1 **REVISION 1**

2 **Ferro-tschermakite with polysomatic chain-width disorder identified in silician magnetite**

3 **from Wirrda Well, South Australia: a HAADF STEM study**

4 CRISTIANA L. CIOBANU[1,*], MAX R. VERDUGO-IHL[1], NIGEL J. COOK[2], KATHY EHRIG[2,3],

5 ASHLEY SLATTERY[4], LIAM COURTNEY-DAVIES[1]

6 *[1] School of Chemical Engineering and Advanced Materials, The University of Adelaide, Adelaide, SA,*

7 *5000, Australia*

8 *[2] School of Civil, Environmental and Mining Engineering, The University of Adelaide, Adelaide, SA,*

9 *5000, Australia*

10 *[3] BHP Olympic Dam, 10 Franklin St., Adelaide, South Australia 5000, Australia*

11 *[4] Adelaide Microscopy, The University of Adelaide, Adelaide, SA, 5000, Australia*

12 **ABSTRACT**

13   Silician magnetite within ~1.85 Ga lithologies hosting the ~1.6 Ga Wirrda Well iron oxide copper

14 gold (IOCG) prospect, South Australia, was examined at the nanoscale. The magnetite is oscillatory-

15 zoned with respect to the density and orientation of nm-scale inclusions, among which Si-Fe-nanorods

16 and Al-rich amphibole (as much as hundreds of nm long and tens of nm wide) form swarms along <111>

17 directions in magnetite. The amphibole is identified as ferro-tschermakite (Ftsk) with the crystal-

18 chemical formula: $^A(K_{0.06}Na_{0.01})_{0.07}{}^B(Ca_{1.65}Na_{0.35})_2{}^C(Fe^{2+}_{2.07}Al_{1.64}Mg_{1.15}Ti_{0.06}Fe^{3+}_{0.04}Mn_{0.04})_5{}^T(Si_{6.48}$

19 $Al_{1.52})_8O_{22}{}^W(OH)_2$. This contains single and double rows of a triple-chain silicate attributed to

20 clinojimthompsonite (Cjt), as coherently intergrown (010) zippers along the entire length of the grains.

21 High-angle annular dark field scanning transmission electron microscopy (HAADF STEM) imaging and

22 simulation of Ftsk and Cjt on the [001] zone axis provide direct visualization of crystal structures. These

23 are defined by the 7- and 10-atom octahedron strips ($B+C$ sites) and flanked by double- and triple-pairs

*Corresponding author. E-mail address: cristiana.ciobanu@adelaide.edu.au

24   of Si atoms (T sites). Remarkably, the sites for light cations and/or vacancies are clearly imaged as single

25   and double, darkest, diamond-shaped motifs separating the octahedron strips showing that A cavities

26   known in amphibole are readily depicted in the wider-chain silicate. *I-beam* models show that nanoscale

27   intergrowths among the two silicates are coherent along zig-zag chains of cations at the edges of the

28   octahedron strips, with single and double rows of the triple-chain silicate corresponding to 1- and 1.5-

29   unit cells of Cjt (27 and 41 Å intervals along the b axis). This type of polysomatic chain-width disorder

30   is widely reported in Mg-rich pyriboles but is shown here in an Al-Fe-rich amphibole. The lack of planar

31   defects and/or reaction fronts at mutual contacts between 3-chain zippers and host amphibole indicates

32   primary co-crystallization growth, promoted by formation of the Si-Fe-nanorods. Co-crystallizing

33   plagioclase is also preserved in close vicinity to the amphibole hosted by magnetite (from a few nm to

34   µm apart). In contrast, replacement of amphibole by phyllosilicates is recognizable as irregular swells

35   along the (010) zippers and results in extensive chloritization of the amphibole during an overprinting

36   event. Pressures of ~11.5 kbar are estimated using Al-in-hornblende nano-geobarometry and calculated

37   Al content in Ftsk (3.16 a.p.f.u.). Assuming the amphibole-plagioclase association buffered by host

38   magnetite fulfils the textural equilibration criteria required for application of this barometer, we interpret

