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Impact ejecta in upper Eocene deposits at Massignano, Italy

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Abstract–Previous workers have shown that an impact ejecta layer at Massignano, Italy contains a positive Ir anomaly, flattened spheroids (pancake spherules), Ni-rich spinel crystals, and shocked quartz with multiple sets of planar deformation features. Because of sample sizes and work by different investigators, it was not clear if the shocked quartz is associated with the Ir anomaly and pancake spherules or if it belongs to a separate impact event. To address this problem, we carried out a high-resolution stratigraphic study of this ejecta layer. The ejecta layer was sampled continuously at 1 cm intervals in two adjacent columns. The carbonate was removed with dilute HCl, and the non-carbonate fraction was gently sieved. Pancake spherules were recovered from the 250–500 μm size fraction and counted. At the peak abundance, the number of pancake spherules in the 250–500 μm size fraction is about 6–7/g of sample. The pancake spherules removed from the 250–500 μm size fraction are mostly translucent to opaque pale green, but some have a grey color or dark opaque patches due to a coating of Ni- and Cr-rich spinel crystals. Energy-dispersive X-ray analysis and X-ray diffraction data indicate that the green spherules are composed of iron-rich smectite, probably nontronite. Black opaque spinel stringers (dark spinel-rich pancake spherules), usually <200 μm across, can be seen in a polished section of a block that includes the ejecta layer. None of the dark spinel-rich pancake spherules were recovered from the sieved non-carbonate fraction due to their fragile nature, but we believe that they are from the same impact event as the green pancake spherules. The <250 μm size fractions from both columns were disaggregated using ultrasonics and re-sieved. The 63–125 μm size fractions were then searched for shocked quartz using a petrographic microscope. At the peak-abundance level, the number of shocked quartz grains in the 63–125 μm size fraction is about 7/g of sample. Some of the shocked quartz grains have a "toasted" appearance. These grains have a brownish color and contain a patchy distribution of faint, densely spaced planar deformation features (PDFs). Polymineralic fragments containing one or two shocked quartz grains with one or two sets of PDFs were observed. They appear to have an organic matrix and are probably fragments of agglutinated foraminiferal tests. We searched for, but did not find, coesite or shocked zircons. We found that the peak abundance of the shocked quartz is within a centimeter of the peak abundance of the green pancake spherules. We conclude that the pancake spherules are diagenetically altered clinopyroxene-bearing spherules and that the shocked quartz, green (and presumably the dark spinel-rich) pancake spherules, and Ir anomaly all belong to the same impact event. This conclusion is consistent with previous suggestions that the cpx spherule layer may be from the 100 km-diameter Popigai impact crater in northern Siberia.

INTRODUCTION

Spherule layers have been found in upper Eocene deposits at numerous sites around the world (e.g., Glass et al. 1985; Sanfilippo et al. 1985; Keller et al. 1987; Vonhof and Smit 1999; Glass et al. 1998; Liu and Glass 2001). The number of upper Eocene spherule layers has been a matter of dispute, with the estimated number ranging from two to eight or more (Glass et al. 1985; Keller et al. 1987; Hazel 1989; Miller et al. 1991). However, more recent studies appear to support the conclusion that there are only two: 1) the North American microtektite layer; and 2) a microkrystite layer, also known as a crystal-bearing or clinopyroxene-bearing spherule layer (e.g., Wei 1995; Whitehead et al. 2000).

The North American microtektite layer has been found in the Gulf of Mexico, the Caribbean Sea, on Barbados, and in the northwest Atlantic Ocean off New Jersey (Glass et al. 1985, 1998; Sanfilippo et al. 1985; Thein 1987; Keller et al. 1987; McHugh et al. 1996). It has an age of ~35.5 Ma (Obradovich et al. 1989) and may have been derived from the Chesapeake Bay impact crater (Poag et al. 1994; Koeberl et al. 1996). Shocked quartz and feldspar with planar deformation features, coesite, stishovite, and reidite (a high-pressure polymorph of zircon) have been found associated with this layer (Thein 1987; Glass 1989; Glass and Wu 1993; Glass et al. 1998; Glass and Liu 2001).

The clinoproxene-bearing (cpx) spherule layer is slightly older (~10 to 20 thousand years) than the North American microtektite layer (Glass et al. 1998) and appears to be global in geographic extent (Glass 2002). Many clinopyroxene-bearing (cpx) spherules contain rare to common Ni- and Cr-rich spinel crystals. In some of the cpx spherules, the spinel crystals are concentrated at the surface (Glass et al. 1985). Furthermore, the cpx spherule layer is associated with a positive Ir anomaly (Alvarez et al. 1982; Glass et al. 1985; Kyte and Liu 2002) but is usually not associated with shock-metamorphosed mineral grains.

