

POLYMETALLIC AND CARBONACEOUS DEBRIS IN PALAEOGEOLOGICAL GLASS STREWN FIELD, SW EGYPT: EVIDENCE OF A COMETARY IMPACT. M. A. G. Andreoli¹, M. Di Martino², V. Pischedda³, R. L. Gibson¹, S. Huotari⁴, A. Kallonen⁴, G. Belyanin⁵, R. Erasmus⁶, A. Ziegler⁷, H. Mouri⁵, T. Ntsoane⁸, R. van der Merwe⁸, M.D.S. Lekgoathi⁸, Z. Jinnah¹, J. Kramers⁵, R. Serra⁹, G. P. Sighinolfi¹⁰, I. Stengel¹¹, L.D. Kock⁸, D. Block¹², L. Chown¹³, M. Bamford¹⁴, K. Rumbold¹⁵ and D. Billing¹⁶. ¹School of Geosciences, University of the Witwatersrand, PO WITS, Johannesburg 2050, South Africa, (Marco.Andreoli@wits.ac.za), ²INAF – Osservatorio Astrofisico di Torino, Pino Torinese, Italy, ³ILM, Univ. Lyon 1, Villeurbanne, France, ⁴Univ. Helsinki, Helsinki, Finland, ⁵Dept. Geology, Univ. Johannesburg, Johannesburg, South Africa, ⁶School of Physics, Univ. Witwatersrand, Johannesburg, South Africa, ⁷Microscopy and Microanalysis Unit, Univ. Witwatersrand, Johannesburg, South Africa, ⁸The South African Nuclear Energy Corp., Pretoria, South Africa, ⁹Dipart. Fisica e Astronomia, Univ. Bologna, Italy, ¹⁰Dipartimento Scienze Chimiche e Geologiche, Università di Modena e Reggio Emilia, Italy, ¹¹NamibGeoVista GeoConsult & Imaging; Namibia University of Science and Technology, Windhoek, Namibia, ¹²Dept. Applied Mathematics, Univ. Witwatersrand, Johannesburg, South Africa, ¹³School of Chemical and Metallurgical Engineering, Univ. Witwatersrand, Johannesburg, South Africa, ¹⁴Evolutionary Studies Institute, Univ. Witwatersrand, Johannesburg, South Africa, ¹⁵School of Molecular and Cell Biology, Univ. Witwatersrand, Johannesburg, South Africa, ¹⁶School of Chemistry, Univ. Witwatersrand, Johannesburg, South Africa.

Introduction: Following the discovery of a diamond-bearing carbonaceous pebble in the Libyan Desert Glass (LDG) area of SW Egypt [1], subsequent investigations accounted for the extraterrestrial origin of this stone, nicknamed Hypatia, either as the shocked relic of a comet impact at $28.5 \text{ Ma} \pm 0.8 \text{ Ma}$ [2, 3, 4] or the relic of a rare type of meteorite [5].

Samples and Methods: Our last expedition in November 2011 to the find area ($25^{\circ}30'E$, and $25^{\circ}20'N$) failed to recover additional hand specimens of Hypatia material, though it returned samples of goethite-cemented, Cenozoic pebbly sandstone with the pedogenic characteristics widely represented in the region. One of these samples (WZER 8B), weighing about 0.8 kg, was collected 3.8 km SSW of the Hypatia sampling site (coordinates: $25^{\circ}29'E$ and $25^{\circ}18.11'N$). The sample was crushed in a jaw crusher mill, with the pulp being later digested in *aqua regia* to remove most of the iron oxides. The insoluble residue was separated using bromoform into a light fraction (mainly consisting of quartz and kaolinite) and a heavy minerals fraction. From the latter, residual goethite and other magnetic minerals were removed using a standard magnetic separator. Our aim was to try and identify evidence of hard amorphous carbon and sub-micron diamonds like those found in the Hypatia pebble in the heavy, non-magnetic, residue.

Results and Discussion: The investigation of the non-magnetic heavy minerals present in sample WZER-8B is on-going and involves several micro-analytical techniques, including SEM-EDX, synchrotron tomography, NanoSIMS and Raman spectroscopy. Some grains were embedded in Epoxy cylinders for quantitative micro- and ion probe analysis, whereas other grains were directly pressed on conductive adhesive tape, mainly for qualitative SEM-EDX analysis.

The greater proportion of the recovered heavy minerals comprises aluminosilicates, ilmenite, zircon and rutile, probably derived from the weathering of the Late Cretaceous Nubian sandstones extensively represented in the region [5]. Fresh pyrite grains are also common, but their origin remains unclear. In addition, a significant proportion of still-to-be-characterised heavy, non-magnetic grains comprises unusual metallic and carbonaceous particles tentatively grouped into 4 types (Fig. 1).

Type I grains and spherules range from 10-20 μm up to $\sim 130 \mu\text{m}$ (Figure 1a, b and c) although Pb grains a few μm long were also observed. SEM-EDX data indicate that the smaller spherules are metallic with a wide compositional range comprising Ti, Ag, Al, and Si in varying proportions, and Ca, O, Na, Mg and S as variable, minor constituents. The largest spherules are pale green and vitreous (Fig. 1c) and consist entirely of P, Si with no detectable oxygen.