39   the Ftsk nanoinclusions in magnetite as preserved evidence for amphibolite facies metamorphism

40   affecting host lithologies at Wirrda Well with subsequent retrograde alteration during the ~1.6 Ga IOCG

41   mineralizing event. Magnetite records petrogenetic processes by accommodating variable ranges of

42   nanomineral inclusions and preserving them over geological time scales. HAADF STEM imaging is

43   ideally suited to depiction of crystal-structural modularity and also provides insights into the evolution

44   of geological terranes with protracted histories.

45   **Keywords:** silician magnetite, ferro-tschermakite, clinojimthompsonite, polysomatic chain-width

46   disorder, pyriboles, HAADF STEM

47   **INTRODUCTION**

48   Scanning Transmission Electron Microscopy (STEM) using a High Angle Annular Dark Field

49   (HAADF) detector provides sub-Ångstrom atomic-scale resolution when combined with contemporary

50   instruments offering improved aberration-correction of the probe forming optics (e.g., van Tendeloo et

51   al. 2012). One of the main advantages of using HAADF STEM over High Resolution (HR) TEM

52   techniques is that the image is formed from a convergent rather than parallel beam (Van Tendeloo et al.

53   2012) and thus, the displayed 'dots' are directly attributable to atoms, with a distribution that is unaffected

54   by focus and thickness as in conventional HR TEM imaging. This enables an unparalleled route to direct

55   imaging of minerals and their intergrowths at the nanoscale, in turn providing insights into petrological

56   processes that cannot be constrained by other methods (Ciobanu et al. 2019a, and references therein). In

57   HAADF STEM mode, the image contrast is correlated with atomic mass, i.e., the atomic number Z-

58   dependence of the contrast is $\sim Z^2$, with application to the smallest U-bearing nanoparticles in

59   environmental studies (e.g., Utsunomiya and Ewing 2003). Recent HAADF STEM studies of Pb-Bi

60   sulfosalts, REE-fluorocarbonates, and Pb-Bi- or Bi-chalcogenides show how we can directly visualize

61   structural blocks defining the homology of a mineral series and layer types in mixed-layer compounds

62   (Medlin et al. 2010, 2013, 2014, 2019; Ciobanu et al. 2016, 2017; Li et al. 2019; Cook et al. 2019).

63   Crystal-structural modularity is a concept widely used in modern mineral classification schemes,

64   including those based on the topology of SiO_4 tetrahedral groups (*T*) defining the major categories of

65   rock-forming silicates (Deer et al. 2013). Among these, biopyriboles form a group that combine *T*-sheet

66   and -chain silicates and have been used to define polysomatism and its application to derive modular

67   series (e.g., Thompson 1978; Veblen 1981). Of interest here are the pyriboles which comprise only chain

68   silicates, in which the number of chains (n) defines pyroxenes (n=1), amphiboles (n=2) and non-classical

69   pyriboles (NCP) with n>2, as well as those with two or more different chains in combinations (Veblen

70   et al. 1977; Veblen and Burnham 1978a, b; Veblen and Buseck 1979, 1980). Pyriboles are well-known

3

71   for their ability to form coherent lattice-scale intergrowths with one another, also called polysomatic

72   intergrowths, as shown by many HR TEM studies of natural or synthetic material (e.g., Veblen 1992;

73   Veblen et al. 1993; Bozhilov 2013, and references therein).

74   To date, none of the studies addressing complex pyribole sequences, their degree of order and

75   disorder, or the diverse range of defects present (stacking faults, dislocations, chain terminations, etc.)

76   has been carried out using HAADF STEM imaging. Using this technique, we identify ferro-tschermakite

77   occurring as nanoinclusions in magnetite. We show the advantages of such an approach to the direct

78   visualization of the building blocks that define their crystal-structural modularity and the presence of

79   polysomatic disorder as lamellar intergrowths with NCP layers.

