, 1920). In the case of the Upper Cretaceous–Paleogene Scaglia Rossa Formation of Italy, the substrate consisted almost entirely of pelagic carbonate (97–98%), with only a minor admixture of terrigenous silt and clay. Acid residues of these limestone samples consist almost exclusively of agglutinated foraminifera that have constructed their tests of silt-sized grains of aeolian quartz. The extremely low background concentration of detrital mineral grains within the Scaglia Rossa Formation increases the probability of impact-derived grains being incorporated into the tests of the agglutinated foraminifera. Additionally, because certain genera of agglutinated foraminifera are known to burrow as deeply as 15-20 cm in deep marine sediments (Kaminski *et al.*, 1988), we postulated that these organisms might be responsible for the subsequent redistribution of ejecta grains across the KPB layer.

The spectroscopic evidence from the microprobe investigation suggests a minor fraction of the minerals contained within the test walls of the studied agglutinated foraminifera are allotropes of carbon that are cathodoluminescence active. This evidence is consistent with the signature of impact microdiamond. In particular, Hough *et al.* (1999) noted a size grading in the impact diamonds away from the impact crater within the North American localities, and speculated that diamonds might be too small to be detected at more distal sites. It is particularly important that the size distribution of diamonds at Monte Cònero (5-10 μm) is consistent with the expected size distribution of impact diamonds from the Chicxulub impact crater, using the first order model proposed by Pope (2002) and Claeys *et al.* (2002) for shocked quartz.

Due to the formation conditions of microdiamonds, their origin uniquely points to an impact, presumably from the Chicxulub crater, which would limit its occurrence during deposition solely to the KPB clay. This implies that diamonds found both above and below the KPB must have been scavenged and redistributed by the burrowing foraminifera. It must be noted that the 6 cm is the post compaction depth which may equate to approximately 10 cm before burial. Such motility of an organism allows for their study as biological vectors of sedimentary particle redistribution.

The discovery of presumed impact diamonds outside of North America is highly significant. The nearby KPB outcrop in Petriccio, Italy, was studied by Gilmour *et al.* (1992), but neither stepped combustion nor TEM analyses revealed any carbonaceous components. Carlisle (1995) believed that the extremely small size of the diamonds would exclude their presence from marine localities, as they would not settle through the water column. However, neither author searched for these grains within the walls of the agglutinated foraminifera. It seems that the ability of these organisms to concentrate the ejecta signal may prove of great benefit to the wider investigation of impact processes at the KPB.

CONCLUSIONS

We have identified microdiamonds and metalliferous Co and Ni-rich grains within the walls of agglutinated foraminifera associated with the KPB interval in the Monte Cònero section in Italy. This is the first report of impact-derived diamonds at this stratigraphic level outside of North America, consistent with derivation from Chicxulub.

Infaunal agglutinated foraminifera (*Reophax* cf. *parvulus*) sampled from 5-6 cm above and below the KPB clay layer were also found to contain microdiamonds. Therefore, scavenging of ejecta grains by agglutinated foraminifera is an important process for the subsequent bioturbation and redistribution of the ejecta material in the deep-marine environment.

ACKNOWLEDGEMENTS

We thank Andy Beard (Birkbeck/UCL) for his assistance with the SEM/EDS and for reviewing the paper. Simone Galeotti and the postgraduate micropalaeontology students at the University of Urbino helped with the fieldwork. This study was supported by travel grants from the EEC Socrates Program. This is contribution nr. 83 of the Deep-Water Agglutinated Foraminiferal Project, and nr. 23 of the Centro di Geobiologia, UU.

