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Atomic worlds: Current state and future of atom probe tomography in geoscience

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ABSTRACT

Atom Probe Tomography (APT) is rapidly finding new applications within the geosciences. Historically connected with materials science and semiconductor device applications, recent years have seen APT established as a useful tool for nanoscale geochemistry, offering unique capabilities when compared with conventional geoanalytical techniques. The ability to characterize 3D nanoscale chemistry with isotopic sensitivity has uncovered intricate details of complex trace element distributions within a variety of minerals. Already these advances are having an impact on long-standing questions within geochronology, planetary science and other fields. Future developments are likely to bring significant expansion in this research space.

1. Introduction

Earth's range of rock types represents different mixtures of over 5000 minerals, the diversity of which has grown over the past 4.4 billion years [33]. Each of these minerals has differing composition and/or crystal structure that reflects the conditions of formation and the subsequent geological evolution that has modified them. Over several hundred years, geoscientists have developed a broad range of analytical techniques to characterize mineral compositions and structures, to shed light on the geological evolution of the planet. However, at a fundamental level, geological processes are governed by the mechanisms that control the nanoscale distribution and mobility of atoms within minerals and their boundaries. Nanoscale analytical techniques thereby underpin our ability to observe, measure and understand such mechanisms. At the sub-nanometer scale, transmission electron microscopy has commonly been used to investigate nanoscale processes in minerals [12,58,64]. However, this approach is limited to the compositional analysis of major elements and cannot identify individual atoms, or provide trace elements or isotopic compositions that are widely used by geochemists. In recent years, atom probe tomography (APT) has been increasingly applied to geological minerals to address this shortfall and to investigate a diverse and growing range of nanoscale features and processes. This contribution gives the authors' assessment of pioneering developments over the last few years, reviews the current state of APT in relation to geoscience applications, and forecasts the future developments and exciting possible applications in this rapidly growing field.

2. Atom Probe Tomography: A short overview

Atom probe tomography, often referred to alternatively as atom probe microscopy (APM), is unique among materials analysis techniques in its ability to provide three-dimensional chemical and isotopic information at near-atomic scales [47]. Such detailed analysis can be achieved over regions of interest of up to 100s of nm in size, carefully positioned at the apex of a needle-shaped specimen (Fig. 1a). In its application to geological samples, which are commonly electrically insulating, the atom probe is usually operated in a 'pulsed-laser' mode, combining a very high electric field at the specimen tip with a short laser pulse focused in the same region [56]. Thermal energy from the laser pulse is sufficient to initiate field-evaporation of atoms from the specimen apex, ideally one atom at a time. The specimen is thereby slowly eroded away as the evaporated ions are accelerated from the tip and impact upon a position-sensitive detector (Fig. 1b). Data from the detector are used to infer the original 3-D location of each atom within the sample, by applying a reverse-projection algorithm to the ion trajectories to generate a three-dimensional point-cloud, or 'atom map' (Fig. 1c). Importantly for geochemical studies, the detector arrival time can be used via time-of-flight mass spectrometry to determine the

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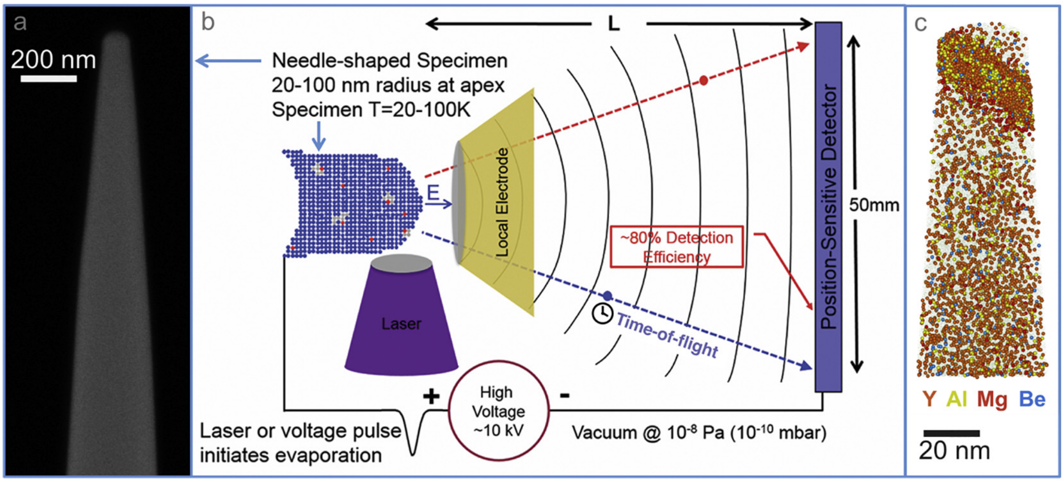