80   Mineral inclusions in magnetite are increasingly reported from nanoscale studies using Z-contrast

81   STEM imaging techniques of minerals from deposits spanning the magmatic-hydrothermal spectrum (Xu

82   et al. 2014; Deditius et al. 2018; Ciobanu et al. 2019b; Gao et al. 2019a, b; Yin et al. 2019; Verdugo Ihl

83   et al. 2021). Whereas crystallographically-oriented inclusions of magnetite are common in pyroxenes

84   from igneous and metamorphic rocks (Fleet et al. 1980), inclusions of magnetite in amphibole, or vice-

85   versa, are largely unreported.

86   Silician magnetite, known from many deposit types, can accommodate vacancy-bearing Si-Fe-

87   nanoprecipitates with widths of multiple d_{111} magnetite, as shown for banded iron formation (BIF) and

88   iron-oxide copper gold (IOCG) deposits (Xu et al. 2014; and review of silician magnetite in Ciobanu et

89   al. 2019b). In the outer shell from the ~1.6 Ga IOCG deposit at Olympic Dam (South Australia), silician

90   magnetite contains abundant nanoscale inclusions of (ferro)actinolite, one of several calc-silicates

91   formed during alkali-calcic alteration of host granite (Ciobanu et al. 2019; Verdugo-Ihl et al. 2020a).

92   Based on trace element geochemistry, silician magnetite is also known from the Cu-(Au) prospect at

93   Wirrda Well, also within the Olympic Dam district where mineralization belongs to the same ~1.6 Ga

94   IOCG event defining the Olympic Cu-Au Province (1598.9 ± 6.3 Ma [207]Pb/[206]Pb age obtained from U-

4

95   bearing hematite; Courtney-Davies et al. 2019). The Wirrda Well prospect is, however, hosted by an

96   older, ~1.85 Ga granite (Donington Suite; DS) that experienced burial metamorphism at conditions from

97   granulite to greenschist facies during the 1735–1690 Ma Kimban orogeny (Reid 2019, and references

98   therein). Numerous mafic dikes, some of which are penecontemporaneous with the DS suite, as well as

99   shear zones, are typical of the geological setting at Wirrda Well (e.g., Courtney-Davies et al. 2019).

100   The present HAADF STEM study addresses amphibole and other nm-scale mineral inclusions in

101   silician magnetite from Wirrda Well. The aim is to understand the petrogenetic significance of such

102   nanoscale inclusions in the context of protracted igneous-metamorphic history. Comparison with

103   magnetite from other deposits/prospects in the district constrains mineral signatures recorded during the

104   early stages of IOCG systems.

<p style="text-align:center">BACKGROUND ON TSCHERMAKITE AND PYRIBOLES</p>

106   Amphiboles are a large group of inosilicates with the general formula: $AB_2C_5T_8O_{22}W_2$, where $A =$

107   vacancy ($\square$), Na, K, Ca, Pb, Li; $B =$ Na, Ca, Mn^{2+}, Fe^{2+}, Mg, Li; $C =$ Mg, Fe^{2+}, Mn^{2+}, Al, Fe^{3+}, Mn^{3+},

108   Ti^{4+}, Li; $T =$ Si, Al, Ti^{4+}, Be; and $W =$ (OH), F, Cl, O^{2-} (Hawthorne et al. 2012). Of these, the Al-rich,

109   calcic amphiboles with $C2/m$ symmetry comprising the solid solution series between the Mg-endmember

110   tschermakite: $^A\square^BCa_2{}^C(Mg_3Al_2)^T(Si_6Al_2)O_{22}{}^W(OH)_2$ (Abdu and Hawthorne 2009) and Fe-endmember

111   ferro-tschermakite, $^A\square^BCa_2{}^C(Fe^{2+}{}_3Al_2)^T(Si_6Al_2)O_{22}{}^W(OH)_2$ (Hawthorne and Grundy 1978; Oberti et al.

112   2018) are rare species documented only from a limited number of localities.

