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

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 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 cathodoluminescence detectors. Photographs were taken so that a point correlation with EDS could be made. Semi-quantitative point analysis was performed on individual mineral grains.
the infaunal species in particular tend to select aeolian quartz, but when presented with a choice materials used by the agglutinated foraminifera is environments, the normal choice of agglutinated organisms allows for their study as biological vectors of sedimentary particle redistribution.

DISCUSSION

Because of the tendency of some species of agglutinated foraminifera to select and concentrate certain mineral grains into their test walls, these organisms constitute an important signal enhancer for other- where 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 construct- ed 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 postu- lated that these organisms might be responsible for the subsequent redistribution of ejecta grains across the KP layer.

The spectroscopic evidence from the microprobe investigation suggests a minor fraction of the min- erals 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 microdia- mond. 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 microdia- monds, their origin uniquely points to an impact, presumably from the Chicxulub crater, which would limit its occurrence during deposition solely to the KP clay. This implies that diamonds found both above and below the KP 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 vec- tors of sedimentary particle redistribution.

The discovery of presumed impact diamonds outside of North America is highly significant. The nearby KP outcrop in Petriccio, Italy, was studied by Gilmour et al. (1992), but neither stepped combus- tion nor TEM analyses revealed any carbona- ceous 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.

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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.