Between defects and inclusions: the fate of tellurium in pyrite

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Abstract

Tellurium (Te) is a critical commodity, essential for renewable energies and high-tech applications. Most Te is currently recovered from copper smelters, but rising demand requires sourcing from alternative supplies. However, the mineralogy of Te-rich ores is poorly understood and hinders their economic potential. Here, we investigate the distribution of Te in pyrite from a high-grade Au-Ag-Te epithermal-type ore to inform metallurgical extraction methods, and secure future Te supply. We identified three distinct modes of Te incorporation in this pyrite, which challenge previous solubility models. (1) Te solid-solution, at concentrations (up to 285 ppma) that significantly exceed previous solubility limits. (2) Nano-telluride inclusions along cracks that formed by intra-grain remobilization. (3) Crystal defects, enriched in Te through pipe diffusion hosting up to 0.5 at.% Te. Our results therefore provide new fundamental insights into the chemical and structural coordination of Te in pyrite, which may guide future efforts for its direct recovery.

1 Introduction

The technical transition towards low-carbon energy production relies on a secure supply of critical elements, which are, however, commonly recovered as by-products. Tellurium, which is an important constituent in high efficiency thin film photovoltaic technology is such an example. Currently, most Te is produced from anode slimes of base metal smelters (e.g., Cu and Pb), as a by-product element. This directly limits the Te supply to the amount of Cu and Pb ores that are processed, however, the Te demand is projected to significantly outpace that of Cu and Pb over the next decade. Tellurium generally has a low crustal abundance (~5ppb), but local enrichments to 0.5 wt. % were reported in world-class low sulfidation epithermal Au-Ag-Te deposits, such as Cripple Creek (Colorado), Porgera and Ladolam (Papua New Guinea), and Vatukoula (Fiji). The formation of these deposits seems to be genetically linked to post-subduction alkaline magmatism. Hydrothermal fluids in the given environments are characterized by neutral to alkaline pH (≥7) due to the high buffering capacity of the alkaline host rocks, which enhances the Te and Au solubility. Large quantities of dissolved Te effectively precipitate through fluid mixing, boiling-induced vapor condensation or fluid-wall rock interaction. Besides Au-Ag tellurides, the precipitated Te is also commonly hosted by sulfides like As-bearing (arsenian) pyrite and galena. Arsenian pyrite may incorporate up to 1.6 wt. % Te and is often already processed for the recovery of ‘invisible’ Au. Conservative mass balance calculations indicate that up to 60% of the bulk Te may be hosted by arsenian pyrite in alkaline-hosted epithermal deposits. However, Te is currently only extracted from three epithermal (like) deposits worldwide (Dashuigou and Majiagou, China; Kankberg, Sweden) and generally without considering Te in pyrite. Hence, even if Te is recovered as a primary product from these deposits, its recovery rate will stay low, as long as arsenian pyrite is not integrated into the processing chain. Most current extraction methods for ‘invisible’ Au in pyrite include roasting and cyanidation, which cannot access associated ‘invisible’ Te, as roasting
would cause a Te loss due to its volatile behavior\textsuperscript{18}. Hence, a full chemical and structural characterization of Te in pyrite down to the nano- and atom-scale is required, to adjust the refining and recovery process.

