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April 18, 2019

Dear Dr. DSouza [Editor JoVE],

Thank you for your additional editorial comments. Please find enclosed with this letter the revised version of the second revision "R2" of the article entitled "Atom Probe Tomography (APT) Analysis of Exsolved Mineral Phases" towards publication in *JoVE*.

We have considered carefully your comments, and we have determined that, for "APT Data Processing", software steps are difficult to be better explained with more words in order to be adequate for scripting and filming. Thus, we followed your recommendation after the first revision of the manuscript and remove the highlighting in this section; if, during filming, it is considered showing this aspect of the protocol, we will be glad to collaborate towards this goal.

Thank you very much for your time and consideration. We hope that changes are already adequate for acceptance of the manuscript.

Sincerely yours,

Alberto Perez-Huerta (On behalf of the authors)

Associate Professor
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1   **TITLE:**
2   Atom Probe Tomography Analysis of Exsolved Mineral Phases
3

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16 **KEYWORDS:**
17 Atom probe tomography, APT, volcanic ash, titanomagnetite, ilmenite, exsolution lamellae, FIB-
18 SEM lift-out, LEAP
19

20 **SHORT ABSTRACT:**
21 Analysis of the morphology, composition, and spacing of exsolution lamellae can provide
22 essential information to understand geological processes related to volcanism and
23 metamorphism. We present a novel application of APT for the characterization of such lamellae
24 and compare this approach to the conventional use of electron microscopy and FIB-based
25 nanotomography.
26

27 **LONG ABSTRACT:**
28 Element diffusion rates and temperature/pressure control a range of fundamental volcanic and
29 metamorphic processes. Such processes are often recorded in lamellae exsolved from host
30 mineral phases. Thus, the analysis of the orientation, size, morphology, composition and spacing
31 of exsolution lamellae is an area of active research in the geosciences. The conventional study of
32 these lamellae has been conducted by scanning electron microscopy (SEM) and transmission
33 electron microscopy (TEM), and more recently with focused ion beam (FIB)-based
34 nanotomography, yet with limited chemical information. Here, we explore the use of atom probe
35 tomography (APT) for the nanoscale analysis of ilmenite exsolution lamellae in igneous
36 titanomagnetite from ash deposits erupted from the active Soufrière Hills Volcano (Montserrat,
37 British West Indies). APT allows the precise calculation of interlamellar spacings (14–29 ± 2 nm)
38 and reveals smooth diffusion profiles with no sharp phase boundaries during the exchange of Fe
39 and Ti/O between the exsolved lamellae and the host crystal. Our results suggest that this novel
40 approach permits nanoscale measurements of lamellae composition and interlamellar spacing
41 that may provide a means to estimate the lava dome temperatures necessary to model extrusion
42 rates and lava dome failure, both of which play a key role in volcanic hazard mitigation efforts.
43

44 **INTRODUCTION:**

The study of chemical mineralogy has been a major source of information within the field of Earth Sciences for more than a century, as minerals actively record geological processes during and after their crystallization. Physio-chemical conditions of these processes, such as temperature changes during volcanism and metamorphism, are recorded during mineral nucleation and growth in the form of chemical zonation, striations, and lamellae, among others. Exsolution lamellae form when a phase unmixes into two separate phases in the solid state. The analysis of the orientation, size, morphology, and spacing of such exsolution lamellae can provide essential information to understand temperature and pressure changes during volcanism and metamorphism[1-3] and the formation of ore mineral deposits[4].

Traditionally, the study of exsolution lamellae was conducted with the observation of micrographs by simple scanning electron imaging[5]. More recently, this has been substituted by the use of energy-filtered transmission electron microscopy (TEM) providing detailed observations at the nanoscale level[1-3]. Nevertheless, in both cases, the observations are made in two dimensions (2D), which is not fully adequate for three dimensional (3D) structures represented by these exsolution lamellae. Nanotomography[6] is emerging as a new technique for the 3D observation of nanoscale features inside minerals grains, yet there is insufficient information about the composition of these features. An alternative to these approaches is the use of atom probe tomography (APT), representing the highest spatial resolution analytical technique in existence for the characterization of materials[7]. The strength of the technique lies in the possibility of combining a 3D reconstruction of nanoscale features with their chemical composition at the atomic scale with a near part-per-million analytical sensitivity[7]. Previous applications of APT to the analysis of geological samples have provided excellent results[8-11], particularly in the chemical characterization of element diffusion and concentrations[9, 12-13]. Yet, this application has not been used for the study of exsolution lamellae, abundant in some minerals hosted in metamorphic and igneous rocks. Here, we explore the use of APT, and its limitations, for the analysis of the size and composition of exsolution lamellae, and interlamellar spacing in volcanic titanomagnetite crystals.

PROTOCOL:

1. Sourcing, selection, and preparation of mineral grains

NOTE: Samples were obtained from the catalogued collection at the Montserrat Volcano Observatory (MVO) and derived from falling deposits originating from a vigorous ash venting episode at Soufrière Hills Volcano that occurred on 5 October, 2009; this was one of 13 similar events over a course of three days[14]. This ash venting preceded a new phase of lava dome growth (phase 5) that commenced on 9 October. Previous analysis of this sample showed it to be a combination of dense dome rock fragments, glassy particles, and accidental lithics[14].

