ORIGIN OF MICRODIAMONDS IN KT BOUNDARY CLAYS; I. Gilmour, S.S. Russell, C.T. Pillinger, Department of Earth Sciences, The Open University, Milton Keynes, MK7 6AA; M. Lee, Department of Physics, University of Essex, Colchester CO4 3SQ; J.W. Arden, Department of Earth Sciences, University of Oxford, Oxford OX1 3PR.

The recent discovery of nanometre sized diamonds in a KT boundary clay from Knudsen's farm, Canada, has led to the suggestion that they may be derived from an interstellar diamond component in the impacting asteroid [1]. Nanometre sized diamonds (C6) found in carbonaceous, ordinary, and enstatite chondrites have a number of very characteristic properties: the presence of the exotic noble gas component Xe (HII), an extremely negative $\delta^{15}N$ value of ca. $-343\pm16\%$o with typical nitrogen concentrations of 2000-15000 ppm, a cubic structure, and $\delta^{13}C$ values of -32 to -40%o. In order to verify the existence of diamonds at the KT boundary, and to examine the hypothesis of a meteoritic origin, we have undertaken detailed carbon and nitrogen isotope plus transmission electron microscopy (TEM) investigations of acid residues from three boundary sites world-wide. Acid residues were prepared using identical procedures to those reported previously for the isolation of meteoritic diamond [2]. The samples studied were of a "fireball" layer and Cretaceous sample from Brownie Butte, Montana; a "fireball" layer and "ejecta" layer sample from Berwind Canyon, Colorado; and a boundary clay sample from Petrieio, Italy.

Examination of the Brownie Butte and Berwind Canyon fireball layer acid residues using TEM indicated that the principal components were high in titanium, zirconium and tungsten presumably due to the presence of acid resistant minerals such as rutile. The diffraction patterns of the carbonaceous component had predominant d-spacings at ~2.06, ~1.26 and ~1.08Å identifying it as cubic diamond; if the hexagonal form does occur it is greatly subordinate. The diamonds occur as clumps with individual crystals being ~6nm in size and vary in morphology from irregular to near-cubic euhedral crystals.

Figure 1 shows the stepped combustion results obtained for carbon and nitrogen isotope analysis of the Brownie Butte fireball layer sample and a "background" sample from 6-8 cm below the boundary. The acid residue obtained represents 113 ppm of the bulk fireball layer and consists mostly of rutile but has 3.2% carbon with an associated 82 ppm nitrogen combusting over the temperature interval 375-700°C. This corresponds to concentrations in the bulk rock of 3.6 ppm C and 9 ppb N. The carbon isotopic release profile reveals two possible components; the first combusts below 450°C and has a maximum $\delta^{13}C$ of ~12%, the second (53% of the total carbon) combusts from 450-700°C and has a $\delta^{13}C$ of ~18%o. The total nitrogen released during stepped combustion has a $\delta^{15}N$ value of +5.5%o. The background residue represents 0.46 ppm of the bulk rock. However, it combusts mainly in the temperature range 200-400°C with a $\delta^{13}C$ of ~26%o and it therefore probably represents a small amount of laboratory contamination introduced during sample handling. Stepped combustion of the fireball layer sample from Berwind Canyon gave comparable results to the Brownie Butte sample with a very similar $\delta^{13}C$ release profile though a slightly narrower range in combustion temperature.

The integrated abundance of diamond in the Brownie Butte fireball layer is 9µg/cm² a factor of 70 higher than reported at Knudsen's Farm [1]. The combustion temperature of the majority of the carbon in both fireball residues is similar to C6 diamonds, but, the carbon and in particular nitrogen isotopic compositions are clearly inconsistent with them being an interstellar diamond component derived from the impacting asteroid or comet. It would seem, therefore, that the diamonds were formed as a result of the impact and there are several possible mechanisms. The most likely would be either production by shock alteration of carbon from the target rock and/or asteroid or by a mechanism such as chemical vapour deposition (CVD) producing diamonds in the fireball. At first sight the cubic structure of the diamonds would apparently exclude shock as a mechanism as "shocked" diamonds of larger grain size are normally hexagonal in structure. However, diamonds produced by the explosive detonation of TNT were also found to be cubic and to have similar morphologies and grain size to the KT diamonds. The isotopic profiles obtained by stepped combustion suggest a more complicated picture. The carbon isotopic compositions do not
match any major crustal reservoir of carbon such as carbonate or organic carbon though could clearly be obtained by mixing. Indeed, the variations in $\delta^{13}C$ and indicative of the presence of more than one component and may suggest the existence of two populations of diamonds perhaps reflecting several formation processes. CVD produced diamonds are isotopically fractionated from their starting materials by a few per mil.

The extent to which the diamonds were distributed globally will also provide clues to their origin. Shocked quartz grains, although concentrated in North America, have also been found in Europe, Asia, and the Pacific Ocean and the Ir anomaly has been found at around 95 sites worldwide. An acid residue of bulk boundary clay sample from Pettriccio in Italy has also been prepared. The carbon concentration in the residue was equivalent to 48 ppm of the bulk clay, however, it combusted at lower temperatures (300-500°C) and gave lighter $\delta^{13}C$ values (~23‰) than the North American samples. TEM examination has yet to be done on this residue to confirm the presence of diamond, however, its combustion properties suggest that it is either very fine grained diamond or another form of carbon.

References

Acknowledgments
We thank Bruce Bohor, Alan Hildebrand and Alessandro Montanari for the provision of samples.