

**SPHERICAL CARBONACEOUS INCLUSIONS IN (DARWIN) IMPACT GLASS AND CO-GENETIC MINERAL (SiO<sub>2</sub> + TiO<sub>2</sub>) GROWTH UNDER IMPACT CONDITIONS.** K.T. Howard<sup>1</sup>, M.J. Bailey<sup>2</sup>, P.A. Bland<sup>1,3</sup>, G. Cressey<sup>1</sup>, L. E. Howard<sup>1</sup>, C. Jeynes<sup>2</sup>, V. Stolojand<sup>4</sup> and S. Verchovsky<sup>5</sup>, <sup>1</sup>Impacts and Astromaterials Research Centre (IARC), The Natural History Museum, Mineralogy Department, London, SW7 5BD, United Kingdom. <sup>2</sup>University of Surrey Ion Beam Centre, Guildford, GU2 7XH, United Kingdom <sup>3</sup>IARC, Dept. of Earth Sci. & Eng., Imperial College, London, SW7 2AZ, United Kingdom. <sup>4</sup>Advanced Technology Institute, University of Surrey Guildford, GU2 7XH, United Kingdom. <sup>5</sup>Centre for Earth, Planetary, Space & Astronomical Research (CEPSAR), Open University, Milton Keynes, MK7 6AA, United Kingdom. E-mail: kieren.howard@nhm.ac.uk

**Introduction:** Impact glasses are formed by the shock melting of target rocks during the earliest stages of meteorite crater formation. Defining features of impact glasses are: extremely high formation pressures >35 GPa and temperatures >1700°C (evidenced by the observation of a pure silica glass called lechatelierite), textures that indicate disequilibrium conditions (evidenced by chaotic flow layering), and a complete absence of co-genetic mineral inclusions or phenocrysts. Although recent experimental impact studies have observed the growth of crystalline sulphide in as little as 10<sup>-4</sup>s [1], natural evidence for co-genetic mineral growth during impacts is limited to a few proximal impactite samples associated with non- and partially-molten components from the target stratigraphy [2,3]. Here the growth of crystalline phases is related to the presence of volatiles bound in sedimentary target rocks [2,3]. Co-genetic crystal growth in widely dispersed impact glass or tektite melt has not been demonstrated. This was the rationale for an extensive ongoing survey of tektite and impact glasses by ultra high brightness micro X-ray diffraction (μXRD).

In some cases when the composition of an impact glass is compared to its target rocks there is evidence for depletion in the concentrations of select elements considered volatile under impact conditions. Carbon is one such element that is generally thought to be lost from the impact site to a gas phase or expanding plume by devolatilization [4,5]. Impact breccias containing significant C (0.2 to 5 wt%) are known from just two out of more than 175 craters on Earth [5,6]. This C exists as diamond, graphite and poorly ordered C, rather than quenched melt, and is explained by impact-related incorporation and shock transformation of graphitic material from target rocks [6]. These occurrences of C-bearing phases are within the stratigraphy of impact craters. It is only relatively recently that carbonate melts have been recognised to form by impact melting, and these tend to exist as immiscible phases intermingled with silicate melts within the crater stratigraphy, or very proximal impactites containing partial and unmelted material [7]. Ejected impact glasses or tektites containing C-rich material have not been described previously.

Darwin glass is a siliceous impact glass found across a 400km<sup>2</sup> strewn field in western Tasmania [8]. The glass source is the 1.2km diameter Darwin Crater; a buried structure located in a narrow rainforested valley [8,9,10]. Relative to the size of the source crater this is the most abundant and widely dispersed impact glass on Earth [8]. Paleoclimatic and biologic evidence indicates a surface swamp was present at the time of the impact at ca. 800ka [8,11]. Abundant volatiles (H<sub>2</sub>O) contained in the surface swamp resulted in an increased magnitude explosion that promoted greater melting and wider dispersion of melt than expected for a crater of this size [8]. This has direct implications for models of tektite origin that require a mechanism to promote melt dispersal.

**Description:** We have discovered rare spheroidal inclusions in Darwin glass that range up to 200 μm diameter. XRD alerted us to the presence of these inclusions that were first observed *in situ* by X-ray Nano-Computed Tomography (Nano-CT), and later in glass thin sections under reflected light. After disaggregation from the bulk glass the inclusions were imaged by Scanning Electron Microscope (SEM). X-ray Nano-CT [Fig. 1] was used to obtain 3D images of the inclusions from which virtual thin slices were extracted, revealing the presence of high-density 'islands' in a low-density matrix, comprised of distinct domains that merge along near-planar boundaries.

