

# SEEING SINGLE ATOMS – THE LAST FRONTIER



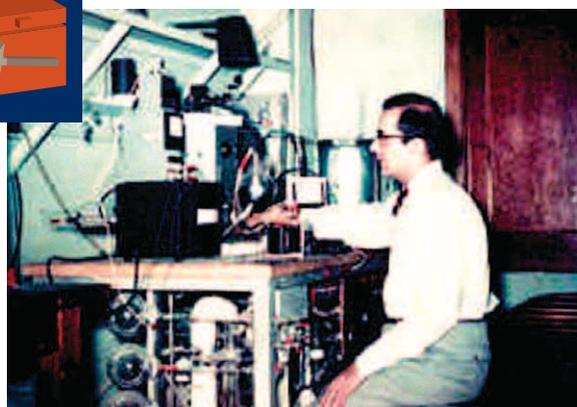
A thorough knowledge of a given natural process often requires a detailed understanding of a suite of mechanisms operating across length scales spanning many orders of magnitude. An example of this phenomenon involves the single seismic event: (1) stress failure is triggered at the micro-scale, (2) mechanical rupture occurs along a fault plane at the kilometre scale, and (3) energy is dissipated at the global scale. For crystallographers and mineralogists, this “scaling factor” challenge manifests itself most acutely at the shortest length scale. Key grain boundary and mineral reaction mechanisms operate at atomic to nanometre scales, and this fact drives the need for analytical techniques with ever improving spatial resolutions. Compared to a few decades ago, the array of analytical technologies now available is impressive:  $\mu$ -XRF (spatial resolution around 100  $\mu\text{m}$ ), laser ablation ICP-MS (100 to 10  $\mu\text{m}$ ), SIMS (20  $\mu\text{m}$  to 100 nm), electron probe and SEM quantification (1  $\mu\text{m}$  to 100 nm), Auger Microprobe (10 nm), and TEM (down to 1 nm or better). Each of these techniques has its advantages and drawbacks. Nonetheless, detailed characterisation of geo-materials is now technically possible at length scales spanning the nanometre to hand specimen range and beyond. The only technology lacking is the ability to evaluate the position and identity of single atoms.

Here I present the 3-dimensional atom probe, an emerging technology that may fill the one remaining gap in our analytical capabilities. Also known as the tomographic atom probe, this high-tech method involves the “evaporation” of individual atoms from the end of an extremely sharp tip made of the material being investigated. A sharp tip with a diameter on the order of <100 nanometres is essential as this provides the extremely high field gradients (on the order of  $10^{10}$  V/m) needed for field emission to occur. Projecting the emitted atoms, whether from a desorbed imaging gas or from the sample itself, in combination with a  $10^6$  magnification between the sample and the imaging detector, allows atomic-scale resolution using a phosphorus screen and a simple hand lens.

Atom probe tomography (APT) had its roots six decades ago when Erwin Müller (1951), then at the Kaiser-Wilhelm-Institute in Berlin, described his theory of the field ion microscope. His device relied on the emission of adsorbed hydrogen molecules, which were subsequently desorbed from the sample tip; these protons were then accelerated onto a phosphorus screen, thereby producing a very weak optical signal that could be observed in the completely darkened laboratory. The device gave information only about the crystallographic structure of the material under investigation, and Müller estimated the spatial resolution of his method to be around 2 or 3 nm, which was certainly impressive for its time. That same year, Müller moved to take up a faculty position at Pennsylvania State College (now University) where he established a research group working on field ion and field electron microscopy.

The next breakthrough came in October 1955 when Kanwar Bahadur, a PhD student in Müller's group, accomplished the first demonstration of lattice-scale resolution using a cooled tip in conjunction with helium imaging gas. Two similar experiments had previously been carried out by the group with limited success. It was thanks largely to the tenacity of Bahadur that success was achieved after he devised minor modifications to both the apparatus and the all-critical tip-preparation procedure (FIG. 1). These busy days in the Penn State lab are described in detail by Melmed (1996) and Kumar (2005). Müller went on to rapidly publish a number of single-author articles related to this achievement, while Bahadur obtained his doctorate in 1956 before returning to his former institute in New Delhi.

Until the mid-1960s the field ion microscope was limited to atomic-scale structural studies. Adsorbed ions from a low-pressure imaging gas were introduced into the sample chamber; these ions were subsequently



**FIGURE 1** Historical photograph of Kanwar Bahadur at the controls of the original 1955 field ion microscope (from Kumar 2005, with permission from *Current Science*)

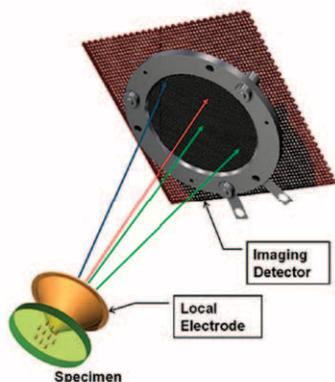
evaporated and ionized through the field emission mechanism. Frequently the sample atoms were not even involved in the actual imaging and, except in the case of pure substances, there was no way of knowing which elements were present. This changed when Müller et al. (1968) coupled a field ion microscope to a time-of-flight (ToF) mass spectrometer, creating the first true atom probe capable of identifying specific elements in the sample material. A key obstacle that had to be overcome was the requirement of ToF mass spectrometry to know with high certainty when a given ion was ejected from the sample, the event against which an ion's flight time would be measured. This challenge was solved by pulsing the voltage applied to the sample tip, increasing the electric potential from some base-level voltage to above the threshold at which field emission can occur. In order to prevent the undesired continuous emission of ions, the voltage then had to be rapidly dropped back below the emission threshold, this entire sequence lasting perhaps 3 ns. By recording the sequence of atomic compositions originating from each single locale, it was possible to build a 3-dimensional map of the sample. Despite the limited field of view of <2 nm provided by this apparatus, it still can be seen as the first true APT instrument capable of determining both the structure and chemistry of a sample material, albeit limited to assessing only around 50,000 atoms (Miller and Forbes 2009).