Fig. 1. a) Scanning electron microscope image of an APT specimen needle. b) Schematic view of the atom probe microscope from Valley et al. [95]. The laser pulse incident on the specimen apex initiates field-evaporation of ions from the surface. Ions are projected by the strong electrostatic field on to the position-sensitive detector, creating a highly magnified 'image' of the specimen surface. Measurement of the ion flight times, from laser pulse to detector impact, allows the ion identities to be determined by time-of-flight mass spectrometry. c) The detector data can be used to reconstruct the original three-dimensional location of each detected atom within the specimen. The atom map here shows the distribution of trace elements within a sample of shocked zircon [77].

mass-to-charge ratio of each ion, which usually allows isotopes to be identified with confidence.

The mass-to-charge ratios are typically presented as a histogram, or 'mass spectrum' (Fig. 2). Interpretation of the data requires the association of intervals, or 'ranges', within the mass spectrum with particular ionic species [27], which may be elemental or molecular. Multiple charge states may also be present for a single species. No pre-selection of elements or isotopes is required as the entire spectrum is recorded for each laser pulse, and every atom may be considered to be ionized and detected with equal probability.

The ability to confidently interpret APT data requires both site-specific targeting from well-characterized locations and non-destructive, correlative imaging of the atom probe specimen. The workflow to identify critical locations commonly involves multiple techniques. In identifying regions of interest, geoscience atom probe studies have so far utilized SEM-based cathodoluminescence (CL) imaging [73,94,95], secondary ion mass spectrometry (SIMS) [95], laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) [73], electron backscatter diffraction (EBSD) [74,77,94], X-ray fluorescence microscopy (XFM) [25], and backscatter electron (BSE) imaging [14,94,95]. Characterization of atom probe specimens by transmission Kikuchi diffraction (TKD) [93] in the SEM has been developed over recent years [4,9,81], and has been used to confirm lattice homogeneity of zircon and baddeleyite reference materials [80], and to identify subgrain boundaries and lattice distortions in zircon [74,77].

3. Geoscience applications of APT

Early work on geological materials was performed with voltage-pulsed atom probes, which require electrically conductive samples for efficient field-evaporation. This limited the quantity of data and the variety of materials that could be analysed [54,67]. The advent of commercial laser atom probe systems in the mid-2000s opened the APT technique to non-conducting samples [11,16,26,39], including geological materials such as sulphides, carbonates and silicates. Combined with the ability to prepare site-specific samples using focused ion

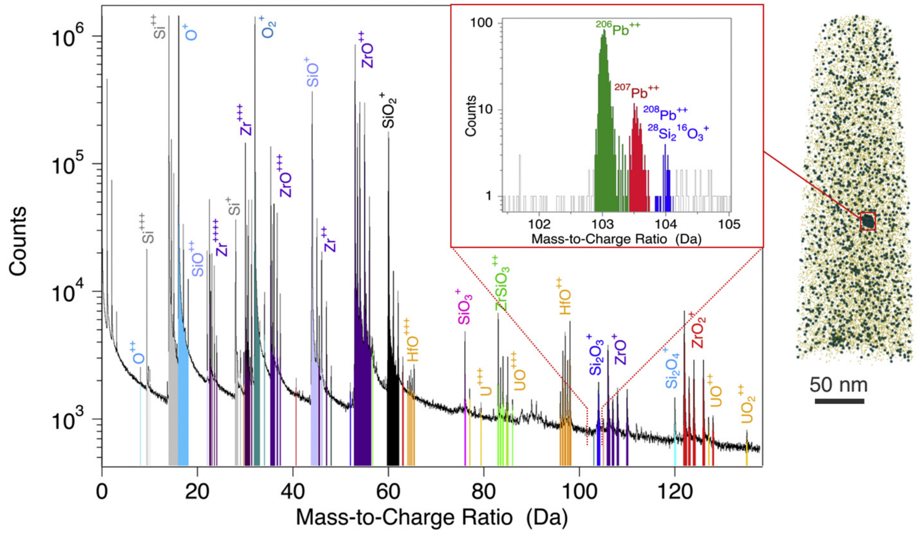

Fig. 2. An APT mass spectrum obtained from a zircon sample, showing the ranges (coloured bands) used to identify each atomic or molecular ion species. The atom map (right side) shows the distribution of Pb atoms within the grain. Selecting only the atoms in close proximity to a ~10 nm Pb-rich cluster allows the Pb isotopes to be clearly identified in the reduced mass spectrum (inset). From Peterman et al. [73]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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