Montanari et al. (1993) reported the discovery of a positive Ir anomaly, with a peak of 156 ± 19 ppt, at 5.61 m in upper Eocene deposits (calcareous nannofossil NP19/20 Zone) at Massignano, Italy. Two other Ir anomalies have been reported at Massignano (see Montanari and Koeberl 2000), but in this study, we only deal with the lower anomaly at 5.61 m. This section has been formally established as the Global Stratotype Section and Point (GSSP) for the Eocene/Oligocene boundary (Premoli Silva and Jenkins 1993). Clymer et al. (1996) discovered shocked quartz grains in a 9 cm-thick layer centered at 5.58 m, which they presumed to be the same age as the Ir anomaly. Pierrard et al. (1998) discovered flattened (or pancake-shaped) spheroids that range from translucent green to dark opaque. According to Pierrard et al. (1998), the dark spherules are spinel-rich and represent ~80% of the spheroids. They state that the green spheroids are composed of smectite and contain rare dendritic and octahedral spinel crystals often concentrated along the outer rim of the spheroids. Pierrard et al. (1998) also measured the Ir content and found a peak concentration of ~280 ± 20 ppt, which is somewhat higher than the value reported by Montanari et al. (1993). Pierrard et al. (1998) found that the spinel and flattened spheroids (pancake spherules) occur at the same level in the section as the Ir anomaly, at least within the sample spacing of 6 to 10 cm.

Although Pierrard et al. (1998) were not sure if the pancake (or flattened) spherules belong to the cpx spherule layer, the North American microtektite layer, or another upper Eocene spherule layer, we believe that the green flattened spheroids are probably diagenetically altered cpx spherules, which are known to contain spinel crystals and to be associated with an Ir anomaly. However, cpx spherules were not known to be associated with shock-metamorphosed mineral grains. Thus, it seemed possible that the shocked quartz might be slightly younger and represent ejecta related to the North American microtektite layer. The sedimentation rate in the upper Eocene section at Massignano was about 6.6 cm/ka (23.3 m/3.5 Ma; Montanari et al. 1993). Thus, if present, ejecta (e.g., shocked quartz) from the North American microtektite event would be only ~7 cm above the pancake spherules and Ir anomaly. Because the shocked-quartz study by Clymer et al. (1996) was made on a different suite of samples than were used for the Ir and spinel studies and because the samples covered vertical intervals of 6–10 cm, there was the possibility that the peak abundance of shocked quartz might be as much as 7 cm above (or below) the Ir anomaly.

The purpose of this investigation was to make a high-resolution stratigraphic study across the ejecta layer at Massignano to determine if the shocked quartz is associated with the pancake spherules and, therefore, with the Ir anomaly or if the peak abundance of the shocked quartz occurs above (or below) the pancake spherule layer. We found that the shocked quartz grains are, indeed, associated with the green pancake spherules

METHODS

A block of rock measuring about 15 cm wide by 15 cm high by 11 cm deep was taken across the ejecta layer at Massignano. The center of the block was about 5.62 m above the base of the section (the peak of the Ir anomaly is at about 5.61 m). In the laboratory, the block was mounted in epoxy to prevent it from falling apart while being cut by a saw. Two vertical columns, about 2.5 cm across, were cut from the block taking care to avoid any obvious burrows that are common in the Massignano section (Huber et al. 2001). The columns were cut horizontally every centimeter to produce a continuous series of slices about 8 mm thick. Each slice was then weighed and placed in a beaker. Dilute HCl was added to dissolve the carbonate and help disaggregate the slices. After reaction ceased, the HCl solution was diluted with water and, after settling, the liquid was siphoned off. This was repeated until the acid was removed and then the samples were gently sieved. The 250–500 μm-size fractions were dried, and the number of pancake spherules in each slice was determined. The <250 μm-size fractions were disaggregated using ultrasonics and sieved into <63, 63–125, and 125–250 μm-size fractions. The 63–125 μm-size fraction from each slice was carefully sprinkled on a petrographic slide and then covered with index oil and a glass coverslip. Each slide was then examined using a petrographic microscope, and the grains containing planar deformation features (PDFs) were counted.

Counting of the pancake spherules was done by one observer, and counting of the grains with PDFs was done by another observer. The results were then compiled and plotted.

The counting of the number of grains with PDFs in each sample was done without knowledge of the sample depth in the section. This procedure was carried out for the two adjacent columns, and the results were compared to determine the effects of bioturbation. Since a well-defined peak in abundance of pancake spherules and shock-metamorphosed grains was found in each column, and since we obtained similar results for both columns, we assume that bioturbation was not a major problem. Many of the samples contained some epoxy, which was recovered and weighed after sieving. The weight of the epoxy was subtracted from the original weight of each slice to give the actual sample weights, which were generally between 15 and 20 g.