1.1) Pour 1 g of volcanic ash sample into a 10 cm diameter glass Petri dish.

1.2) Wrap a small (3 cm x 3 cm) sheet of weighing paper around a 10 G magnet.

1.4) Use a paper-wrapped magnet to pull magnetite-rich grains between 100 μm and 500 μm in diameter from the ash sample and place in a 32 μm (5 φ), 8 cm diameter stainless-steel sieve.

1.5) Rinse in deionized water for 20–30 s using a squeeze bottle to remove smaller, adhering ash particles (which will pass through the sieve), and air-dry for 24 h.

1.6) Affix clean and dry ash particles to sample mounts suitable for the secondary electron microscope (SEM). Image in secondary electron mode at a 15–20 kV accelerating voltage and at a working distance of 10 mm to select the 5–10 best candidates for further analysis. Selected grains should be predominantly (>50%) magnetite (**Figure 1a,b**).

1.7) Affix selected ash grains to clear tape, surround with one-inch diameter hollow mold (metal, plastic, or rubber) that has been internally coated with vacuum grease, and pour in epoxy resin to fill the mold (2 cm^3). Allow epoxy to cure according to the specific epoxy instructions.

1.8) Once epoxy has cured, remove from mold and peel tape from the bottom. Ash grains should be partially exposed.

1.9) Polish the epoxy-cast ash grains using SiC grinding paper of five different grit sizes (400, 800, 1200, 1500 and 2000 grit).

1.9.1) Polish the sample with each grit size, from highest (400) to lowest (2000) in a figure eight motion for at least 10 min. In between grit sizes, sonicate the sample in a bath of deionized water for 10 min.

1.9.2) Check the sample under a microscope to ensure that the polishing grit is not present, and the sample surface is free from scratches. If scratches are present, repeat the polishing procedure with the previous grit size before sonicating and moving to the next grit size.

1.10) Polish the epoxy-cat ash grains with alumina polishing suspensions of 1.0 μm and then 0.3 μm on polishing cloths.

1.10.1) Polish the sample with each suspension in a figure eight motion for at least 10 min. In between suspension sizes, sonicate the sample in a bath of deionized water for 10 min.

1.10.2) Check the sample under a microscope to ensure that the suspension is not present and the sample surface is free of scratches. If scratches are present, repeat the polishing procedure with the previous suspension before sonicating and moving to the next suspension size. At the end of the polishing procedure, the epoxy surface should be smooth and the ash grains should be flat and well-exposed.

1.11) Coat the sample surface with a conducting coat of ~10 nm thick carbon using an available sputter coating device.

1.12) Obtain backscattered electron images of the ash grains with the electron microscope at a 15–20 kV accelerating voltage and a working distance of 10 mm to determine the location of exsolution lamellae in the magnetite (**Figure 1c**), as conducted in previous studies[5].

[Place Figure 1 here]

2. Atom probe tomography (APT) sample preparation

2.1) APT samples will be prepared from a wedge of material that reveals the presence of exsolution lamellae (**Figure 1d**) employing a FIB-based lift-out protocol[16] (**Figure 2**). Prior to FIB work, sputter coat the sample surface with 15 nm layer of Cu to avoid electron charging and sample drifting.

2.2) Using a focused ion beam in a dual beam scanning electron microscope (FIB-SEM), deposit a rectangle of platinum (Pt) (3 μm in thickness) on the polished section of interest containing the lamellae over a 1.5 μm x 20 μm region using a gallium (Ga$^+$) ion beam at 30 kV and 7 pA.

NOTE: This platinum layer is deposited to protect the region of interest (ROI) from ion beam damage.

2.3) Mill three wedges of material below three sides of the Pt rectangle using the ion beam (30 kV, 1 nA). See **Figure 1d** and **Figure 2**.

2.4) Insert the gas injection system (GIS) and weld the wedge to an in situ nano-manipulator using GIS-deposited Pt before cutting the final edge free (**Figure 2a**).

2.4) Using the Ga$^+$ ion beam (5 kV and 240 pA), cut ten 1–2 μm wide segments from the wedge and sequentially affix them with Pt to the tops of Si posts of a microtip array coupon (**Figure 2b–d**).

2.5) Shape and sharpen each specimen tip using annular milling patterns of increasingly smaller inner and outer diameters (**Figure 3**). Initially, perform the milling at 30 kV to produce the specimen geometry necessary for APT (**Figure 3**, left panel).

2.6) Perform the final milling at an accelerating voltage of 5 kV in order to reduce Ga+ implantation and obtain a consistent tip-to-tip shape (**Figure 3**, right panel).

2.7) By applying the measuring tools of the SEM to the figure, ensure that the diameter at the top of the tips ranges 50–65 nm, while the shank angle of the tips ranges from 25° to 38°.

NOTE: Further details have been previously published, describing the conventional lift-out protocol[16].

[Place Figures 2 and 3 here]

177
3. APT data acquisition

3.1) Perform analysis with a local electrode atom probe (LEAP) equipped with a pico-second 355 nm UV laser. See specific LEAP running parameters in **Table 1**.

NOTE: Analyses were performed with a LEAP equipped with a pico-second 355 nm UV laser, housed in the Central Analytical Facility (CAF) at The University of Alabama.