113   The tschermakite crystal structure was refined from a specimen at the contact between anorthosite and

114   amphibolite from Fiskenaesset, Greenland (Abdu and Hawthorne 2009; Table 1). However, Oberti et al.

115   (2018) discredited the Fiskenaesset specimen as being a magnesiohornblende variety, based on

116   redefinition of tschermakite within a narrower compositional field: $1.5 < {}^C(Al+Fe^{3+}+2Ti) < 2$ a.p.f.u and

117   $0 < {}^A(Na+K+2Ca) < 0.5$ a.p.f.u (Hawthorne et al. 2012). The ferro-tschermakite crystal structure was

118   refined by Hawthorne and Grundy (1973) and the formal description of the mineral given by Oberti et

119   al. (2018) from a specimen in the Ploumanac'h granitic complex, France (Table 1).

120   When projected along the c axis, the basic amphibole structure (Fig. 1a) can be visualized as two

121   double-chains of SiO_4 tetrahedra [$T(1)$ and $T(2)$] sandwiching an octahedron strip of C-group cations

122   [$M(1)$, $M(2)$ and $M(3)$], collectively making up what is known as an *I-beam* stack, two chains in width

123   (Papike and Ross 1970). The B-group cations occupy the $M(4)$ site and link the octahedron strip to the

124   tetrahedron double chain, whereas the A-group cations occupy the A cavity with several distinct sites of

125   which only the $A(m)$ and $A(2)$ sites are occupied (Hawthorne et al. 2005, and references therein). These

126   authors discuss order and disorder phenomena in amphiboles in terms of site occupancy, whereby Short-

127   Range Order (SRO) is defined as local clusters of atoms, either in excess or deficit, over a single site. Of

128   interest here are the A sites that can be depicted by HAADF STEM imaging since these contain light

129   cations (±vacancies) thus contrasting with the cations filling the other sites defining the I-beam stacks in

130   the structure.

131   Aside from pyroxenes and amphiboles (1- and 2-chains wide, respectively), NCP pyriboles include

132   those with triple chains of *I-beams* (jimthompsonite and clinojimthompsonite) and alternating double

133   and triple chains (chesterite) identified in metamorphic rocks from Chester, Vermont (Veblen and

134   Burnham 1978). Of interest here is clinojimthompsonite with the ideal formula: ^{Oct}(Mg,

135   Fe)$_{10}$^{Tet}Si$_{12}$O$_{32}$(OH)$_4$ (Oct=octahedral; Tet=tetrahedral), described as a Mg-Fe-rich variety from the type

136   locality: Na$_{0.04}$^{Oct}(Mg$_{7.59}$Fe^{2+}$_{2.07}$Mn$_{0.13}$Ca$_{0.11}$)$_{\Sigma9.95}$^{Tet}(Si$_{11.97}$Al$_{0.07}$)$_{\Sigma12}$O$_{32}$(OH)$_4$ (Veblen and Burnham 1978;

137   Fig. 1b). A calcic analogue of clinojimthompsonite: K$_{0.054}$Na$_{0.029}$(Mg$_{7.783}$Ca$_{1.958}$Fe^{2+}$_{0.222}$Mn$_{0.014}$)$_{\Sigma9.977}$

138   (Si$_{11.970}$Al$_{0.028}$)$_{\Sigma11.998}$O$_{32}$(OH)$_4$ was identified from Oeyama ophiolite, Japan (Konishi et al. 1993).

139   Modularity in pyriboles has been conceptualised by defining two main building blocks: mica (**M**) and

140   pyroxene (**p**), each with a dimension of ~4.5 Å along the b axis, so that the structures can be visualised

141   as a combination of such modules when viewed down the c axis (Thompson 1978). Considering the

142   structural symmetry comprising c-glide planes that pass through individual silicate chains, such blocks

6

143   are only one-half unit cell wide along the *b* axis, and therefore a mirrored **p** module was introduced as

144   the **q** module (Bozhilov 2013 and references therein). This can be used to formalise generic pyribole

145   sequences for single chain sequences as $\mathbf{p2M}_{(n-1)}\mathbf{q}$, and for mixed chain sequences as $\mathbf{pM_nqM}_{(n-1)}$, where

146   n is a positive integer. Representation of such sequences for ferro-tschermakite and clinojimthompsonite

147   are shown on Figure 1.