Some of the pancake spherules were studied by X-ray diffraction, scanning electron microscopy (SEM), and energy dispersive X-ray (EDX) analysis. A JEOL 6335S, cold cathode field emission SEM with an attached JEOL backscattered electron (BSE) detector and a PGT energy dispersive X-ray spectrometer were used in this study. The SEM was operated at 15 kV.

While counting the grains with PDFs in the samples, it was noted that some polymineralic fragments contained quartz grains with PDFs. To determine if the polymineralic grains are rock fragments or agglutinated foraminiferal test fragments, the 125–250 μm fraction of a sample from the ejecta layer was mounted in epoxy on a 2.54 cm (1 inch) diameter glass disc, ground down, and polished to make a polished grain mount. The grains were observed using a petrographic microscope, and polymineralic fragments containing quartz grains with PDFs were photographed at different magnifications. The photographs were then used to locate the polymineralic fragments containing shocked quartz grains using a binocular microscope with up to 50× magnification. Arrows pointing to the grains were scratched into the epoxy and numbered so that they could be correlated with the photographs. The grains were then studied by SEM and EDX.

X-ray diffraction (XRD) patterns were obtained for some translucent, colorless to white opaque quartz grains using a Gandolfi camera to determine if coesite was present.

RESULTS

The pancake spherules that we recovered from the 250–500 μm-size fraction are all green, but some have grey to black regions due to a coating of spinel crystals. A few of the pancake spherules are almost completely coated with spinel crystals (Fig. 1). No completely dark spherules were recovered from this size range. The green pancake spherules are up to about 600 μm in diameter with thicknesses varying between 10 and 100 μm. There is a rough positive correlation between thickness and diameter. Some are oval in shape, but teardrop and dumbbell forms were not observed. A few irregular pancake spherules may have originally been fragments or may have been broken during processing. SEM/EDX analysis of one pale green spherule and XRD study of another indicate that they are iron-rich smectite, probably nontronite.

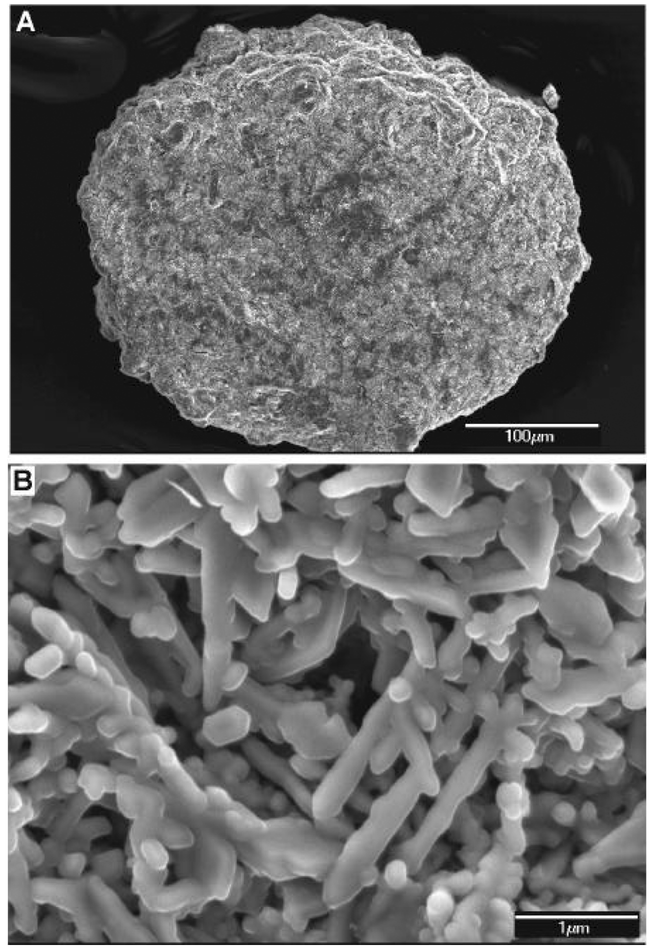

Fig. 1. Scanning electron microscope images of a pancake spherule from the impact ejecta layer at Massignano, Italy: a) pancake spherule; b) Ni-rich spinel crystals on the surface of the pancake spherule in (a).

Because we did not find any dark pancake spherules in the 250–500 μm-size fraction, while Pierrard et al. (1998) reported that most of the spherules are dark opaque and generally in the 100–200 μm-size range, we processed another column and recovered the 125–250 μm-size fraction without use of ultrasonics. We only recovered a few dark pancake spherules in the 125–250 μm-size fraction. We then examined a polished section through the section of interest. We observed a few green pancake spherules, some with a dark layer of spinel crystals on the surface, within the level of highest concentration based on the processed samples. We also observed numerous thin (10 μm or less) streaks or stringers of spinel crystals, usually <200 μm in length; some are irregular in shape and up to a millimeter in length (overlapping smaller stringers?). These stringers, like the green pancake spherules, have their long axes parallel to bedding. They seem to be scattered throughout the section without any obvious peak in abundance, but it is difficult to get a good count in the polished section. These dark spinel-rich stringers appear to be the dark pancake spherules discussed by Pierrard et al. (1998), and they make up at least 80% of the pancake spherules as stated by Pierrard et al. However, they are very fragile and fall apart during acid treatment and sieving.

