USING ATOM PROBE TOMOGRAPHY TO UNRAVEL THE AGE AND VOLATILE COMPOSITION OF LUNAR SAMPLES.

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Introduction: The development of laser-assisted atom probe tomography (APT) has allowed for the analysis of non-conductive materials, including mineral specimens [1]. The ability for APT to generate 3D chemical reconstructions from < 100 nm crystallographic domains at high spatial (± 0.1 nm) and mass (1000 FWHM) resolution has provided fundamental insights into the mobility of radiogenic isotopes [2], volatile (Cl) fractionation and loss [3], and the distribution of H_2O in nominally anhydrous olivine [4]. Recently, the technique has been applied to meteoritic and returned lunar samples, constraining the chemical artifacts induced by space weathering within lunar regolith [5] and quantifying Pb mobility and clustering in shocked zircon [2]. Here, we explore the ongoing applications of APT to lunar samples and highlight the importance of the technique going forward in unravelling nanoscale variations which are fundamentally linked with kilometre scale recent and ancient mechanisms on the Moon.

Samples: A range of lunar samples have been analysed using APT, with an aim of targeting various isotopic or compositional signatures within a suite of mineral species. Northwest Africa (NWA) 3163 is a brecciated lunar meteorite, while Apollo samples 60500 (soil) and 78236 (shock deformed norite) represent samples returned by the Apollo missions. A range of mineral specimen were targeted within the samples (baddeleyite (ZrO_2), anorthite ($CaAl_2Si_2O_8$), and apatite ($Ca_5(PO_4)_3(Cl,OH,F)$)) to measure bulk chemistry and trace element abundances and target radiogenic (Pb) and volatile (Cl, F, OH) isotopic reservoirs within isolated nanodomains.

Results: *NWA 3163:* A baddeleyite grain within a feldspathic clast in NWA 3163 contains two discrete microstructural domains: a polysynthetically twinned core (~90°/<401>) and a uniquely oriented rim domain interpreted to represent overgrowth during a later metamorphic event. Targeted analysis of these domains yields resolvable Th and Pb isotopic signatures by APT, allowing the generation of Th-Pb ages from each microstructural domain. The core, which appears to retain igneous microstructure, records a ^{232}Th/^{208}Pb age of 4328 ± 309 (2σ) Ma. The < 2 µm wide overprinting rim yields a ^{232}Th/^{208}Pb age of 2175 ± 143 Ma (2σ).In combination, APT has allowed for robust isotopic dating of both the oldest and youngest events in NWA 3163 within a single baddeleyite grain less than 5 µm in total length [6]. *Apollo 78236:* An apatite grain within the highly shocked Mg-suite norite 78236 reveals various microstructural domains, including crystal plastically deformed crystalline areas and quasi-amorphous domains. Dating of the apatite and merrillite populations by SIMS reveal a discordant array of U-Pb ages between 4210 ± 14 Ma (upper intercept) and 504 ± 24 Ma (lower intercept) [7]. APT analysis of the quasi-amorphous apatite domains reveals polygonal grains separated by Mg-decorated subgrain boundaries which act as diffusion pathways to allow radiogenic isotope loss at lower temperatures than solid state diffusion through the crystal lattice. Correlative APT analysis is thus critical to accurately interpreting *in-situ* isotopic and chemical datasets, here placing empirical constraints on a young (500 Ma) lunar impact crater while also providing evidence for an ancient (4.2 Ga) formation age, interpreted to reflect formation of the Serinitatis basin [7]. *Apollo 60500:* An individual feldspar grain was targeted from the lunar soil. Initial data reveal the homogenous distribution of Al, Ca, Si, and trace elements throughout the 300 nm long microtip specimen. Species of isotopic importance, such as Ar, Pb, Sr, Rb and Sm, could not be confidently measured within the mass spectrum due to mass overlaps with complex AlSiO species and compounds, in agreement with previous APT measurements of feldspar [8]. Work is ongoing to constrain the influence of solar wind implantation within the surficial regions of the sample.

Discussion: APT is a rapidly emerging tool in the geological and planetary sciences, holding great promise in answering large planetary scale questions with (sub) nanometre scale measurements [e.g., 6]. The minimally destructive nature of the technique (consuming less material than a typical LA-ICP-MS or SIMS spot) coupled with the potentially all-encompassing scientific yield (measuring the entire mass spectrum, with no mass bias or fractionation effects) is particularly critical for returned samples, where small amounts of material (from grams to single grains) are only available [7-9]. Future and ongoing sample return missions to the Moon, such as Chang’e 5, would benefit greatly from the inclusion of atom probe tomography in planned workflows of returned samples.

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