2 Samples & Methods

The studied high-grade ore sample (VM-17-12.3) originates from the world-class low-sulfidation epithermal Au-Ag-Te deposit of Vatukoula (formerly Emperor), Fiji. In a previous study, the bulk composition of the sample was determined by XRF (~ 500 µg/g Au, ~ 800 µg/g Te) and the trace element composition of the hydrothermal pyrite by Laser Ablation – Inductively Coupled Plasma – Mass Spectrometry\textsuperscript{6}. The Vatukoula deposit sits on the intersection of two large fault zones, the Viti Levu lineament and the Nasivi shear zone (Fig. 1a). The ~ 10 Moz Au mineralization is located at the western margin of the Tavua caldera and is associated with caldera contact breccias and high-K calc-alkaline volcanic rocks (i.e., shoshonite, absarokite, Fig. 1b). The Au-Ag-Te mineralization is mostly related to native gold, electrum and tellurides, such as sylvanite [(Au,Ag)\textsubscript{2}Te\textsubscript{4}] and minor calaverite [AuTe\textsubscript{2}], petzite [Ag\textsubscript{3}AuTe\textsubscript{2}], hessite [Ag\textsubscript{2}Te], and native Te\textsuperscript{19,20}. In addition, arsenian pyrite, as the most abundant sulfide mineral, also hosts significant amounts of Au, Ag and Te reaching 1,000 to 10,000 µg/g. One pyrite grain from the high-grade ore sample VM-17-12.3 was selected for the following micro- and nano-analytical study due to its good preservation, growth zoning (Fig. 1c) and available trace element data of other pyrite grains from this specimen that are characterized by high Te contents reaching up to 600 ppma (Supplementary Fig. 1a-c; Supplementary Table 1)\textsuperscript{6}.

2.1 Electron probe microanalysis (EPMA)

The EPMA (n = 13) was performed by a JEOL JXA-8200 Superprobe at the GeoZentrum Nordbayern. Wavelength-dispersive x-ray spectrometry (WDX) was used to quantify the major and trace element contents in the selected pyrite grain (Supplementary Fig. 1a). The analyses were performed with a focused beam, an acceleration voltage of 20 kV and a beam current of 50 nA. Count times for the WDX were set to 20 and 10 s (S, Cu, Fe); 140 and 70 s (As, Ag, Au, Te) for the peak and background measurements, respectively. The WDX was calibrated by the following reference materials: FeS\textsubscript{2} (Fe, S), CuFeS\textsubscript{2} (Cu), InAs (As), Ag\textsubscript{2}Te (Ag, Te), Au (Au). Qualitive element maps were acquired by WDX (Fig. 1c-f) with a pixel size of 0.5 µm at a dwell time of 50 ms; all other measuring conditions were identical to the WDX spot analysis.

2.2 Transmission Electron Microscopy (TEM)

An electron-transparent lamella of ~ 220 nm thickness for TEM was prepared by a standard lift-out technique (Fig. 1c), using a Helios NanoLab 660 dual beam focused ion beam scanning electron microscope (FIB-SEM). Bright field and high-angle annular-dark field scanning transmission electron microscopy (BF-STEM and HAAD-STEM, respectively), energy dispersive X-ray spectroscopy combined with STEM (STEM-EDXS) and high-resolution STEM (HR-STEM) were performed at 300 kV using a Titan Themis\textsuperscript{3} 300 (Thermo Fisher Scientific) equipped with an ultrabright X-FEG electron source and spherical...
aberration correctors (both probe forming and imaging sides). All HR-STEM analyses were conducted after a thinning of the sample to ~100 nm by FIB. The EDXS spectra and the corresponding element maps were obtained by a Super-X detector. The measurements were performed at the IMN, IZNF and CENEM at Erlangen.