Type II grains are much larger (length: 60 μm to 1.2 mm) and consist of a) sintered aggregates of Pb metal particles; b) strongly sintered clusters of α -Ti (+ ~ 1.0 at.% Al) subgrains; and c) more brittle aggregates of seemingly submicron, Sn-Ca alloy particles (Fig. 1d, e respectively). The Ti metal grains in places host clusters of quenched gas bubbles, blobs of Ti aluminide, veinlets of non-stoichiometric Ti nitride, Al oxycarbonitride, and particles of Zr, Ag, and Zn. Ti isotopic ratios were measured by E. Zinner (deceased), and found to be not significantly different from the standard used, suggesting a terrestrial or solar system derivation of the metal. A distinctive feature of the Type II grains is their localized coating by (C, O bearing) carbonaceous films and filaments up to $\sim 300 \mu\text{m}$ in length (Figure 1h). Although these resemble fungal

hyphae and tendrils in SEM images, Raman spectra prove that they comprise partly graphitized kerogen.

Type III grains are shard-like in shape and occur either as partly oxidized branching ($70\ \mu\text{m} \times 50\ \mu\text{m}$) Al particles decorated by μm -size Bi granules (Fig. 1f), or as lace-textured Ti particles partly enveloped by Type II grains. Petrographic textural analysis of multiple 3-D sections of the shard shown in Fig. 1g indicate that the Type II (and perhaps Type I) grains were derived from the partial to complete melting of the Type III shards.

Type IV grains are morphologically and compositionally diverse, with common characteristics being C as the major constituent, a hardness ≥ 9 , and density $>2.84\ \text{g}\cdot\text{cm}^{-3}$. Moissanite (SiC) grains were the first to be positively identified (Figure 1j) from petrography and Raman spectra. Other grains display a range of textures, including one resembling a honeycomb (Figure 1i) with N as second major constituent and minor, varying amounts of S and Cl. The Raman spectra of these N-rich grains show faint, indistinct D and G bands but distinctive peaks in the $3000\ \text{cm}^{-1}$ region, indicative of C:H bonds.

Conclusions: A variety of origins have been evaluated to account for the association of Type I to IV particles including that they may represent anthropogenic or geological products, fulgurites, cosmic spherules, metal-rich meteorites, or impact-related melts and carbonaceous matter. As far as we have been able to ascertain, with the exception of the moissanite grains, the residual grains from sample WZER 8B have yet to be described in natural materials of extraterrestrial or terrestrial origin, including impactites. However, grains of metallic silver, aluminium and filaments of Ti-metal, the latter up to 1 mm in length, also occur in the Hypatia stone [3, 6]. The data presented support the hypothesis by [2, 3] that the LDG area of SW Egypt represents the strewn field of an impacted comet. However, apart from moissanite, current knowledge of meteoritics and astromineralogy cannot explain the origin of the Type I-IV particles described above.

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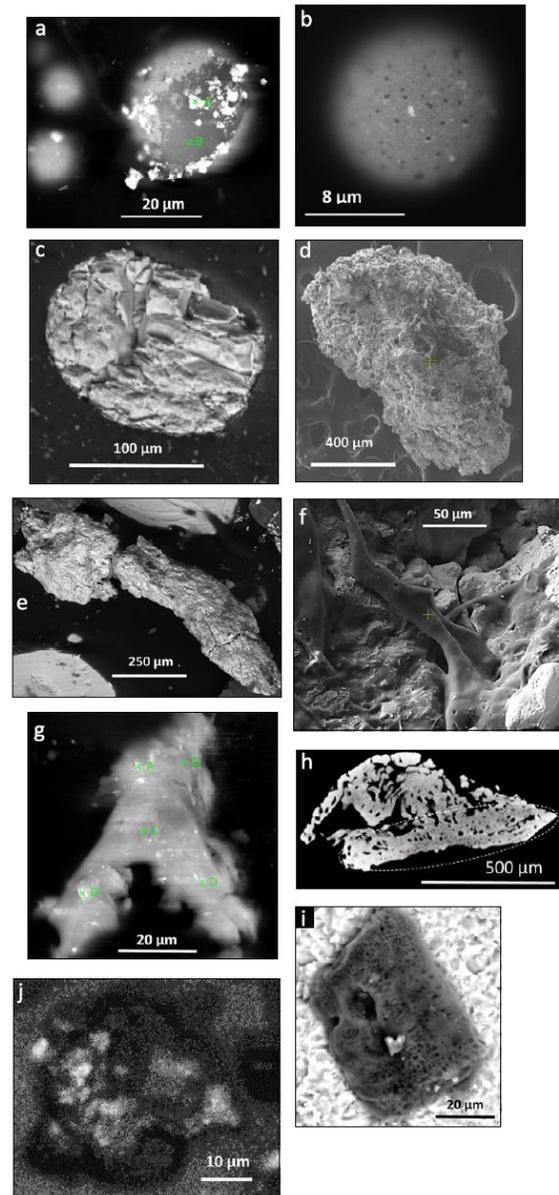


Figure 1: Backscatter SEM images of acid-resistant grains (density $>2.84\ \text{g}\cdot\text{cm}^{-3}$) recovered from sample WZER 8B, Libyan Desert Glass area, SW Egypt; a) and b), Type I (Ag, Si $>$ S, Ca, O; and Ti, Al, Ag) spherules; c) Type I PSi spherule; d), e) Type II clustered grains (Ti-metal, SnCa alloy, respectively); f) kerogen (C, O) filaments and films partially coating a Type II Ti-metal cluster; g) Type III Al \pm O shard with bright Bi speckles; h) Type III Ti shard (enclosed in ellipse) melting to a cluster of synered Ti metal droplets (top section of grain); i) Type IV carbon nitride grain (with dust particle in grain centre); j) Type IV SiC grain (optic microscope image).