3.2) Mount the micro-coupon with the sharpened tips, welded to the Si posts, in a specimen puck and load into a carousel for placement inside the LEAP.

3.3) Insert the carousel inside the buffer chamber of the LEAP.

3.4) Turn the laser head on and perform a laser calibration.

3.5) After achieving vacuum in the analysis chamber at or below 6 x 10^{-11} Torr, insert the puck specimen into the main analysis chamber. For this use a transfer rod; this is operated with a series of automatic steps and manual insertion.

3.6) Before analysis, select the tip by moving the specimen puck to align the micro-coupon with the local electrode and update the database to indicate the tip number.

NOTE: Four out of six tips were analyzed successfully (two fractured during analysis) and resulted in a variable amount of acquired data ranging from 26 to 92 million total detected ions, which corresponded to the removal of a 160–280 nm-thick layer of magnetite (see specific LEAP running parameters in **Table 1**).

[Place Table 1 here]

4. APT data processing

4.1) Open the dataset in the processing software (see the **Table of Materials**) and perform the following steps for data analysis.

4.1.1. Review the information setup.

4.1.2. Select ion sequence range based on the voltage history plot. Select the detector region of interest (ROI).

4.1.3. Perform time-of-flight (TOF) correction. Use peaks corresponding to oxygen and iron for the TOF correction.

4.1.4. Perform mass calibration with the identification of main peaks.

221

222   4.1.5. Perform the ranging of ions for their assignments to specific masses.

223

224   4.1.6. Perform the reconstruction of the tip profile.

225

226   4.2) Show the data into the two main formats: 1) mass-to-charge state ratio (Da) chemical spectra
227   (**Figure 4**); and 2) 3D reconstructions of tip specimens (**Figure 5**).

228

229   4.3) Define peak ranges as the entire visible peak, or adjust manually when large thermal tails are
230   present, for each mass-to-charge state ratio spectrum (**Figure 4**). These peaks represent single
231   elements or molecular species, and the decomposition of peaks provides the overall chemical
232   composition for each tip or feature (i.e., clusters and exsolution lamellae) inside each tip (**Table
233   2**).

234

235   4.4) Perform three-dimensional (3D) tip reconstructions using the "voltage" tip profile method[17]
236   to determine the reconstructed radius as a function of analyzed depth (**Figure 5** and **Movie 1**).

237

238   4.5) Reconstruct isosurfaces of exsolution lamellae to conduct interlamellar spacing
239   measurements (**Figure 5**) and establish the host mineral-lamella chemical relationship using
240   proxigrams[17-18] (**Figure 6**).

241

242   4.6) Measure interlamellar spacings with image analysis software.

243

244   [Place Figure 4 and Table 2 here]

245

246   **REPRESENTATIVE RESULTS:**
247   Like many titanomagnetite crystals from various stages of the Soufrière Hills Volcano (SHV)
248   eruption, the crystal analyzed here contains exsolution lamellae <10 µm in thickness, visible in
249   secondary SEM images (**Figure 1d**), which separate zones of Ti-rich magnetite, indicating a C2
250   stage of oxidation[18]. Based upon the SEM images, spacing between these lamellae ranges from 2
251   to 6 µm (n = 15). Four titanomagnetite specimen tips, referred as 207, 217, 218, and 219, were
252   successfully extracted from this single crystal and analyzed by APT (**Figure 5**). Two of the
253   specimens (207 and 218) showed homogenous concentrations of both Fe and Ti throughout
254   (**Figure 5a**), indicating that lamellae were not intersected. The other two specimens (217 and
255   219) showed zones with variable concentrations in Fe, O, and Ti (**Figure 5b–e**). These features
256   are parallel to each other and have tapered terminations, indicative of trellis ilmenite[18]. Specimen
257   219 contains a larger proportion of the intersected lamellae than specimen 217. 3D
258   reconstructions of the APT data (**Figure 5c–e**, **Movie 1**) permit a precise measurement of the
259   interlamellar spacing (λ) and provide length scales that average 29 nm for specimen 219 (n = 30)
260   and 14 nm for specimen 217 (n = 15), with a 1σ value of 2 nm for both. In addition to these
261   measurements, APT permits extraction of chemical information across these lamellae at high
262   spatial resolution (nanoscale) through the analysis of proxigrams, taking the point 0 as the
263   intersection between the lamella and the host mineral (**Figure 6**). Proxigram diffusion profiles
264   through these zones are smooth. Atomic concentrations of Ti in the crystal, 17% in specimen 217