2.3 Atom Probe Tomography (APT)

Tip M15 for APT was prepared by a ZEISS Crossbeam 540 FIB-SEM (Fig. 1c), using the standard site-specific lift-out procedure. A pillar of ~1 µm in diameter was milled by FIB using a 3 nA and 30 kV Ga-ion beam, removed with a micromanipulator and attached to a tungsten substrate using the platinum gas injection system (GIS) in the FIB-SEM. The pillar was then sharpened to the required tip-shape at 100 pA and 10kV. Tips M14 and M16 were extracted using a Tescan LYRA3 FIB-SEM with a Ga+ ion source following the Pt fiducial targeting approach\textsuperscript{21} (Fig. 1c). Atom probe tomography experiments were performed on CAMECA LEAP 4000X HR instruments at the Department of Materials Science and Engineering at Erlangen, Germany (sample M15) and the Geoscience Atom Probe Facility, at the John de Laeter Centre of Curtin University, Australia (samples M14 and M16)\textsuperscript{22}. The APT analyses were conducted in laser-assisted mode using an ultraviolet laser (\(\lambda = 355\) nm) and under cryogenic base temperatures (50 to 60 K). The laser pulse energy was set between 35 and 50 pJ and the laser pulse rate at 125 kHz. An automated detection rate was maintained at 0.01 ion/pulse. Atom Probe Tomography data were reconstructed in 3 dimensions using CAMECA's APsuite 6 software. Voltage evolution mode reconstructions were performed with an atomic volume of 0.01325 nm\(^3\)/atom and an empirically determined electric field of 19.1 V/nm\textsuperscript{23}.

3 Results

3.1 Micro-scale results - EPMA

Back-scattered electron (BSE) imaging revealed three distinct growth zones (1, 2, 3) in the investigated pyrite, as reflected by different grey scales (Fig. 1c). Zone 1 in the center of the pyrite grain resembles a hexagon with relatively similar side length hosting up to 3.25 at. % As, 250 ppma Au and 22 ppma Te (Supplementary Fig. 1a; Supplementary Table 1). An internal epitaxial zoning is visible in the BSE contrast of zone 1, and the crystal growth appears to have been obstructed in parts at the top right facet (Fig. 1c). Growth zone 2 also shows elevated As contents (up to 2.26 at. %; Fig. 1d; Supplementary Table 1) and the As zoning of the left and right facet follows the shape of the hexagon defined by zone 1. In addition, the arsenic zoning in zone 2 is irregular and obstructed following the pattern of zone 1 at the upper part of the pyrite, whereas it is very thin to absent in the lower part of the grain (Fig. 1d). Zone 3 approximately resembles the 110 facet of a rhombitri truncated pyrite cube (Fig. 1c), with a ~29° clockwise rotation relative to the core (i.e. zone 1). Tellurium is decoupled from As and Au in zone 3, as indicted by rather low As (up to 0.4 at. %) and Au (up to 40 ppma), but high Te (up to 600 ppma) contents (Fig. 1d-f, Supplementary Table 1). We note that the As and Te concentrations in this pyrite (obtained by WDX), are in the range of other pyrite analysis from sample (VM-17-12.3) from a previous Laser Ablation –
Inductively Coupled Plasma – Mass Spectrometry study (Supplementary Fig. 1b). Multiple cracks of various scales intersect the pyrite without showing a preferential orientation (Fig. 1c).

### 3.2 Micro- to nano-scale results - TEM

Element maps of the TEM lamella that were extracted at the contact of zone 2 and 3 (Fig. 1c) by STEM-EDXS revealed finer epitaxial As zoning between zone 2 and 3 on the nano-scale (Fig. 2a-c). The zoning is parallel to the direction of crystal growth and is superimposed with the As zoning on the micro-scale that defines the transition between zone 2 and 3 (Fig. 1d). Three types of crystal defects can be distinguished in the bright field (BF; Fig. 2a) and the high annular dark field (HAADF; Supplementary Fig. 2b) image.