In one column, the total number of quartz grains observed was ~19,300. At the peak abundance, ~5% of the quartz grains contained PDFs. Of the grains with PDFs, approximately 21% had one set of PDFs, ~37% had two sets, and the remaining 42% had three or more sets (Figs. 2a–2c). A number of the grains have a "toasted" appearance (Short and Gold 1996). These grains are translucent with a brownish color and contain multiple sets of faint, closely packed indistinct PDFs in patches (Fig. 2d). Furthermore, a number of polymineralic fragments were observed that contain one or more quartz grains with up to two sets of PDFs (Fig. 3).

Because the samples contain agglutinated foraminifera, it seemed possible that some, or all, of the polymineralic fragments might be fragments of agglutinated foraminiferal tests. Another possibility was that the grains are rock fragments, which could indicate the type of target rock present at the source crater. However, SEM and EDX studies show that the matrix material in the polymineralic fragments is carbon-rich with a high Cl content (Cl/C ratio of ~0.4). The

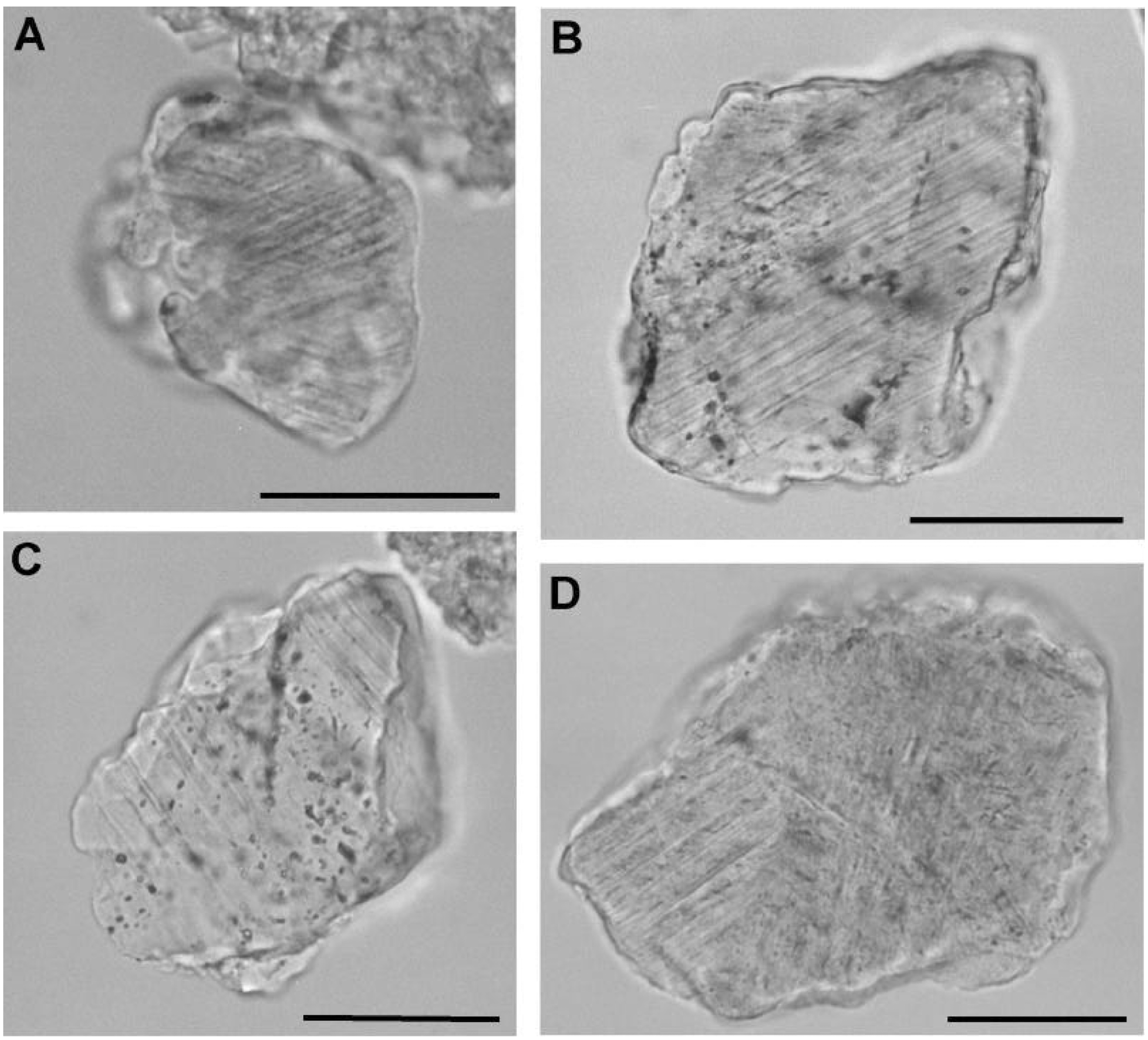

Fig. 2. Photomicrographs of shocked quartz from the impact ejecta layer at Massignano, Italy: a) shocked quartz with two sets of PDFs; b) shocked quartz with one set of planar features; c) shocked quartz with two sets of PDFs; d) "toasted" quartz with at least three sets of faint PDFs in a patchy distribution. (a) and (c) are from the 5.64–5.65 m level, (b) is from the 5.62–5.63 m level, and (d) is from the 5.61–5.62 m level. All scale bars are 50 μm.

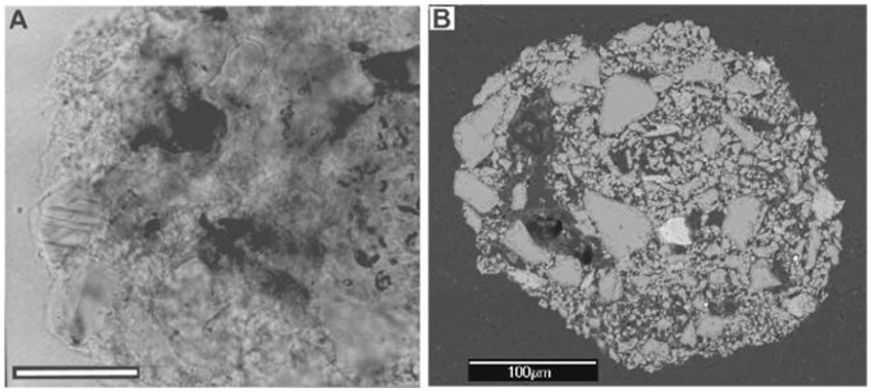

Fig. 3. Polymineralic fragment from the impact layer at Massignano, Italy: a) petrographic microscope image in transmitted light. Note the grain with two sets of planar features on the left side just below the center. The scale bar is 50 μm; b) backscattered electron image of same fragment as in (a) with approximately the same orientation. The light grey grains are mostly quartz, but a few are Na-rich feldspar. The brighter grain near the center is K-feldspar. The darker grey matrix material is carbon- and chlorine-rich. It is similar in appearance and composition to the epoxy that the fragment is mounted in but has a higher Cl/C ratio.