265 and 16.5% in specimen 219 (**Figure 6**), confirm that it is a titanomagnetite and are consistent with
266 previous petrologic analyses of SHV eruptive products[18]. These proxigrams also confirm that the
267 composition of lamellae matches that of ilmenite (**Figure 6**).
268
269 [Place Figures 5 and 6 here]
270
271 **FIGURE AND TABLE LEGENDS:**
272
273 **Figure 1: Example of magnetite-rich ash grains from venting episodes at the Soufrière Hills**
274 **volcano.** (**a**, **b**): Backscattered electron images (BSE) of both reacted and unreacted textures in
275 magnetite grains. (**c**) BSE image of a polished magnetite grain showing the presence of exsolution
276 lamellae (light grey laths; red arrows) of potential ilmenite composition. (**d**) Secondary electron
277 image of a polished magnetite grain prepared for atom probe tomography (APT) analysis,
278 showing the location of some exsolution lamellae (dashed red lines), which are distributed all
279 along the grain surface, and the location of the wedge extraction (blue arrow).
280
281 **Figure 2: Example of FIB-SEM sample preparation protocol for APT analysis.** (**a**) Wedge (W) lift-
282 out extraction with the nanomanipulator (Nm). (**b**) Lateral view of the micro-coupon array of
283 silicon posts mounted on a copper clip. (**c**) Top view of the micro-coupon array of silicon posts
284 showing the nanomanipulator for mounting the wedge sections. (**d**) Wedge fragment (S),
285 showing a portion of the protective platinum cap (Ptc), mounted on a silicon post after welding
286 with platinum (Ptw).
287
288 **Figure 3: Example of tips prepared for APT analysis.** (**Left**) Image of tip after the first stage of
289 sharpening. (**Right**) Image of the same tip after low kV cleaning, indicating the tip radius (67.17
290 nm) and the shank angle (26°).
291
292 **Figure 4: Example of a representative APT mass-to-charge spectrum.** Spectrum for the analyzed
293 magnetite crystal with individual ranged peaks showing examples of the identification of peaks
294 corresponding to single elements (e.g., oxygen (O) or iron (Fe)) or molecules (e.g., FeO).
295
296 **Figure 5: Example of 3D atomic reconstructions of magnetite tips analyzed (z values in nm)**. (**a**)
297 Specimen 218, showing homogenous concentrations of O, Fe, and Ti. (**b**) Specimen 219,
298 displaying regions depleted in Fe and enriched in O and Ti (lighter areas). (**c**) Elemental
299 isoconcentration surfaces of specimen 219, showing intralamellar concentrations of Fe < 30.0%
300 in blue, Ti > 25.0% in yellow, and O < 51.5% in purple. (**d**) View of same area in panel c, but rotated
301 90° to reveal the measured lamellar spacing (λ). (**e**) Specimen 217, showing a relatively smaller
302 portion of exsolution lamellae in the lower left (intralamellar concentrations: Fe < 19.0%, Ti >
303 33.0%, O < 49.0%).
304
305 **Figure 6: Proxigrams of APT data showing atomic concentrations of O, Fe and Ti in specimens**
306 **217 and 219, respectively**. A distance of zero on the x-axis (dashed vertical line) represents the
307 boundary between the titanomagnetite on the left and the ilmenite lamellae on the right. Across
308 this boundary, Ti concentrations increase from 17.0% to 44.0% and from 16.5% to 42.5% in

309   specimens 217 and 219, respectively. Fe contents decrease from 37.7% to 0.8% and from 38.5%
310   to 0.6% in specimens 217 and 219, respectively. O concentrations increase from 40.0% to 50.2%
311   and from 38.8% to 50.6% in specimens 217 and 219, respectively. Ti and O diffuse toward the
312   lamellae (to the right) and Fe is diffusing away from the lamellae (to the left). Error in all
313   measurements is < 2 atomic %.

315   **Figure 7: Schematic representation of different possibilities for capturing exsolution lamellae**
316   **in APT tips, and the implications for measuring lamellar spacing (λ).**

318   **Table 1. Atom probe tomography data acquisition settings and run summary.**

320   **Table 2. Atom probe tomography bulk compositional data for all analyzed specimens.**

321   **Movie 1. 3D elemental isoconcentration reconstruction of specimen 219, showing intralamellar**
322   **concentrations of Fe < 30.0% in blue, Ti > 25.0% in yellow, and O < 51.5% in purple, and rotated**
323   **360° along the longitudinal (z) axis.**

325   **DISCUSSION:**
326   3D APT data reconstructions allow a precise measurement of the interlamellar spacing in the
327   analyzed crystal at a resolution three orders of magnitude higher than those measured from
328   conventional SEM images. This indicates that atomic variations in chemistry occur over a spatial
329   extent three orders of magnitude smaller than optically observable mineralogical changes. Also,
330   the measured interlamellar distances (29 nm and 14 nm), are consistent with the length scale for
331   oxyexsolution as opposed to that for nucleation and growth of a separate phase, the latter of
332   which occurs over length scales an order of magnitude greater[19-20]. Oxyexsolution of the
333   titanomagnetite examined here may have resulted from either heating of the magma within the
334   chamber due to mingling events, or oxidation induced by atmospheric exposure during ascent
335   through the conduit and emplacement at the vent. The titanomagnetite crystal used in this study
336   displays numerous lamellae on the order of 10 μm or less in diameter, indicating sufficient time
337   for partial exsolution of the entire 0.06 mm^2 crystal. That observation, in conjunction with the
338   ash-venting origin of the sample, suggests that the lamellae were formed from oxidation of the
339   lava dome following emplacement at the vent.