Long and straight defects 1 that are perpendicular to the growth facet of the crystal only occur in zone 3 (Fig. 2a, d). By contrast, the direction of the shorter defects 2 and 3 is unrelated to the crystal facet (Fig. 2a, d). Elongated high density nanophases mostly occur parallel to the direction of the crystal defects 3 (Fig. 2d). Cracks of up to 500 nm in width and 5 µm in length are documented in zone 2 and 3. The healed cracks resemble an en echelon structure in zone 2 (Fig. 2b, d), whereas in zone 3 the cracks are preferentially oriented along the intersection of defects 1 and 3 (Fig. 2d). Both types of cracks are partly healed by pyrite and tellurides with variable Te-Ag-Au contents, but also feature voids (Fig. 2b, d; Supplementary Fig. 3). After thinning of the TEM lamella from ~ 250 to ~ 100 nm, the porous triangular Ag-telluride (#1, Fig. 2d) disappeared (Supplementary Fig. 2c) and the Ag-Au-telluride in #2 (Fig. 2d) revealed a porous texture (Fig. 2f). High-resolution element mapping by STEM-EDXS within area #2 displayed an unequal distribution of Te, Ag and Au in the porous telluride (Fig. 2f, g). A ternary diagram (Au, Ag, Te) containing all STEM-EDXS results of this study and all SEM-EDXS results of measured tellurides from a previous study on the same thin section are provided in Supplementary Fig. 3e.

### 3.3 Nano-scale results - APT

A homogeneous trace element distribution on the nano-scale in the As-rich growth band of zone 1 (Fig. 1d) is confirmed by APT tip M14 (Fig. 3c). By contrast, the APT tips M15 and M16 from zone 3 show discrete planar features (#4 and #5; Fig. 3a-b) and line defects (#1 to #3; Fig. 3a) rich in Te, Sb, Cu, As and Pb (up to 3.5 at. %) relative to the surrounding pyrite matrix (Fig. 3 and Supplementary movies 1–4). Planar feature #4 (Fig. 3a) is rich in Au and Te but lacks elevated contents in the other trace elements. By contrast, planar feature #5 shows high As, Cu, Te and Sb but lacks Au, and therefore shows a composition comparable to the line defects #1 to #3. A nanophase (#6) with high Au, Pb and Te contents, as well as minor amounts of As, Cu, Sb is associated with planar feature #5 (Fig. 3b). Animations of the APT reconstructions for As, Au and Te of M15 and M16 can be found in the electronic supplement (Supplementary Movies 1–4), which provide a better 3D understanding of the aforementioned features.

### 4 Discussion

#### 4.1 Crystal growth and revision of the Te solid-solution limit
Sharp compositional contrasts in zoned pyrite crystals are typically the result of trace element incorporation from hydrothermal fluids of varying trace element composition during crystal growth, as reflected by the sharp Te contrast between zone 2 and 3 (Fig. 1f). In the given low-sulfidation epithermal setting, the fluid conditions and compositions commonly vary strongly, for example, through fluid mixing, boiling and vapor condensation. This includes temperature, pH and salinity variations, inducing changes in trace element (e.g., As, Te, Au, Ag) solubility, which also affects their incorporation during crystal growth. This is also supported by the different crystal habits between zone 2 and 3, which are indicative for changing fluid conditions. In addition, we argue that the enrichment of Te in zone 3 is not related to supergene processes, such as infiltration-precipitation or coupled dissolution-reprecipitation reaction (CDRR), as this would not lead to the sharp Te contrast between zone 2 and 3. Such a mechanism would have been preserved by a Te enrichment along µm- to mm-scale cracks, accompanied by larger dissolution domains that would not be confined to a specific growth zone on the mm- to µm-scale. Accordingly, no enrichment or depletion in Au, As, or Te that could indicate such a supergene process was detected in relation to the µm-scale cracks by BSE imaging and WDX mapping (Fig. 1c-f). Neither did adjacent mineral phases show a pronounced Te enrichment in the outer rim compared to the core, as would be expected for an enrichment related to a supergene incorporation mechanism (e.g., CDRR). Hence, the Te enrichment of zone 3 relative to zone 2 must directly be related to its growth history and the composition of the related hydrothermal fluids (Fig. 1f).