same composition was observed in the matrix material in the agglutinated foraminiferal tests. In addition, the mineralogy of the fragments containing shocked mineral grains is similar to that of the agglutinated foraminiferal tests; i.e., ~80% quartz, 15% K-feldspar, and 5% Na-rich feldspar by number. Thus, it appears that the fragments containing shocked mineral grains are probably fragments of agglutinated foraminiferal tests.

White opaque grains consisting of mixtures of quartz and coesite have previously been found associated with the Australasian and North American microtektite layers. X-ray diffraction patterns were made for 23 translucent cloudy to white opaque quartz grains from the Massignano samples, but none of the patterns indicated the presence of coesite. Four zircons were recovered, but none showed evidence of shock metamorphism as indicated by their appearance (i.e., they were transparent) and XRD patterns (i.e., no sign of X-ray asterism, baddeleyite, or reidite).

We determined the distribution of the green pancake spherules (250–500 μm in diameter) and shocked quartz grains (125–250 μm in size) in the two adjacent columns. In both columns, the peak abundance of the pancake spherules (~6–7/g of sample) occurs at the 5.62–5.63 m level, and the peak abundance of quartz grains with PDFs (~5–9/g of sample) occurs at 5.61–5.62 m, or about 1 cm below the peak abundance of the pancake spherules (Fig. 4). Thus, it seems that the shocked quartz grains do not belong to a younger event as we had hypothesized before this study, but rather, it appears that the shocked quartz and pancake spherules (and presumably the Ir anomaly) were all produced by the same event.

