MAJOR, MINOR, AND TRACE ELEMENTAL VARIABILITY OF RIES IMPACT GLASS: IMPLICATIONS FOR HABITABILITY. H. M. Sapers\textsuperscript{1,2}, T. Ota\textsuperscript{2}, E. Nakamura\textsuperscript{2}, G. R. Osinski\textsuperscript{2,3}, N. R. Banerjee\textsuperscript{1}, R. L. Flemming\textsuperscript{1}, K. Kobayashi\textsuperscript{2}, T. Kunihiro\textsuperscript{2}, R. Tanaka\textsuperscript{2}, T. Tsujimori\textsuperscript{1,}\textsuperscript{4}Centre for Planetary Science and Exploration / Dept. of Earth Sciences, University of Western Ontario, London, ON, Canada. \textsuperscript{3}Pheasant Memorial Laboratory, Institute for Study of the Earth’s Interior, Okayama University, Misasa, Japan. \textsuperscript{4}Dept. of Physics and Astronomy, University of Western Ontario, London, ON, Canada, \textsuperscript{5}Center for Northeast Asian Studies/ Dept. of Earth Science, Tohoku University, Sendai Japan (hsapers2@uwo.ca)

Introduction: Impact cratering is a ubiquitous geological process on solid planetary bodies. One of the most characteristic products of impact events is the generation of large volumes of melt, which cools to form impact melt rocks and/or glass-bearing breccias depending on cooling rate. Once formed, impact glasses, in particular, are subject to alteration by impact-generated hydrothermal systems [e.g., 1]. Such impact-induced environments may be conducive to microbial colonization [e.g., 2]. Examination of glasses from the Ries impact structure, Germany, has revealed tubular textures with remarkably similar morphologies to textures observed in volcanic glasses [3].

Tubular morphologies include bifurcation, regular segmentation, spirals, loops, and complex curving forms. Using energy dispersive spectroscopy previous work has shown the presence of a Mg, Fe, Ca and Na depletion zone surrounding the tubules [3]. Fourier transform infrared spectroscopy (FTIR) has identified the presence of organic compounds spatially associated with the tubules. Syncrotron near edge X-ray absorption fine structure (NEXAFS) spectroscopy at the carbon K-edge also indicates the presence of organically bound carbon in the glassy matrix surrounding the tubules, but absence in the glassy matrix hosting only canonical quench crystallites. NEXAFS spectroscopy at the iron L\textsubscript{1} and L\textsubscript{2}–edges indicates distinct bull’s eye patterns of iron speciation in the tubules. Such iron speciation patterns are not present in the iron-rich quench crystallites [4].

The biogenicity of the tubular features has been assessed through a multi-analytical approach [3, 4]. Tubule morphologies are biologically consistent and lack a parsimonious abiotic formation mechanism. The elemental depletion zone surrounding the tubules has been identified as a biological processing signature [5]. The organic carbon spatially associated with the tubules combined with an Fe speciation pattern consistent with iron reducing bacteria lends further evidence to a biological origin of the tubule features. Geochemical variability has significance implications for colonization and for the recognition of biosignatures. Many elements present in natural glasses are essential macro and micronutrients [e.g., 6, 7]. Lithotrophic microorganisms extract micro and macro nutrients from lithic substrates affecting the geochemistry as bioessential elements are actively or passively accumulated. Conversely, the presence (or absence) of certain nutrients and or toxic accumulations of elements will influence habitability. Here we present the first high resolution trace-element geochemistry of the Ries glasses comparing areas containing high concentrations of quench crystallites, tubules, both, or neither.

Methods: Tubules and matrix were analyzed with high-resolution backscatter electron (BSE) imaging and EDX spectroscopy carried out with a Leo 1540 FIB/SEM CrossBeam field emission SEM equipped with an Oxford Instruments INCA EDX at the Nanofabrication Laboratory, University of Western Ontario. A defocused 10 \textmu m beam was used to collect EDX spectra of the matrix glass on a Cameca SX100 electron microprobe at the Electron Microprobe Laboratory at the University of Alberta to determine preliminary chemical difference between crystallite and tubule hosting glass. Micro X-ray diffraction XRD data were collected using a Bruker D8 Discover micro X-ray diffractometer (\textmu XRD) at the University of Western Ontario.