341   [Place Figure 7 here]

343   These measurements of the interlamellar spacing were only possible in two of the four tips
344   analyzed and this sampling bias could induce error. As we only analyze nanoscale volumes of the
345   crystals, each tip could capture partial representation of the distribution of lamellae, potentially
346   leading to an erroneous calculation of interlamellar spacing (λ) (**Figure 7**). Nevertheless, with the
347   analysis of sufficient tips and the 3D tomography capabilities of APT, our approach provides a
348   novel method to precisely measure λ, which can be fundamental to understand a variety of
349   igneous and metamorphic processes. For example, analysis of Fe-Ti diffusion in magnetite
350   crystals has been used to characterize magma mingling events and changes in magma
351   temperature at Soufrière Hills Volcano[19]. The interdiffusion rate of Fe and Ti could be modeled

352 from accurate measurements of the interlamellar spacing if the timescale of diffusion can be
353 constrained. Previous studies have utilized exsolution lamellae to deduce cooling rates in igneous
354 intrusions[21-22], and the novel approach of using APT can potentially be utilized to constrain
355 element interdiffusion and improve calculations of magma and lava dome temperatures in active
356 volcanic systems[23-24]. Besides the precise measurement of 3D structures at nanoscale, APT
357 provides chemical information at the atomic scale for the same spatial resolution. This has
358 resulted in demonstrating that the transition from titanomagnetite to ilmenite is gradual and
359 smooth (**Figure 6**). This is in contrast to previous studies suggesting sharp and distinct contacts
360 between the exsolving lamellae and the host phase, based on microscopy observations (SEM and
361 TEM) without the chemical information. Consequently, only the addition of APT can accurately
362 provide the geochemical characteristics of these phase transitions.
363
364 Atom probe tomography (APT) is still an emerging technique for geological applications[25], yet our
365 case study demonstrates the usefulness of applying this approach for the study of exsolution
366 lamellae, quite common in minerals hosted in igneous and metamorphic rocks. In particular for
367 understanding volcanic processes, future studies can examine multiple samples with exsolution
368 lamellae throughout lava domes (derived from either ash venting episodes or dome collapse
369 events) in order to better constrain variations in temperature during eruptive episodes with
370 calculated diffusion rates.
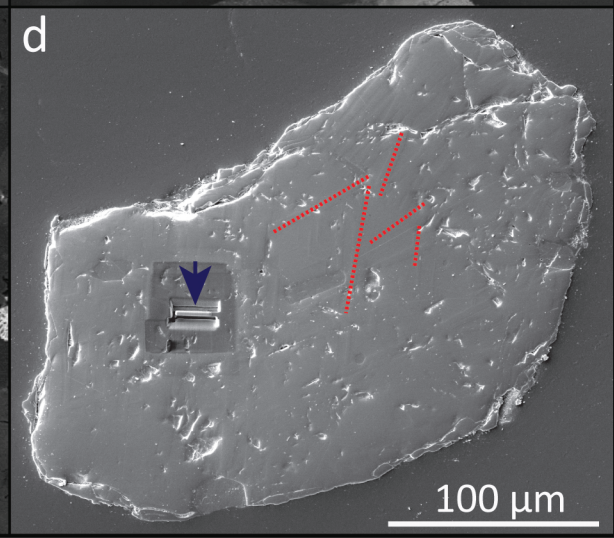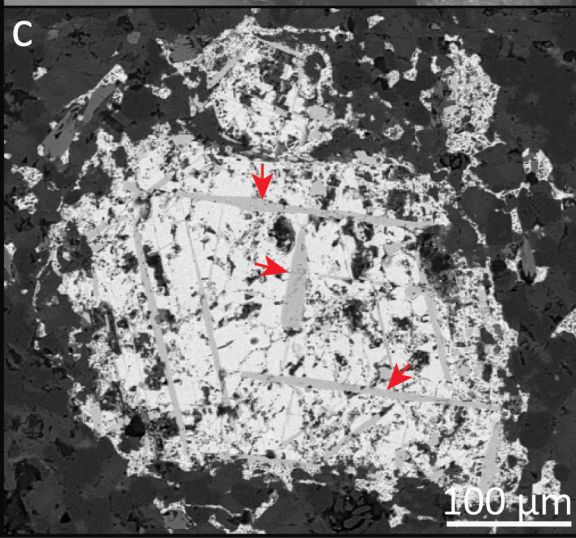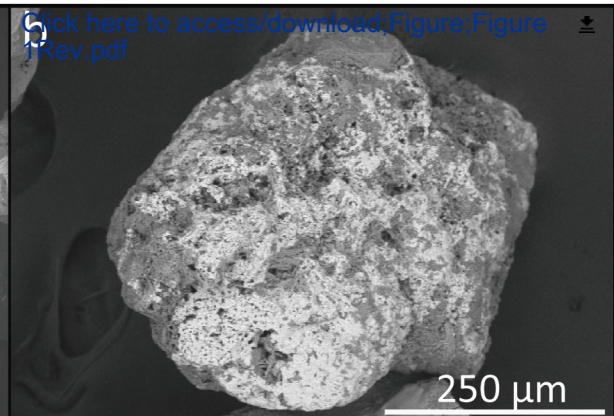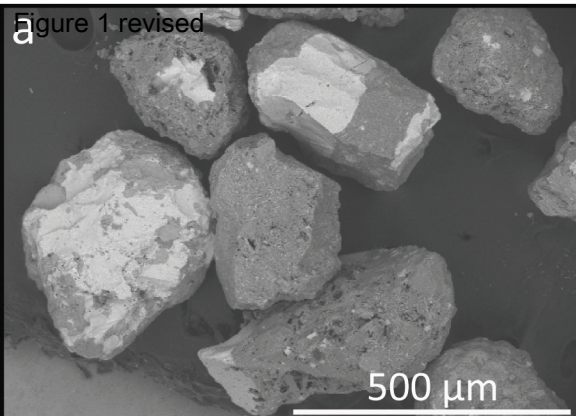371