DISCUSSION

Clymer et al. (1996) reported a maximum of 1.6 ± 0.4 quartz grains with planar deformation features (PDFs) per cubic centimeter of sediment. We found a peak abundance of 7 ± 2 quartz grains with PDFs per gram of sample. We estimate that the specific gravity of the Massignano samples is about 2.4 g/cm^3. This means that at the peak abundance, the number of shocked quartz grains is about 16.8 ± 4.8/cm^3 of sample (i.e., about an order of magnitude higher than reported by Clymer et al. [1996]). Part of the difference is due to the large samples used by Clymer et al. (1996). The peak abundance that Clymer et al. reported was for a 9 cm-thick layer. In contrast, we obtained a continuous series of samples at 1 cm intervals through the ejecta layer. Our average over a 9 cm-thick section centered on Clymer et al.'s (1996) layer is closer to what Clymer et al. found but still about three times higher. This might be due to the identification of "toasted" quartz in this study, which was not mentioned by Clymer et al. (1996).

Some of the upper Eocene cpx spherules have a coating of spinel crystals similar to that observed on the Massignano pancake spherules, especially the small dark cpx spherules found at Site 709 in the western Indian Ocean (Fig. 5). The ratio of cpx spherules that are heavily coated with spinel crystals to those that have few or no spinel crystals at the surface seems to be much lower than the ratio between black and green pancake spherules at Massignano. However, it appears that more of the cpx spherules at Site 709, as well as other sites, originally had a heavy coating of spinel crystals that was partially or almost completely removed due to solution of the adjacent and underlying glass. We have often observed cpx spherules with a high concentration of spinel crystals at their surfaces (Fig. 5). In some cases, spinel crystals are sitting on glass pedestals (Fig. 5). Just a little more solution and they would have been freed from the surface of the spherule. Thus, it is likely that many of the cpx spherules had a thick coating of spinel crystals before dissolution of the glass matrix at the surface of the spherules. If the cpx spherules all originally had the same thickness of spinel crystals on their surfaces, then the smaller ones would have a higher ratio of spinel to glass (and clinopyroxene).

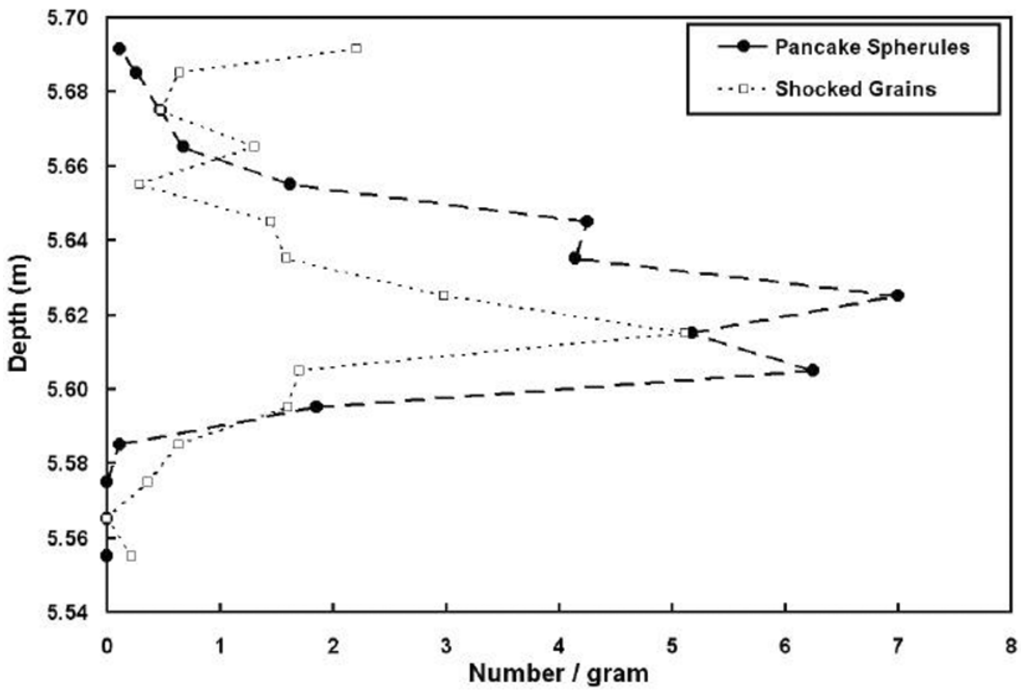

Fig. 4. Plot of abundance of pancake spherules and shocked quartz through the impact ejecta layer at Massignano, Italy.