A coupling in the Au and As enrichment in the investigated pyrite is bound to oscillating crystal growth on the µm-scale as reflected by zone 1 and 2 (Fig. 1d, e). The homogeneous distribution of Au and As down to the atom-scale in zone 1, as revealed by the APT data of tip M14, suggests that these elements are bound in the pyrite lattice by solid-solution. Importantly, the incorporation of Te into the pyrite is decoupled from As and Au, as indicated by the WDX mapping (Fig. 1d-f; Supplementary Fig. 1b-c). The homogenous distribution of Te on the atom-scale in APT tip M14 from the Te-poor zone 1 is indicative for Te solid-solution, which agrees with its position below the Te solubility limit in the As-Te system (Fig. 3c and 4). By contrast, the Te content in the Te-rich zone 3 significantly exceeds the Te solubility limit, suggesting the occurrence of Te-rich inclusions (Fig. 4). However, the homogenous distribution of Te in these areas, as revealed by APT (tip M15 and 16, notably excluding the Te-rich features; Fig. 3a, b), provides direct evidence for Te solid solution. This indicates that at least half (285 ppma by APT) of the highest measured Te content (up to 600 ppma by EPMA) in zone 3 is bound in the crystal lattice (Table 1; Supplementary Table 1), significantly exceeding the previously proposed solubility limit for Te in arsenian pyrite (Fig. 4; Supplementary Fig. 1b).

We therefore propose that the current solid-solution limit of Te into the pyrite lattice, controlled by As, should be dismissed.
Table 1
Element concentrations of matrix and selected features in M14, M15, and M16. Values in ppma unless indicated otherwise. * Au value corrected for overlap with FeAsS2

<table>
<thead>
<tr>
<th></th>
<th>M15 #1</th>
<th>M15 #2</th>
<th>M15 #3</th>
<th>M15 #4</th>
<th>M15 matrix</th>
<th>M16 #5</th>
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<td>S (at%)</td>
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<td>61.2</td>
<td>61.2</td>
<td>60.2</td>
<td>58.0</td>
<td>60.1</td>
<td>56.8</td>
<td>56.3</td>
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<td>Fe (at%)</td>
<td>35.5</td>
<td>37.0</td>
<td>37.0</td>
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<td>41.6</td>
<td>37.0</td>
<td>42.7</td>
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<td>2571</td>
<td>33734</td>
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<tr>
<td>Cu (ppma)</td>
<td>10626</td>
<td>10567</td>
<td>11117</td>
<td>2470</td>
<td>1987</td>
<td>13916</td>
<td>2938</td>
<td>520</td>
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<td>Te (ppma)</td>
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<td>2723</td>
<td>4788</td>
<td>10492</td>
<td>285</td>
<td>4051</td>
<td>229</td>
<td>36</td>
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<td>Pb (ppma)</td>
<td>2222</td>
<td>2697</td>
<td>698</td>
<td>290</td>
<td>81</td>
<td>4015</td>
<td>-</td>
<td>-</td>
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<tr>
<td>Sb (ppma)</td>
<td>280</td>
<td>1088</td>
<td>132</td>
<td>87</td>
<td>-</td>
<td>1274</td>
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<td>-</td>
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<tr>
<td>Se (ppma)</td>
<td>103</td>
<td>138</td>
<td>107</td>
<td>101</td>
<td>136</td>
<td>-</td>
<td>-</td>
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<td>Ni (ppma)</td>
<td>244</td>
<td>94</td>
<td>113</td>
<td>417</td>
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<td>159</td>
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<td>Au (ppma)</td>
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<td>1452</td>
<td>3528</td>
<td>-</td>
<td>65</td>
<td>-</td>
<td>71*</td>
</tr>
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</table>

4.2 Evidence and origin of telluride inclusions

Nano-scale telluride inclusions in pyrite, have been documented in various ore forming environments (e.g. porphyry, epithermal, orogenic, VMS)\textsuperscript{30,32–34} and constitute an important incorporation mechanism of Te in pyrite.