**Chemistry:** Detailed ion beam analysis (IBA) by both lateral mapping with particle induced X-ray emission (PIXE), and resonant elastic (non-Rutherford) backscattering spectrometry (EBS) was used to determine the major element composition of the matrix [12]. Elemental depth profiles were obtained from self-consistent fitting of the EBS/PIXE data, confirming both the high carbon content of the inclusions with the 1734 keV <sup>12</sup>C(p,p)<sup>12</sup>C resonance and the presence of density inhomogeneity consistent with SiO<sub>2</sub> inclusions in the C-rich matrix. The average composition of one representative spherical inclusion is: (C, O, Si) = (28, 56, 16) at.% with S, K, Ca, Ti and Fe as minor elements, and Cr, Mn, Ni, Cu, Zn, and Br as trace elements - this is an average 'bulk' composition demonstrating the high C content, not the true composition of any actual point. The PIXE maps indi-

cate that these inclusions are highly heterogeneous and contain “hotspot” concentrations of Si but also Ti, Fe (with Mn & Cr), Cu, Al, P, S, K, and Ca set in the C-rich matrix. Rutherford backscattering spectrometry (RBS) and EBS demonstrates that O tends to correlate with Si and anticorrelate with C, reflecting a preference for bonding of O with Si consistent with the presence of SiO<sub>2</sub>. Heavily zoned variation of the O/C ratio (between zero and around unity) is observed with Energy-Filtered Transmission Electron Microscopy (EFTEM).

**Structure:** The crystallographic properties of the spherical inclusions were investigated *in situ* using an ultra-high brightness  $\mu$ XRD attached to a curved position sensitive detector (PSD). High-density islands in the nano-CT images are crystalline quartz, consistent with the compositional data. At the resolution of  $\mu$ XRD the carbonaceous material is X-ray amorphous, and this was confirmed by Scanning Transmission Electron Microscope (STEM) nano-diffraction and high-resolution TEM (HRTEM) images, which show it is entirely amorphous. Therefore this carbonaceous material is a glass quenched from a melt and/or vapour. HRTEM also reveals the presence of micro- and nano-crystalline particulate material identified as TiO<sub>2</sub> (rutile) by Fast Fourier Transform (FFT) diffraction.

**Source of C:** Carbon isotopes (<sup>13</sup>C) were studied by stepped combustion. Most of the carbon was released at low temperature (300-500°C with maximum release at 400°C), as is characteristic of organic matter. The carbon isotopic composition ( $\delta^{13}\text{C} = -24\text{--}26\%$ ) indicates that C has a terrestrial source, but the possibility of fractionation prevents further inferences. The target rock (quartzite) is not associated with carbonaceous material or carbonate, and even if the presence of carbonate were speculated, the carbon isotope compositions of west coast Tasmanian carbonates are much heavier ( $\delta^{13}\text{C} -3$  to 2%) [13]. Contamination can be ruled out. The only possible major source of C is the swamp and rainforest at the impact site i.e. biomass.

**Origin:** C-rich melt would have been immiscible from the bulk silicate Darwin glass melt. The pervasive occurrence as filled vesicle space suggests late-stage infiltration by “frothing” [4] through the bulk glass (although direct condensation from vapour segregations cannot be ruled out). The SiO<sub>2</sub> and TiO<sub>2</sub> micro/nano inclusions are only found in association with the carbonaceous spheres and are not present in the bulk silicate glass. This suggests that the C-rich material acted as an insulator to buffer rapid cooling and allow growth of the crystalline phases.

**Conclusion:** This is the first example of a carbonaceous impact melt formed from organic carbon

derived from biomass, and the first example of a C-rich impact melt found outside the source crater. Congenetic crystalline SiO<sub>2</sub> and TiO<sub>2</sub> have also never been described in an ejected impact glass or tektite before. This discovery challenges the usual definition of an impact glass, and appears to confirm the suggestion of [2] that volatile-rich target materials promote formation of crystalline mineral phases during impact – although the exact mechanism of formation remains unclear. These unique inclusions further highlight the ability of organic C to survive impact processing in an amorphous form that is much more reactive than crystalline C-phases known from impacts elsewhere [5,6]. Upon weathering, organic C will readily be released from the amorphous glass and available for consumption in pre-biotic chemical systems or incorporation by biologically relevant organic molecules [5]. This supports the known ability of meteorites to transport C throughout the solar system. Incorporation of reactive C into widely dispersed impact glasses may also provide a C source to “kick-start” primitive biologic and chemical systems post impact, thereby yielding an in-built recovery mechanism for the receiving environment.

**References:** [1] Wozniakiewicz P.J. et al. (2008) *LPS XXXIX*, Abstract #1791. [2] Osinski G.R. et al. (2007) *EPSL*, 253, 378-388. [3] Horz F. et al. (2002) *MAPS*, 37, 501-531. [4] Kieffer S.W. and Simmonds C. H. (1980) *Rev. Geophys. & Space Phys.*, 18,143-181. [5] Parnell J. and Lindgren P. (2006) *Geology*, 34,1029-1032. [6] Gilmour J. et al. (2003) *GCA*, 67,3889-3903. [7] Osinski G.R. and Spray J. (2001) *EPSL*, 194,17-29. [8] Howard K.T. (2009) *MAPS*, 44,115-129.[9] Howard K.T. (2008) *MAPS*, 43, 473-496. [10] Howard K.T. and Haines P.W. (2007) *EPSL*, 260,328-339. [11] Loh C.H. et al. (2002) *MAPS*, 37,1555-1562. [12] Bailey M. J. (2009) *NIMB* 267,2219-2214. [13] Rao C.P. and Wang B. (1990) *Aus. J. Earth. Sci*, 37, 305-316.

**Figure 1:** Raw X-ray projection nano-CT image of a carbonaceous inclusion mounted on a pin. Lower contrast =lower density.