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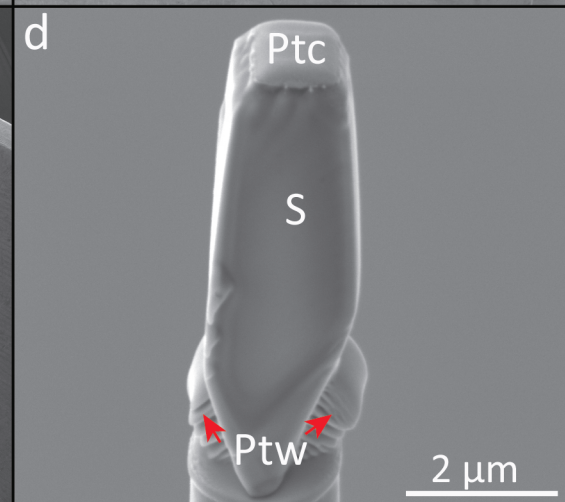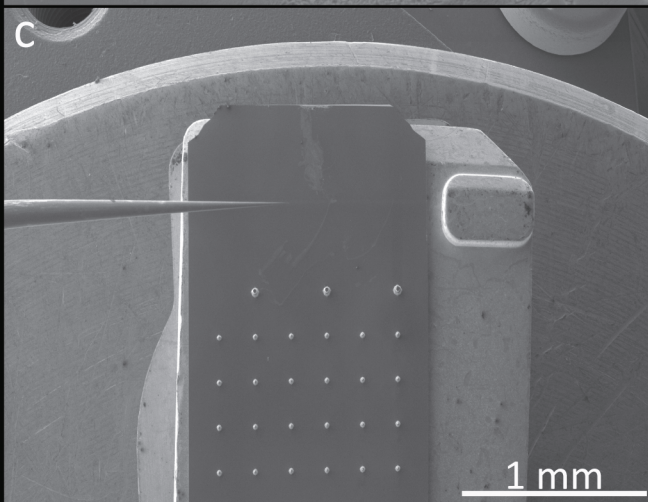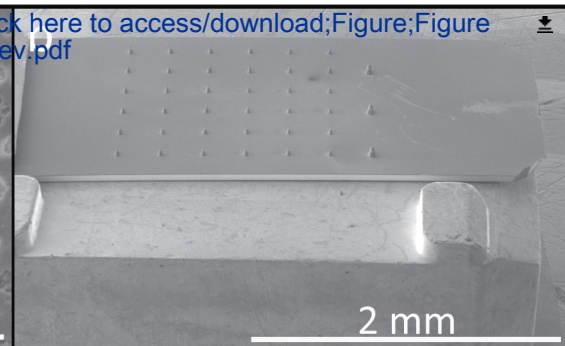447
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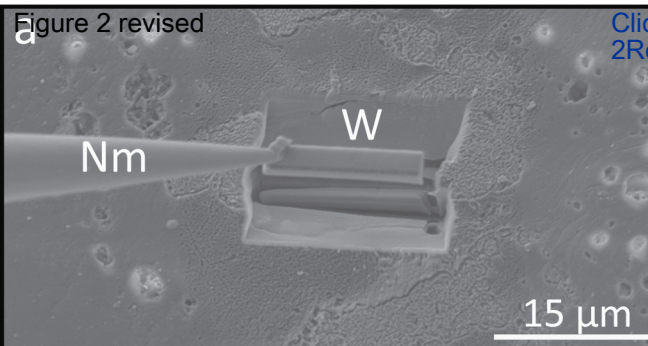
Figure 1 revised

a 500 μm

b 250 μm

c 100 μm

d 100 μm

Figure 2 revised

a — Nm, W, 15 μm

b — 2 mm

c — 1 mm

d — Ptc, S, Ptw, 2 μm

Figure 3 revised

2.5 μm

ß1 = 26° 24'