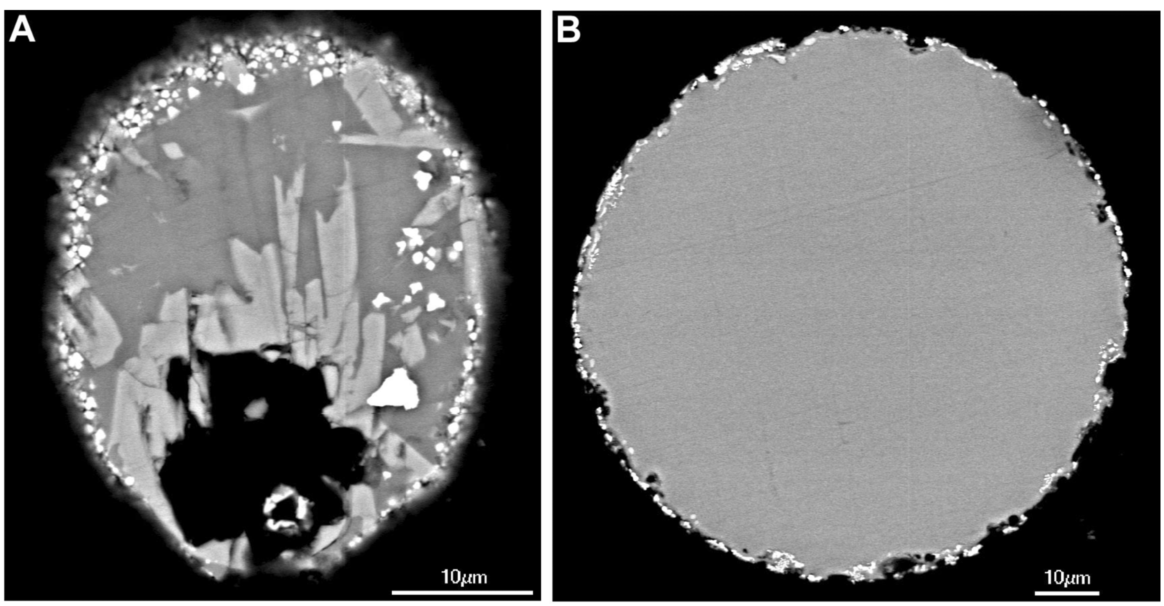

Fig. 5. Backscattered electron images of spherules from the upper Eocene cpx spherule layer at Site 709 in the western Indian Ocean, with spinel crystals concentrated at the surface: a) oval-shaped dark grey cpx spherule. The white crystals near and on the surface are spinel. The light grey bladed crystals are clinopyroxene. The darker grey matrix is glass; b) translucent brown sphere with spinel crystals (white) concentrated at the surface. Many of the spinel crystals are on glass pedestals. Additional dissolution would have freed the spinel crystals from the spherule.

After diagenetic alteration, the smaller spherules would be darker and more friable as a result of their higher concentration of spinel crystals.

We used the present sizes of the green pancake spherules to estimate their original diameters before diagenesis and compaction, assuming that they were originally spherical in shape. This was done by calculating the volumes of the pancake spherules and then determining the diameters of spheres having the same volumes. This indicates that pancake spherules at Massignano had diameters up to ~360 μm and that the number of spherules increases with decreasing diameter. This agrees with the size distribution of cpx spherules found at other sites. Cpx spherules are most abundant in the 63–125 µm-size fraction and range up to about 400 µm in diameter (Glass et al. 1985; Keller et al. 1987). Using the pre-compaction diameters and the number of pancake spherules per cubic centimeter, we determined that the number of spherules (>125 µm)/cm^2 at Massignano is ~46. This concentration is lower than that found in the northwest Atlantic and Indian Ocean sites (e.g., Glass et al. 1985, 1997). The volume of the spherules may have been reduced during diagenesis and compaction. It is also possible that some of the spherules were destroyed during processing, even though we tried to be very careful. Thus, the concentration (number/cm^2) may be higher than calculated. Because of their small diameters and thinness, the original diameters of the black pancake spherules before compaction would have generally been less than 125 µm and, thus, even though they are more abundant, would not have contributed much, if any, to the number of spherules (>125 µm)/cm^2 at this site.

The data seem to support the conclusion that the green pancake spherules in upper Eocene deposits at Massingano are diagenetically altered and compacted cpx spherules. First, the pancake spherules appear to be the appropriate age. The age of the Ir anomaly and pancake spherules is 35.7 ± 0.4 Ma (Montanari et al. 1993; Pierrard et al. 1998). The cpx spherule layer is about 10–20 ka older than the North American microtektite layer (Glass et al. 1985, 1998), which is about 35.5 ± 0.3 Ma (Obradovich et al. 1989). Thus, within the limits of radiometric dating, the pancake spherules are the same age as the cpx spherules. Second, the pancake spherules, like the cpx spherules, are associated with an Ir anomaly and contain both dendritic and octahedral Ni- and Cr-rich spinel crystals (Glass et al. 1985; Glass 2002; Keller et al. 1987; Pierrard et al. 1998). In addition, some of the pancake spherules, like the cpx spherules, are coated with spinel crystals. Third, before compaction, the pancake spherules seem to have been similar in size to the cpx spherules. Fourth, none of the pancake spherules appear to have been teardrop or dumbbell shaped before flattening. Likewise, the cpx spherules do not exhibit teardrop or dumbbell shapes (Glass et al. 1985; Glass 2002). Fifth, the pancake spherules at Massignano may, like the cpx spherules, be from the Popigai impact crater. Langenhorst (1996) made a detailed study of shocked quartz from Massignano and concluded that the source material was probably a quartz-rich, nonporous, near-surface target rock similar to the late Proterozoic to Cambrian quartzite known to be a major lithology in the upper 1000 m of the Popigai crater (Masaitis 1994). In addition, the presence of "toasted" quartz in the Massignano impact layer is consistent with derivation from the Popigai crater. Whitehead et al. (2002) suggested that "toasted" quartz may be due to the presence of submicron fluid inclusions and listed the Popigai crater as one where "toasted" quartz has been observed. "Toasted" quartz grains are also found in the ejecta layer from the Chesapeake Bay structure, but here, they are associated with microtektites not with cpx spherules (except for some reworked from the underlying cpx spherule layer).