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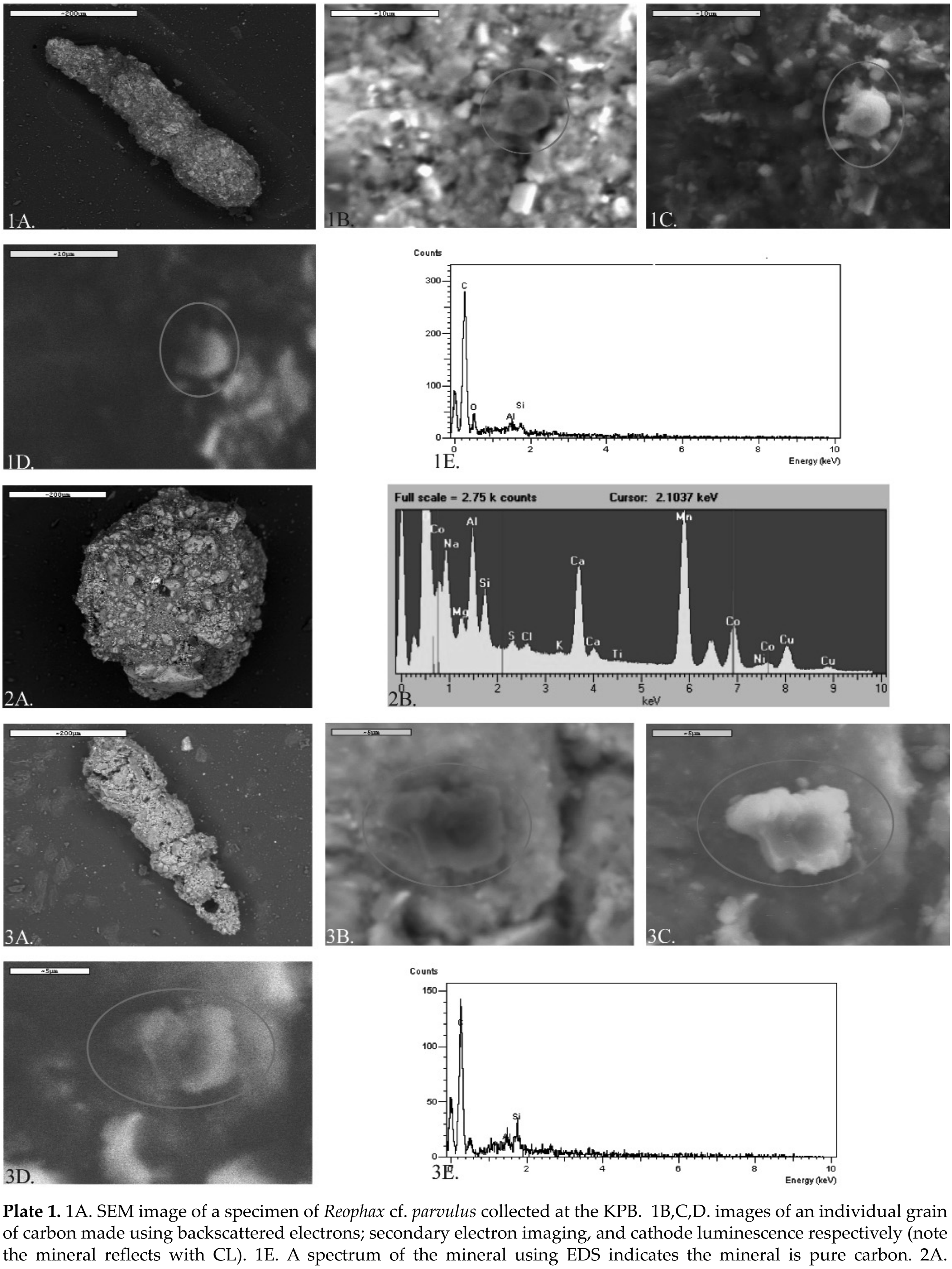

Plate 1. 1A. SEM image of a specimen of *Reophax* cf. *parvulus* collected at the KPB. 1B,C,D. images of an individual grain of carbon made using backscattered electrons; secondary electron imaging, and cathode luminescence respectively (note the mineral reflects with CL). 1E. A spectrum of the mineral using EDS indicates the mineral is pure carbon. 2A. Specimen of *Psammosphaera fusca* collected at the KPB. Similar carbon grains were also identified in this test. In addition, several fractionated siderophile element residues with Co and Ni and spectra similar to that in figure 2B were observed in the test. 3A. Specimen of *Reophax* cf. *parvulus* collected 5-6 cm above the KPB. 3B,C,D. One of several carbon grains illustrated with electron backscatter, secondary electron imaging and cathodoluminescence respectively. 3E. The spectrum indicates this mineral is pure carbon.