C1
r = 67.17 nm

1 μm

Figure 4 revised

Figure 5
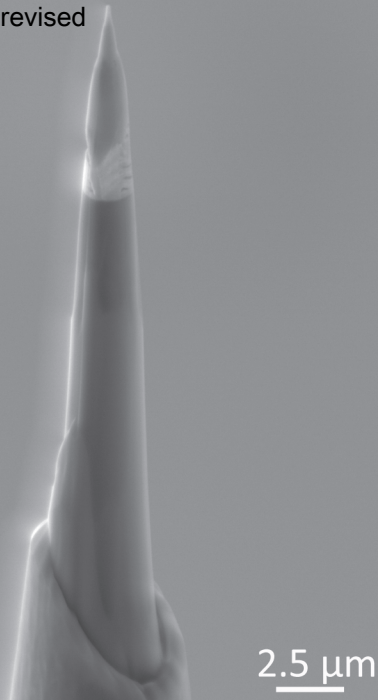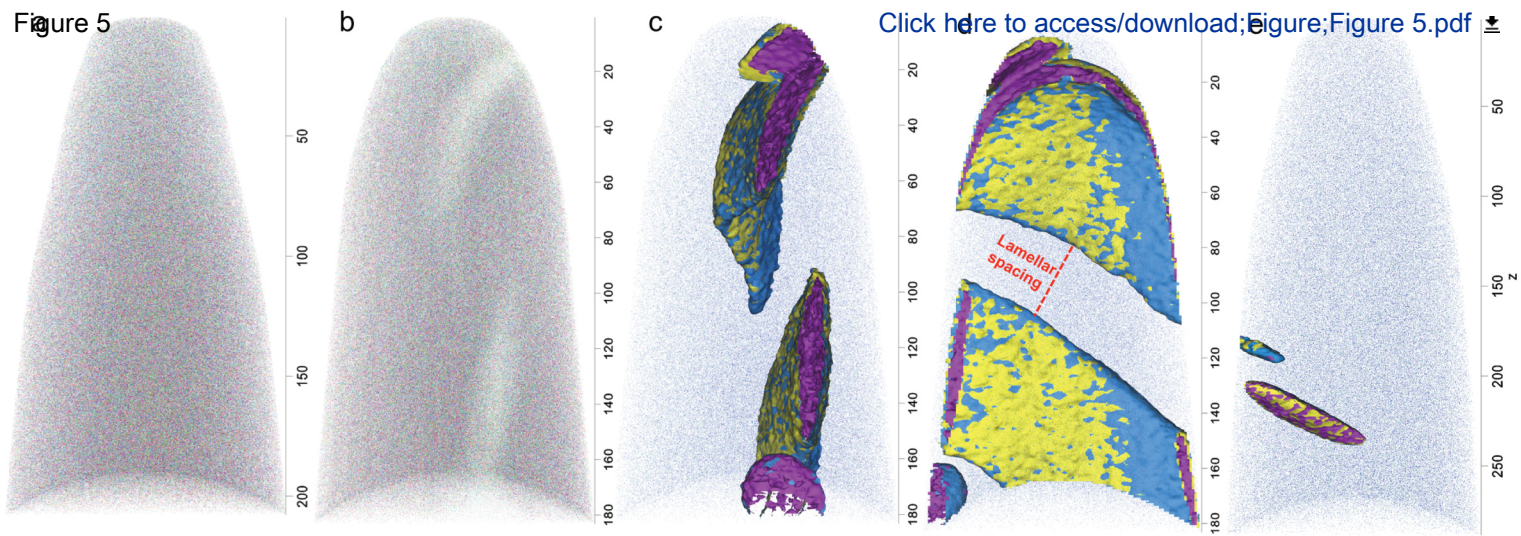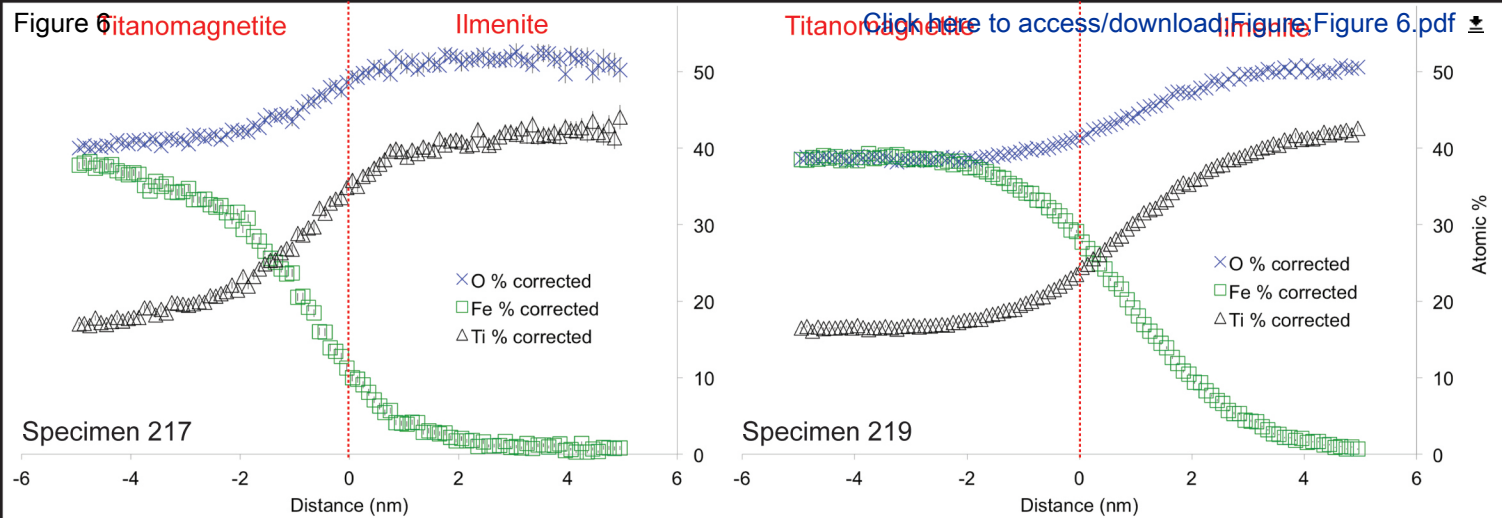
Figure 6

