A TOF-SIMS INVESTIGATION OF THE VOLATILE INVENTORY OF LITHIC AND MINERAL CLASTS IN LUNAR REGOLITH SAMPLES.

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Introduction: The last 15 years of lunar exploration have revealed that there are volatiles on the Moon's surface [1-4]. These volatiles are generally divided into 3 categories: (i) water-ice and other volatiles preserved in high latitude cold traps, (ii) volatiles bound to the surfaces of minerals, and (iii) indigenous volatiles. In parallel, recent reinvestigation of lunar samples has unambiguously shown that rocks from the Moon's interior do contain water, overturning the 40 year-old 'dry-Moon' paradigm [5-6]. While these new missions and laboratory results have transformed our knowledge on lunar volatiles, there remain lots of unanswered questions. One of the next steps to further our understanding of lunar volatiles, and characterize their composition, distribution, abundances, and sources, will be undertaken by *in situ* prospecting missions on the lunar surface [7-8].

These missions will collect samples from the lunar (sub)surface and heat them up to release the volatiles they contain (e.g., H_2, H_2O, CO, CO_2, N_2, HCl, etc). These volatiles released from bulk soil and regolith samples will necessarily contain a contribution from a mixture of phases with unique volatile budgets and sources. These phases include glass agglutinates, pyroclastic glass beads, impact-melt and mineral clasts, and possibly trapped-ice. Therefore, it is crucial to characterize the volatile inventory of each of these components to be able to interpret bulk analyses of regolith samples, and for this we are using Time-Of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS).

Sample & Methods: To establish our analytical protocol, we selected the lunar meteorite Northeast Africa (NEA) 001, which is a feldspathic regolith breccia that comprises a large range of mineral clasts (plagioclase, pyroxene, olivine, oxides, sulfides) and lithic clasts (feldspathic impact melt, anorthosite, very-low titanium basalt) [9]. We first obtained back-scattered electron images and x-ray element maps over the whole polished section of NEA 001 (3×5 mm) using scanning electron microscopy. We then imaged the distribution of volatile species on selected areas using the IDLE-3 TOF-SIMS instrument installed at the University of Manchester [10]. A ~1 nA (DC) beam of Au^+ ions focused to a spot size of ~1 µm was used to sputter clean the sample surface over areas typically 150 µm across. Following this, high mass resolution ($m/\Delta m > 4000$) secondary ion mass spectra were acquired over ~120×120 µm areas. Mass resolved images in positive secondary ions and negative secondary ions were acquired over areas of interest for ~15-30 min.

Initial results: Apatite [$Ca_5(PO_4)_3(F,Cl,OH)$], which is the only mineral hosting volatiles into its crystal structure identified in lunar samples to date [e.g., 6], is easily detected using TOF-SIMS, being enriched in F, and in some cases in OH, compared to its surroundings. Unexpectedly, TOF-SIMS imaging of selected areas in NEA 001 also shows that some major rock-forming mineral clasts such as pyroxene, olivine or ilmenite can be significantly enriched in F and/or Cl, the abundances of these two halogens being generally decoupled. TOF-SIMS investigation of the volatile inventory of lunar soils and breccias thus has great potential for serendipitous discoveries.

Perspectives: TOF-SIMS allows the imaging of the distribution of volatile species such as OH, S and the halogens F and Cl across ~100-150 µm² areas, and, therefore, constitute a powerful tool to survey a wide range of sample types. This will provide key data to select target minerals and clasts in which volatile concentrations and isotopic compositions (e.g., H, S, Cl) will be precisely measured *in situ* using complementary SIMS techniques. Combining data on volatile distribution, abundances and isotopic compositions obtained through complementary SIMS approaches will eventually allow characterizing the volatile inventory of a range of regolith samples collected across different locations on the Moon's surface. These data, obtained on 'dry' lunar soil end-members (i.e. devoid of delivered water-ice), will provide essential baseline information for interpreting bulk measurements obtained *in situ* on the lunar surface by future missions. Crucially, they will also provide us with a better understanding of the sources and transfer of volatiles across the Solar System.

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