We note that several primary processes may lead to the inclusion of nano-scale tellurides in pyrite, this includes: (1) polymetallic melts, (2) colloids in Te saturated fluids, (3) exsolution from the crystal lattice upon cooling (Fig. 2; Fig. 5a-c)\textsuperscript{32,33,35–37}. However, due to telluride remobilization-recrystallization in this sample, the primary process can only be constrained to be directly linked to the formation of zone 3, and to cracks which propagate from zone 3 into zone 2 (Fig. 2). The abundance of tellurides within the nano-scale cracks and their habit, which is controlled by the shape of the cracks and the related crystal defects (Fig. 2d), indicates that a remobilization-recrystallization like process within zone 3, resulted in crack healing by tellurides (Fig. 2b, d; Fig. 5c).
Importantly, the orientation of the nano-scale cracks seems to rather be controlled by the direction of post-depositional mechanical stress, than by crystal facets or growth boundaries (Fig. 2 and Fig. 5). Probable sources of mechanical stress in epithermal environments are hydrothermal fracturing in relation to fluid boiling or tectonic movements, which are common in the vicinity of a caldera margin, as it is the case for Vatukoula. We propose that in response to mechanical stress, the formation of crystal defects 2 and 3 (Fig. 2a; Fig. 5c) were triggered. Ultimately, nano-scale cracks formed in response to peak pressures (c.f. section 3.2, Fig. 2a, b, d). Such cracks naturally originate in the weakest zone of a material, if the stress is evenly distributed. We note that the defects 2 and 3 post-date the defects 1, which formed in relation crystal growth (cf. section 4.3). Besides the defects and their intersections (Fig. 2a, d), the telluride inclusions are points of structural weakness in the host pyrite, due to pronounced hardness contrast (Mohs hardness: ~3 for tellurides; ~6-6.5 for pyrite).

Jian et al. showed that partial melting of polymetallic crystalline material (e.g., stützite and Te or sylvanite and stützite) forming telluride melts may already occur temperatures as low as 135°C. This temperature is below the suggested depositional temperatures of 180 to 250°C for Vatukoula, and implies that telluride inclusions could have been incorporated as (nano-)melts, and may have remained a melt even after pyrite precipitation with respect to the aforementioned temperature range. This in turn would produce zones of even more pronounced structural weakness in the crystal, facilitating both, the crack formation, and remobilization of the tellurides along these cracks. This is further supported by the STEM-EDXS results of the telluride inclusions in the investigated pyrite, which are constrained by the endmembers stützite, sylvanite, and Te (Supplementary Fig. 3e). These results are congruent with their crystallization from a telluride melt with low melting point, as described by Jian et al. The nano-phases that are oriented along the crystal defects 3 (Fig. 2d), may represent such nano-melt inclusions, which were deformed in response to the mechanical stress which induced the formation defects 3. Additionally, recrystallized tellurides from such polymetallic melt inclusions, are characterized by sharp compositional contrasts, which were observed on the nano-scale tellurides that heal the cracks (Fig. 2e, g; Supplementary Fig. 3). This sharp intragrain compositional contrast and the porous nature of the tellurides could in parts only be revealed after the thinning of the TEM lamella (Fig. 2e-g). This indicates a strong heterogeneity of the tellurides on the scale of a few nanometers, suggesting the tellurides only occur in thin, crack-filling, layers, as confirmed by their partial disappearance after thinning (Supplementary Fig. 2c). Further, a remobilization-related deposition of tellurides along the nano-scale cracks in pyrite could explain how tellurides were transported into the otherwise Te depleted zone 2 in very close (~ 1µm) proximity to zone 3 (Fig. 2a, b). Based on the textures and chemical composition of the tellurides as well as the host pyrite and in consideration of the geological context (formation temperature and mechanical stress), we propose that a crystallization of the remobilized telluride (nano-)inclusions from telluride (nano-)melts formed the crack-filling tellurides.