Figure 7

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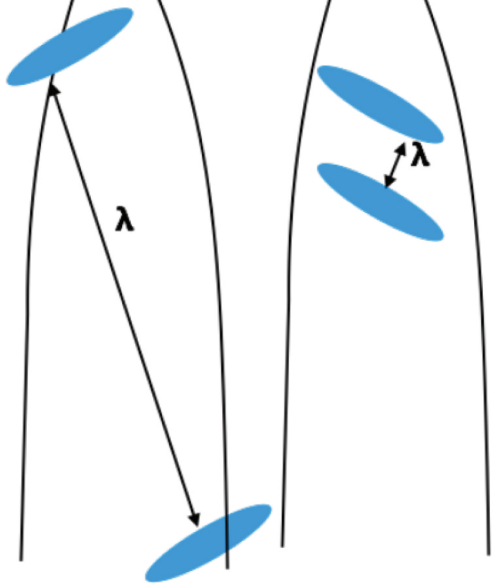
Table 1

Table 1. Atom Probe Tomography data acquisition settings and run summary.

Specimen	207	217
Sample Description	**SHV Magnetite**	**SHV Magnetite**
Instrument Model	**LEAP 5000 XS**	**LEAP 5000 XS**
Instrument Settings		
Laser Wavelength	355 nm	355 nm
Laser Pulse Rate	60 pJ	30 pJ
Laser Pulse Energy	500 kHz	500 kHz
Evaporation Control	Detection Rate	Detection Rate
Target Detection Rate (%)	0.5	0.5
Nominal Flight Path (mm)	100	100
Temperature (K)	50	50
Pressure (Torr)	5.7×10^{-11}	6.0×10^{-11}
ToF offset, t_o (ns)	279.94	279.94
Data Analysis		
Software	IVAS 3.6.12	IVAS 3.6.12
Total Ions:	26,189,967	92,045,430
Single	15,941,806	55,999,564
Multiple	9,985,564	35,294,528
Partial	262,597	751,338
Reconstructed Ions:	25,173,742	89,915,256
Ranged	16,053,253	61,820,803
Unranged	9,120,489	28,094,453
Background *(ppm/nsec)*	12	12
Reconstruction		
Final tip state	Fractured	Fractured
Pre-/Post-analysis Imaging	SEM/n.a.	SEM/n.a.
Radius Evolution Model	"voltage"	"voltage"
$V_{initial}$; V_{final}	2205 V; 6413 V	2361 V; 7083 V

218	219
SHV Magnetite	SHV Magnetite
LEAP 5000 XS	LEAP 5000 XS
355 nm	355 nm
30 pJ	30 pJ
500 kHz	500 kHz
Detection Rate	Detection Rate
0.5	0.5
100	100
50	50
6.1×10^{-11}	6.1×10^{-11}
279.94	279.94
IVAS 3.6.12	IVAS 3.6.12
40,013,656	40,016,543
24,312,784	23,965,867
15,331,670	15,716,119
369,202	334,557
38,415,309	39,120,141
25,859,574	26,598,745
12,555,735	12,521,396
12	12
Fractured	Fractured
SEM/n.a.	SEM/n.a.
"voltage"	"voltage"
2198 V; 6154 V	2356 V; 6902 V

Table 2

Table 2. APT background corrected values for atomic % of elements.

Specimen	207			217		
Element	Atom count	Atomic %	1σ error	Atom count	Atomic %	1σ error
O	9459276	40.263	0.0155	36679256	40.724	0.0080
Fe	9424298	40.114	0.0155	35948593	39.913	0.0079
Mn	15954	0.068	0.0005	72884	0.081	0.0003
Mg	123755	0.527	0.0015	486732	0.540	0.0008
Al	85598	0.364	0.0013	329602	0.366	0.0006
Si	13855	0.059	0.0005	39307	0.044	0.0002
Na	166	0.001	0.0001	1254	0.001	0.0000
Ti	4360052	18.558	0.0097	16478946	18.296	0.0049
H	10657	0.045	0.0004	30522	0.034	0.0002
Total	23493611	100.00	0.04	90067097	100.00	0.02
Fe+Ti+O		98.94			98.93	
Fe/Ti		2.16			2.18	

218			219		
Atom count	Atomic %	1σ error	Atom count	Atomic %	1σ error
15396155	41.010	0.0124	16212281	41.224	0.0122
14829905	39.502	0.0121	15006853	38.159	0.0116
28166	0.075	0.0004	31450	0.080	0.0005
203596	0.542	0.0012	234231	0.596	0.0012
134637	0.359	0.0010	154779	0.394	0.0010
16278	0.043	0.0003	25750	0.065	0.0004
447	0.001	0.0001	1468	0.004	0.0001
6920481	18.434	0.0076	7645849	19.442	0.0077
12899	0.034	0.0003	14478	0.037	0.0003
37542563	100.00	0.04	39327140	100.00	0.03
	98.95			98.82	
	2.14			1.96	

Table of Materials

Name of Material/Equipment	Company	Catalog Number	Comments/Description
InTouchScope Secondary Electron Microscope (SEM)	JEOL	JSM-6010PLUS/LA	
Focus Ion Beam (FIB) Secondary Electron Microscope (SEM)	TESCAN	LYRA XMU	
Local Electrode Atom Probe (LEAP)	CAMECA	5000 XS	
Integrated Visualization and Analysis Software (IVAS, version 3.6.12).			processing software

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