148   Many TEM studies have addressed classic and NCP pyribole intergrowths as potentially metastable

149   polysomes that are intrinsic to growth processes in which kinetic steps are preserved within their fine

150   microstructures. Veblen and Buseck (1980) postulated that most common defects are the terminations of

151   (010) slabs, so called 'zippers'. They further stipulated that coherent terminations must obey two rules:

152   (1) the chain sequences on both sides of that termination must have either an even or odd number of

153   chains; and (2) the number of sub-chains must be equal on both sides of the zipper termination, lest planar

154   faults with displacements occur at slab terminations. Reaction schemes and kinetic models were

155   developed for constraining chain width distributions in biopyribole based on such transformation rules

156   corroborated with observations of zipper terminations (e.g., Grobéty 1997).

157   The biopyribole microstructures could thus be used to interpret physicochemical processes recorded

158   during overprinting events in terranes with protracted geological histories (see reviews by Champness

159   2002 and Bozhilov 2013).

160   **METHODOLOGY**

161   Two S/TEM-foils were extracted from one magnetite grain using established dual-beam FIB-SEM

162   methods with a FEI Helios Nanolab 600 instrument (see Ciobanu et al. 2011). High Angle Annular Dark

163   Field (HAADF) STEM imaging and energy-dispersive X-ray spectrometry (EDX) spot analysis/mapping

164   of the foils were conducted with an ultra-high resolution, probe-corrected FEI Titan Themis S/TEM

165   instrument operated at 200 kV. Simultaneously Bright Field (BF) and HAADF STEM imaging was also

166   undertaken during the experimental sessions. This is equipped with a X-FEG Schottky source and Super-

7

167   X EDX geometry. The Super-X EDX detector provides geometrically symmetric EDX detection with an

168   effective solid angle of 0.8 Sr. Probe correction delivered sub-Ångstrom spatial resolution and an inner

169   collection angle greater than 50 mrad was used for HAADF imaging with a Fischione detector. Indexing

170   of diffraction patterns was conducted with WinWulff© (v1.6) and publicly available data from the

171   American Mineralogist Crystal Structure Database (http://rruff.geo.arizona.edu/AMS/amcsd.php).

172   Crystal structure models were generated in CrystalMaker® (v10.4.6) and STEM for xHREM™ (v4.1).

173   Magnetite composition along transects close to the FIB-cut samples was obtained using electron probe

174   microanalysis (EPMA) using a CAMECA SX-Five electron probe microanalyzer. Analytical procedures

175   are given in Supplemental [1] Table A1. All instruments are housed at Adelaide Microscopy, The

176   University of Adelaide.

177   **RESULTS**

178   The studied magnetite derives from a cm-wide band intersecting the contact between altered

179   Donington granite and a mafic dyke (?) at a depth of ~1,891 m RL (drillhole WRD33, sample

180   WW33.12B; Fig. 2a, b). Fine-grained sulfides (pyrite+chalcopyrite) form trails crosscutting the

181   magnetite band. Alteration comprises chlorite with various Fe/Mg ratios and K-feldspar/sericite.

182   Magnetite displays zonation patterns with respect to dusty, Si-bearing inclusions, and is marginally

183   replaced by hematite and infilled by sulfides and secondary chlorite+quartz, as seen along the distinct

184   zone boundaries in the analyzed grain. The STEM study was carried out on two foils, extracted from: (i)

185   across a sharp boundary -foil #1; and densely-mottled inclusion core-foil #2 (Fig. 2c, d). The two

186   locations were selected so as to probe the changes across the magnetite grain, from primary zoning (foil

187   # 1) to overprint within the core (foil # 2).