Major limitations, however, still hampered the technology. The requirement that the voltage on the specimen tip be rapidly pulsed limited analyses to electrical conductors: semiconductors and insulators remained off limits. This situation changed in the 1970s (see review by Kelly and Miller 2007) with the realisation that short-duration laser pulses, focused on the sample tip, could be used to excite sample atoms to above the energy threshold at which field emission ionization occurs. Tsong (1978) reported photon-stimulated field ionization from a metal tip. Kellogg and Tsong (1980) were the first to successfully couple a ToF system to a pulsed-laser evaporation source. This new system had two major advantages over earlier pulsed-voltage field evaporation techniques. First, it brought the analysis of semiconductors into the realm of the possible. Second, it largely eliminated the broad energy distributions inherent to the emission of ions during either the voltage-pulse rise or drop that degrades the ToF spectrum. In hindsight, the major advance of photo-assisted field emission did not initially have many followers: lasers were expensive and difficult to align, and the thermal pulse was too protracted to give really precise start times for the emission process. In the early 2000s, more robust laser systems were developed. Also, the development of ultrafast lasers greatly improved the time resolution of the affiliated ToF spectrometer because the duration of thermally coupled emission could be reduced to below a few tens of picoseconds.

Another drawback of APT technology was the many problems associated with specimen preparation. Electropolishing had long been a preferred option, but it was not site specific and it generally required a



**FIGURE 2** Basic layout of a local-electrode ion optical design. IMAGE COURTESY OF CAMECA

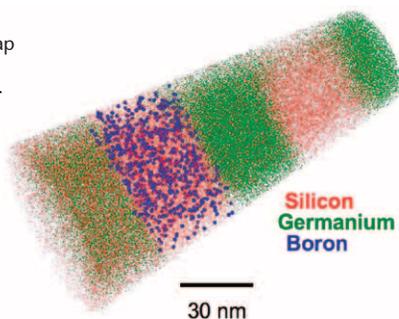


wire-like geometry for the starting material (see also Kelly and Miller 2007); also, the taper angle and diameter of the tip were difficult to control. In the 1980s, new ion-based methods of sample preparation were devised, and focused ion beam (FIB) technology was developed. The FIB technique has now become a must-have tool for many TEM applications, as the area to be investigated can be precisely selected and the geometry of the final specimen – whether a foil or a tip – can be controlled with nanometre precision. The first application of FIB sample preparation to APT technology was reported by Waugh et al. (1984), which opened up an entirely new world of possibilities for materials studies.

At the turn of the 21<sup>st</sup> century, the most common complaint of the atom probe user community was probably the slow data-collection rate: repetition rates were only on the order of 10 kHz, leading to the practical limit that a given experiment could only observe perhaps  $10^6$  ions. After correcting for ion-detection efficiency, this would translate into an available volume for a single analysis of only around  $10^4 \text{ nm}^3$ . This tiny sample size excluded many applications for which APT was otherwise well suited. This began to change with the advent of “local electrode” technology whereby the specimen tip is positioned in front of a funnel-shaped extraction electrode with an aperture diameter of only a few tens of microns (FIG. 2). By placing the local electrode close to the sample – again we are speaking of a few tens of microns – much higher electric field gradients are achieved relative to “traditional” ion optic geometries operating at the same absolute potential. This yields a number of advantages when operating in pulsed-voltage mode, including better mass resolution for the ToF spectrometer and repetition rates well beyond 100 kHz (see Kelly et al. 1996). Other advantages of using a local electrode are that (1) the field of view of the system can exceed 100 nm, (2) it is possible to employ a planar microtip sample geometry and (3) one can load many sample tips on a single specimen holder as only the single tip in close proximity to the local electrode will undergo the field emission process. Thanks to this new ion optical design, experiments involving over  $10^8$  atoms and volumes in excess of  $10^6 \text{ nm}^3$  became realistic (FIG. 3).

What challenges remain? Obviously it would be valuable to couple the local-electrode geometry with the pulsed-laser evaporation technique, thereby making state-of-the-art ion optics applicable to poorly conducting specimens. Exactly such studies have recently been reported.

**FIGURE 3** An example of a 3-dimensional map of a semi-conductive structure acquired using pulsed laser APT. IMAGE COURTESY OF CAMECA



**FIGURE 4** Cameca’s laser-assisted atom probe, like the one used by Bachhav et al. (2011) to investigate wüstite. This particular instrument design has recently gone out of production, having been superseded by the “LEAP 4000X” model. IMAGE COURTESY OF CAMECA

Bachhav et al. (2011) used a 350 fs pulse-width laser operating at 100 kHz (FIG. 4) to analyse iron oxide grains glued to tungsten supports, which were then subjected to ion milling. Using this approach, these authors were able to quantify the Fe/O ratio in non-conducting wüstite at atomic-scale resolution. Equally interesting is a report by Gordon and Joester (2011), who used laser-assisted APT to investigate the nano-scale properties of organic fibres buried within the tooth of the marine mollusc *Chaetopleura apiculata*. Their data reveal a previously undocumented level of hierarchy within this organic scaffold.

APT sample preparation remains rather tedious, requiring expensive technology. For electrically non-conducting samples, many analytical parameters still need to be optimized. Nonetheless, atomic-scale mapping of non-conductors is nearly within our grasp. So how long will it be before this highest of high-tech methods will be taken up in the Earth sciences? I suspect that it is only a matter of time ... and money.

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