4.3 Effect of dislocations on the Te distribution
Recent studies have shown the importance of crystal defects (e.g. stacking faults and dislocations) on the incorporation of trace elements into pyrite\textsuperscript{44–47}. Three different directions of crystal defects have been identified in the investigated pyrite (cf. section 3.2, Fig. 2a). The long and straight, as well as the strictly perpendicular alignment of defects 1 to the crystal facet implies that they have formed in relation to, or shortly after, the crystal growth (Fig. 2a; Fig. 5c). Defects 2 and 3 are shorter and appear in swarms (Fig. 2d), making their appearance on the μm-scale more uneven (Fig. 2a). Cross cutting relations indicate that defects 1 formed prior to defects 2 and 3 which formed in response to mechanical stress (cf. section 4.2, Fig. 2a, d).

Creep and glide of crystal defects are deformation mechanisms consistent with fast strain-rates\textsuperscript{48}, which are typical for fracturing related to fluid boiling or to tectonic movements\textsuperscript{39,49,50}, as observed at Vatukoula\textsuperscript{50,51}. The TEM images records that this high mechanical stress ultimately resulted in the formation of the nano-cracks (Fig. 2a; Supplementary Fig. 2b) and the APT data confirms the presence of line defects, which we interpret to be dislocations (#1, #2, #3, Fig. 3a, Supplementary Movie 1, 2). Therefore, defects 2 and 3 are likely dislocations, which, as suggested by APT (Fig. 3a), in zone 3 are rich in various trace elements (Fig. 5f, g). Interestingly, the dislocations in Fig. 3a feature high levels of Cu, As, Te, Sb, and Pb, but without any elevated Au or Ag contents relative to the surrounding pyrite matrix. No depletion of Cu, As, Te, Sb was detected in the vicinity of the dislocations #1, #2, and #3 (Fig. 3a,b), as would be expected for scavenging of trace elements from the crystal lattice during the movement (creep) of the dislocations\textsuperscript{45}.

Instead, we propose that the enrichment in trace elements in dislocations #1, #2, and #3 was achieved through pipe diffusion (Fig. 3a,b). It has been shown that migrating dislocations are immobilized, when they encounter a fluid inclusion and pipe diffusion of trace elements from the inclusion into the dislocations is induced\textsuperscript{52,53}. If the nano-phases in the pyrite matrix were present as polymetallic melts\textsuperscript{33}, (pipe-) diffusion rates may have been significantly increased compared to solid inclusions, and may have been close to the diffusion rates of fluid inclusions. We argue that a comparable mechanism occurred in this investigated pyrite, when the migrating dislocations were immobilized by nano-melt inclusions rich in Cu, As, Te, Sb, Pb. The compositional difference to the larger telluride grains in the cracks may be explained by different primary compositions of the included nano melts, as well as different diffusion rates for different elements\textsuperscript{32,46}. Due to the lower melting point of polymetallic melts with more components\textsuperscript{42,54}, a common diffusion into dislocations is likely, which is consistent with the abundance of nano-phases in the trails of the dislocations (e.g., defects 3, Fig. 2d and Fig. 5g). Hence, the incorporation of Te into dislocations in pyrite may play a previously underestimated, but important role in the overall distribution of Te in pyrite.

5 Conclusions

We have established/refined three crucial mechanisms for Te incorporation into pyrite: (1) Tellurium in solid-solution, that significantly exceeds previously proposed solubility limits. (2) Nano-telluride
inclusions formed by intra-grain remobilization of telluride-melts, along nano-cracks. (3) Crystal defects, enriched in Te through pipe diffusion hosting up to 0.5 at. % Te. Knowledge of these incorporation mechanisms builds the foundation for an effective future recovery, helping to avoid a Te supply gap in the transition towards a low-carbon economy.

**Declarations**

**Funding**

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**Author contributions**

The EPMA work was carried out by FB and MK. TEM work was conducted by TY and FB. FIB work for APT analysis in Erlangen was carried out by CM, APT runs and data reduction in Erlangen were carried out by CM and PF. FIB, APT and respective data reduction in Perth was carried out by DF. DF, CM and TY wrote the respective methods sections of the manuscript. FB drafted the manuscript. MK conceptualized the study and received the funding. All authors contributed to manuscript revision, read, and approved the submitted version.