---

[1] Deposit item

188   EPMA data for magnetite (Supplemental[1] Table A1) shows up to 4.39 wt.% SiO_2, 2.33 wt.% Al_2O_3,

189   and measurable concentrations of MgO, CaO, TiO_2 and V_2O_3 (<1 wt.% each), elements that, with the

190   exception of SiO_2, are all common to spinel group minerals. Calculation of magnetite composition in

191   a.p.f.u. terms on a 32 O atom basis shows no significant difference between the two transects placed

192   across zone boundaries with the highest contrast in inclusion density, representing the same domains

193   sampled for the nanoscale study (Fig. 2d). Three possible types of magnetite substitution with respect to

194   Si *vs.* Fe exchange are shown in Figure 2e:

195   (1) $2Fe^{2+} \Leftrightarrow Si^{4+}+Fe^{2+}$, leading to $Fe^{2+}_{16}Si_8O_{32}$ (fayalite);

196   (2) $4Fe^3 \Leftrightarrow 3Si^{4+} + \square$, leading to $\square_4Fe^{2+}_8Si_{12}O_{32}$ ($\square$= vacancy);

197   (3) $Fe^{2+}+2Fe^{3+} \Leftrightarrow 2Si^{4+}+ \square$, leading to γ- $\square_4Fe^{2+}_4Fe^{3+}_8Si_8O_{32}$.

198   Substitution (1) preserves metal saturation, whereas the other two types require metal vacancies thus

199   leading to vacancy-bearing spinel phases such as maghemite or γ-Fe_2O_3: $(\square_{0.33}Fe^{3+}_{0.67})Fe^{3+}_2O_4$ or

200    $(\square_{2.64}Fe^{3+}_{5.36})Fe^{3+}_{16}O_{32}$ (Bosi et al. 2019). Substitution (3), was considered by Xu et al. (2014) to define

201   the formation of γ-$\square_{0.5}Fe_{1.5}SiO_4$ nanoprecipitates (space group $P4_332$), one of the Si-Fe-bearing phases

202   typifying silician magnetite with ordered metal vacancies. In this case, Si replaces Fe^{3+} in tetrahedral

203   sites and vacancies are introduced in the octahedral Fe^{2+} sites of the magnetite structure.

204   When considering the ΣMe^{4+} (Si+Ti±U) *vs.* ΣFe diagram, the data plots close to the substitution line

205   defining the γ-$\square_{0.5}Fe_{1.5}SiO_4$ phase (Fig. 2f). The offset is due to the presence of other silicate inclusions

206   but the linear trend nonetheless suggests that inclusion nucleation is preferentially controlled by the

207   magnetite structure.

208   HAADF STEM imaging of the two foils shows zonation with respect to inclusions in foil #1, but

209   pervasively distributed inclusions in foil #2 (Fig. 3). In both foils, there are also coarser inclusions/clots,

210   which are identified from STEM EDX spectra and element maps as plagioclase, rutile, chlorite and

211   sericite (Supplemental[1] Figs. A1-3). Primary zonation (foil # 1) shows the sharp contact between

9

212   inclusion-free and -mottled bands in magnetite (Fig. 3a). A change in inclusion orientation occurs over

213   an interval of ~15 μm from this boundary to the other end of the foil. The junction to the last zone is

214   marked by larger mineral clots comprising phases that are not present throughout the mottling in

215   magnetite (e.g., plagioclase, rutile and fluorite; Fig. 3a; Supplemental[1] Fig. A2). The largest clot, several

216   μm in width, is present in the sample obtained from the core (foil #2; Fig. 3b). The core overprint is

217   highlighted by presence of sericite+chlorite+quartz whereas nm-scale rutile and plagioclase inclusions

218   are also present within discrete fields (Supplemental[1] Figs. A2, A3). There is also a subtle change in

219   inclusion orientation along the length of the foil.