Correlated contextual analyses (optical, EDX, SIMS) were used to obtain a comprehensive set of chemical analyses. 21 optically defined regions of interest (ROIs) were selected (containing tubules, crystallites, both, or neither) and entered into the visual stage linkage (VSL) system, a unique analytical software tool available at the Pheasant Memorial Laboratory for Geochemistry and Cosmochemistry, Institute for Study of the Earth’s Interior, Okayama University SEM was carried out with a JEOL JSM-7001F FE-SEM in BSE mode equipped with an Oxford X-max EDX detector. Approximately 1500 EDX analyses were conducted for quantitative determination of major elements (Na, Mg, Al, Si, K, Ca, Ti, Mn, Fe, Ni). A subset of 91 EDX spots was statistically selected to represent each of the major element trends for secondary ion mass spectrometry (SIMS) to access trace element variation. A suite of 18 trace elements (Ba, Nb, La, Ce, Pr, Sr, Nd, Sm, Zr, Hf, Eu, Gd, Dy, Li, Y, Er, Yb, Lu) was analyzed using a Cameca ims-5f SIMS, Fig. 1).

Results: The bulk chemistry, mineralogy and crystallites of the Ries glasses has been extensively studied [8] and others. The glasses are isotropic, holohyaline to cryptocrystalline schlieren-rich and are characterized by complex flow textures and often dense assemblages of
quench crystallites. Quench crystallites are dominated by Ca- and Al-rich pyroxene. It is noted that at Si concentrations >80% there is a significant decline in the presence of both tubules and crystallites.

The fresh glass varies in colour from colourless to brown, yellow, pink or green, yellow-brown being dominant. The glass typically has a cloudy appearance, which increases with tubule density. High tubule density, increasing alteration, and hydration also darken the glass; highly altered glass clasts may appear dark brown to black. Microprobe analyses suggest SiO$_2$ contents range from ~50% in regions devoid of partially resorbed grains (glassy zones) to 80% in relic quartz grains (SiO$_2$ rich). In areas dominated by tubular features the average SiO$_2$ composition was the lowest at ~50 wt%. The average total for these regions is ~90% indicating a relatively high volatile content consistent with hydrous alteration. In general, areas dominated by pyroxene quench crystallites had higher SiO$_2$ contents (ave ~60%). The areas devoid of tubules and crystallites also have a high average SiO$_2$ content (~60%) The values of the other major elements are comparable between all regions with the notable exception of Na$_2$O and K$_2$O. In the areas hosting the tubular features, Na$_2$O content is enriched and K$_2$O depleted relative to regions dominated by quench crystallites or regions with neither feature. In general, it appears that tubule features tend to be associated with lower SiO$_2$ contents and appear in areas showing lower totals, reflecting hydrous alteration. Tubules are not present in Si-rich regions of the glass nor are they concentrated in areas dominated by partially resorbed quartz grains. This distribution suggests a preference for a glass substrate enriched in the transition metals and alkali elements.

Micro-XRD conducted on 3 glassy clasts suggests the presence of a complex suite of micro-crystalline material. Clay minerals include montmorillonite, illite and nontronite. There is also evidence for chlorite, zeolites, carbonates, and iron sulphides. Peaks indicative of quartz, orthoclase and K-feldspar are also present.

Relative to the glassy matrix the tubules are depleted by ~5X in Na, ~2X in K, ~1.5X in Al and Si. The tubules are enriched by ~6X in Mg and Fe, and ~1.5X in Ca. The glassy matrix is Si rich. In areas where tubules are densely concentrated, they are surrounded by a zone of alteration depleted in Mg, Fe, Ca and Na and enriched in K. There are three types of quench crystallites present, distinguished by morphology and elemental chemistry. Most abundant are skeletal pyroxene dendrites followed by tabular laths of plagioclase, and rare, rounded Ti, Mg, and Fe oxides. Partially absorbed quartz grains are scattered throughout the matrix. Tubular features are generally associated with areas containing crystallites chemically consistent with pyroxene. Areas dominated by relict quartz, have low tubule density if tubules are present at all.

Major element trends were as follows: Al$_2$O$_3$, MgO, and CaO decrease with increasing SiO$_2$; K$_2$O increases with increasing SiO$_2$ and decreases once SiO$_2$ approaches 75 wt%; there is no trend observed for Cr$_2$O$_3$, NiO, or Na$_2$O with respect to SiO$_2$ content. Trace element data was both chondrite normalized and normalized to an area of fresh glass. In a chondrite-normalized space the Ries impact glasses generally have a trace-element abundance with relative enrichment of light rare-earth and large ion-lithophile elements. When normalized to fresh glass it is noted that tubules are not observed in the glass exhibiting a Nb-positive anomaly, although crystallites occur irrespective of Nb-abundances. The light rare-earth and large lithophile element enrichment is consistent with the Hercynian crystalline basement from which the glasses derive.

Studies have shown Nb to increase the antimicrobial properties of copper [9] and organic Nb(V) complexes are of interest as anti-microbial drug agents [10,11]. If the tubules are formed as a result of microbial activity, the toxic properties of Nb complexes could explain the absence of tubule features in areas with Nb enrichments.

![Figure 1: Chondrite normalized trace element composition of Ries impact glasses. 91 analysis spots.](image)

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**References:**