If the black spinel-rich stringers represent diagenetically altered and flattened spinel-rich spherules, then they must either belong to the cpx spherule layer or they must be from a different layer, which could be slightly older or younger. If they are from a different impact event, then the impact must have been small and close to Massignano, since spinel-rich spherules have not been found just above or below the cpx spherule layer at any other site. If the dark spinel-rich pancake spherules are part of the cpx spherule layer, then the question is: why haven't spinel-rich cpx spherules been found at other sites? One possibility is that different spherule types have different distributions within the strewn field. Another possibility is that spinel-rich cpx spherules were deposited at other sites but have lost most of their spinel crystals as discussed above.

Thus, our data support the conclusion that the pancake spherules at Massignano (at least the green ones and probably the dark spinel-rich ones) are diagenetically altered cpx spherules and that they are associated with shock-metamorphosed mineral grains. Since shock-metamorphosed mineral grains had not previously been found associated with the cpx spherule layer, this conclusion was unexpected. However, since this study began, one of us (S. Liu) found coesite associated with the cpx spherule layer at DSDP Site 216 in the eastern equatorial Indian Ocean and Site 709 in the western equatorial Indian Ocean (Liu and Glass 2002; Liu et al. 2002). In addition, shocked quartz with one to two sets of PDFs was found at Site 709. This is also the site where we found that many of the small dark cpx spherules appear to be coated with spinel crystals.

At the time of the impact, Massignano was closer to the Popigai crater (~6010 km or 60 crater diameters) than to the Chesapeake Bay crater (~6600 km or 78 crater diameters). Some researchers have suggested that the diameter of the Chesapeake Bay crater may be much less than the often quoted 85 km (e.g., Grieve and Therriault Forthcoming; Collins and Melosh 2004). Grieve and Therriault (Forthcoming) suggest that a diameter of ~40 km is more consistent with the residual gravity anomaly over the structure. Radial variations in thickness of the North American microtektite layer are also more consistent with a smaller crater diameter (Glass et al. 1998). If the Chesapeake Bay crater is only ~40 km in diameter, then Massignano would have been 165 crater diameters away at the time of the impact—i.e., more than twice as far as from the Popigai crater.

Massignano was also the closest known cpx-spherule-bearing site to the Popigai crater at the time of the impact. Sites 216 and 709 were about 9880 and 10,100 km (~99 and 101 crater diameters) from Popigai, respectively. Shocked quartz has been found at least 14,000 km (~77 crater diameters) from Chicxulub (Bohor 1990) and may very well be global in extent (i.e., up to 111 crater diameters). Thus, it should not be surprising that shocked quartz from the Popigai crater is found at Massignano and Sites 216 and 709 in the equatorial Indian Ocean but not at other cpx spherule sites that were farther from Popigai at the time of the impact.

SUMMARY AND CONCLUSION

Green flattened spheroids (pancake spherules) containing and sometimes coated with Ni- and Cr-rich spinel crystals are found associated with an Ir anomaly at Massignano, Italy. They appear to be diagenetically altered cpx spherules that were flattened by compaction. The silicate portion of the cpx spherules was altered to Fe-rich smectite. We believe that the generally smaller, black, spinel-rich pancake spherules are from the same impact event as the green pancake spherules, but because of their fragile nature, we were not able to accurately determine their vertical distribution in the section. Our data support previous conclusions that the pancake spherules at Massignano are associated with shocked quartz. A search for coesite and shocked zircons was negative. Polymineralic grains containing shock-metamorphosed mineral grains, with up to two sets of PDFs, are also present but appear to be fragments of agglutinated foraminiferal tests. The shocked quartz, pancake spherules (diagenetically altered cpx spherules), and an Ir anomaly at Massignano all appear to belong to a single impact event. This conclusion is consistent with previous conclusions that the cpx spherule layer was probably derived from the 100 km-diameter Popigai crater in northern Siberia.

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Editorial Handling—Dr. Uwe Reimold

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