220   Stubby grains of Al-rich amphibole, each up to several hundred nm in length and tens of nm wide

221   (Fig. 4a-c) are present at the contact to the inclusion-free zone in magnetite (Fig. 3a). On HAADF STEM

222   images, stacking disorder in the amphibole is observed as darker, single or double strips that extend along

223   the entire length of each grain but with irregular distribution across their width (Fig. 4d-f). A second

224   population of larger inclusions, consisting of chlorite+quartz, occurs in the same area with the amphibole

225   grains (Fig. 4g-i). Some longer strips of chlorite contain relics of amphibole (Fig. 5a).

226   The host magnetite is typified by dense mottling with respect to Si-Fe-nanorods, each a few nm in

227   width, positioned along $<111>_{magnetite}$ (Fig. 5a, b). Fast Fourier transform (FFT) patterns obtained from

228   amphibole tilted on the [001] zone axis shows streaks along $b*$ indicating disorder due to the presence

229   of the darker strips stacked along this direction (Fig. 5c, d). At the same tilt, host magnetite is oriented

230   on [11$\bar{2}$] zone axis (Fig. 5c). High resolution images show epitaxial relationships between the two

231   minerals, whereby $a_{amphibole}$ is parallel to $<111>_{magnetite}$ along their mutual contact (Fig. 5e). Away from

232   the boundary between the zones of clean and inclusion-rich magnetite, longer Si-Fe-nanorods are the

233   only major inclusions observed (Fig. 6a, b). EDX mapping of areas from both foils show that the Si-Fe

234   bearing precipitates can also contain minor, albeit variable, Al-Mg-Ca content (Supplemental[1] Fig. A2).

10

235   An integrated STEM EDX spectra across one of the mapped amphibole grains gives the mean formula

236      $^A(K_{0.06}Na_{0.01})_{0.07}{}^B(Ca_{1.65}Na_{0.35})_2{}^C(Fe^{2+}{}_{2.07}Al_{1.64}Mg_{1.15}Ti_{0.06}Fe^{3+}{}_{0.04}Mn_{0.04})_5{}^T(Si_{6.48}Al_{1.52})_8O_{22}{}^W(OH)_2$,

237   corresponding to ferro-tschermakite (Fig. 6d-e; Table 1). Total a.p.f.u. Al is 3.16, comparable with the

238   3.18 total a.p.f.u. Al in ferro-tschermakite reported from Ploumanac'h (Oberti et al. 2018), both slightly

239   lower than the 3.3 total a.p.f.u. Al in ferro-tschermakite reported by Hawthorne and Grundy (1973). The

240   composition of the Wirrda Well amphibole is within the limits of the tschermakite field as defined by

241   Hawthorne et al. (2012), i.e., $^A(K+Na) = 0.07$ a.p.f.u (no Ca present in this site) and $^C(Al+Fe^{3+}+2Ti)=1.8$

242   a.p.f.u.

243   High resolution imaging of (i) the amphibole and (ii) stacking defects as double-rows of a 3-chain

244   silicate shows a good match with HAADF STEM simulations and crystal structure models for (i) ferro-

245   tschermakite (Ftsk) and (ii) clinojimthompsonite (Cjt) obtained for [001] zone axis in both species (Fig.

246   7). This allows interpretation of the images in terms of atom distributions and crystal structural motifs.

247   Most prominent on the images and simulations are the arrays of 7 and 10 bright dots (Fig. 7a, b), for

248   Ftsk and Cjt, respectively. These correspond, on the crystal structure models, to the octahedron strips

249   (with the same number of atoms as dots on the images) in the middle part of each unit cell (Fig. 7c, d).

250   The pairs of SiO_4 tetrahedra (T) are recognized as the second brightest dots on the images and simulations

251   and correspond to the topology of the 2- and 3-pairs of T placed on both sides of the octahedron strips in

252   Ftsk and Cjt, respectively. In the case of Ftsk, the atoms in the B position, at the edges of the octahedron

253   strips, are slightly less bright than the rest of the strip with an excellent match between the image and

254   simulation using the crystal structure of Hawthorne and Grundy (1973) for Ftsk (Fig. 7a, c). The match

255   between the images and simulations for the atoms along the octahedron strip is not as good in terms of

256   relative HAADF signal intensity. Considering that the structure used for Cjt is a Mg-rich specimen

257   (Veblen and Burnham 1978), we can assume a higher proportion of heavier atoms occupying the

258   octahedron strip, e.g., higher Fe, Ca and less Mg, in the Wirrda Well sample (Fig. 7b, d).