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**References**


Figures

Figure 1

a) Simplified geological and tectonic overview of Viti Levu, Fiji, showing the location of the Vatukoula (formerly Emperor) deposit. Modified after Orovan et al.\textsuperscript{55}. b) Schematic map presenting the different
lithological units of the Vatukoula deposit. After Fornadel et al.\textsuperscript{19} c) Backscattered Electron (BSE) image of the investigated pyrite grain, with zones 1-3 separated by the white dotted lines and the locations of the TEM lamella and the APT tips (M14-16). d-f) Wavelength-dispersive x-ray spectrometry element maps of As (d), Au (e), and Te (f) of the pyrite grain presented in (c).

Figure 2

a) Bright field (BF) scanning transmission electron microscopy (STEM) image of the lamella from the contact of zone 2 and 3, showing different types of defects, cracks, and inclusions. b) High-angle annular dark field (HAADF-STEM) image of a partially healed crack between zone 2 and 3 (see red rectangle in a). c) STEM- Energy Dispersive X-Ray Spectroscopy (EDXS) map of (b) displaying the As and Te distribution. d) HAADF-STEM image of a crack in zone 3 (see red rectangle in a). e) STEM-EDXS map of displaying the distribution of Ag, Au and Te (see red rectangle in d). f) High resolution (HR)-HAADF-STEM image of area #2 in (d) after thinning of the lamella from ~250 to ~100nm. g) STEM-EDXS map of the area marked in (f) displaying the heterogenous distribution of Ag, Au and Te on the nano-scale.
Figure 3

a) Reconstruction of APT tip M15 from zone 3 (Fig. 1c) showing the dislocations #1, #2 and #3, as well as planar feature #4. b) Reconstruction of APT tip M16 from zone 3 (Fig. 1c) showing planar feature #5, the Au-teguride nanophase #6 and the As depleted zones that are perpendicular to the planar feature #5. c) Reconstruction of APT tip M14 from zone 1 (Fig. 1c) showing the homogeneous distribution of all displayed elements, no Sb signal could be detected.
Figure 4

Bivariate diagram of Te vs. As in parts per million atoms (ppma). The corresponding data is presented in Table 1 (APT) and in supplement Supplementary Table 1 (EPMA) and Supplementary Table 2 (TEM). The dashed line represents the solid-solution limit for Te in pyrite as a function of As proposed by Keith et al.\textsuperscript{13}
Figure 5

a) Schematic model of the micro- and nano-scale features in pyrite after crystal growth and prior to mechanical stress. b) Schematic model of the TEM lamella between zones 2 and 3, illustrating the defects 1 and telluride inclusions, most likely as polymetallic melt inclusions, prior to mechanical stress. c) Schematic model of the TEM lamella between zone 2 and 3 showing defects 2, 3 (swarms of dislocations), cracks, nanophases and recrystallized telluride inclusions concentrated in the nano-cracks after the mechanical stress. d-i) Observations by TEM and APT that underpin the schematic model, and which refer to the areas in the red rectangles shown in (c). d) STEM-EDXS map of crack-filling tellurides in zone 3. e) HAADF-STEM image of crack-filling tellurides in zone 2. f) HAADF-STEM image of nanotelluride inclusions and defects #3; g) STEM-EDXS map for Te of the area shown in (f). h) APT reconstruction of tip M16 displaying the nano-phase and planar features. i) APT reconstruction of tip M15 displaying the dislocations and planar features.

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- Electronicannex170123.pdf
• Supplementarymovie1M15AsSblue.mp4
• Supplementarymovie2M15AuturquoiseTeSyellow.mp4
• Supplementarymovie3M16AsSblue.mp4
• Supplementarymovie4M16AuturquoiseTeSyellow.mp4