11

259   The third prominent feature on the images and simulations obtained for the amphibole are the dark,

260   'diamond-shaped' motifs separating the octahedron strips (Fig. 7a, c, e). These correspond to the *A*

261   cavities which host alkaline atoms ± vacancies on the crystal structure model (Fig. 7g). Double-diamond

262   shaped motifs, with the same geometry as in the amphibole, are present on the images and simulations

263   obtained for Cjt (Fig. 7b, d, f). This implies that such *A*-type cavities should be also present in the Cjt, as

264   marked on the simulation and crystal structure model in Figure 7f, h.

265   The STEM simulations show that the atoms at the edges of the octahedron strips (*B* site) form a zig-

266   zag array, 'zipper' terminations along the boundaries between the 2- and 3-*I beams* structures (Fig. 8a).

267   The *I-beam* stacks can be identified also on high resolution images obtained for such intergrowths,

268   whereby the octahedron strips of 7- and 10-atoms, as well as the *A* cavities are the most prominent

269   features (Fig. 8b). In detail, the relationships between the unit cells and the topology of *I-beam*s for Ftsk

270   and Cjt show that insertion of single and double arrays of *3-I beam*s correspond to 1 and 1.5 units of Cjt

271   (Fig. 9).

272   In contrast, irregular swells observed along some of the (010) zippers in the amphibole show stepwise

273   terminations and changes to the structure of the triple-chain silicate (Fig. 10a, b). In detail, alternating

274   brighter and darker strips with ~9.2 Å spacing, correspond to the *c* parameter of phyllosilicates such as a

275   2:1 mixture of pyrophyllite (P) and talc (T) (Drits et al. 2012 (Fig. 10b). The *I-beam* model for such areas

276   shows that the (010) boundary between the amphibole and inferred phyllosilicate mixture is coherent

277   along a "normal" biopyribole structure ('**p**' slab; Fig. 10c) but other planar orientations entail gaps (Fig.

278   10c). Wider chlorite patches in which no relict amphibole is preserved display disordered intergrowths

279   with other phyllosilicates, likely P/T mixtures as along the zippers in the amphibole (Fig. 10d). The

280   chlorite itself also displays irregularities in layer stacking (Fig. 10e). Indexing of phyllosilicates was done

281   using models of P/T mixtures (Drits et al. 2012) and one of the *C*2/*m* chlorite structures (Zanazzi et al.

282   2007) projected onto the [100] zone axis (Fig. 10 f, g).

283   DISCUSSION

284   *Significance of polysomatic disorder in ferro-tschermakite*

285   The Ftsk inclusions displaying single- and double-rows of a 3-chain silicate identified as a Ca-bearing

286   variety of Cjt represents the first report of pyriboles displaying polysomatic disorder within magnetite.

287   Isolated triple- or quintuple-chains in amphiboles are a type of chain-width disorder that have been

288   debated in terms of primary growth mechanisms (Cressey et al. 1982) and replacement with rapid growth

289   kinetics (Veblen 1981). The presence of isolated triple-chains showing no displacive planar defects at

290   the terminations of the (010) slabs in host amphibole from Wirrda Well (Figs. 4d, 5d) breaks the

291   termination rules of Veblen and Buseck (1980). In addition, the *I-beam* intergrowths, documented from

292   [001] HAADF STEM imaging, which extend along the entire length of the Ftsk inclusions, without

293   reaction fronts at mutual contacts between 3-chain zippers and host amphibole (Figs. 4, 5 and 9), are

294   suggestive of primary co-crystallisation rather than replacement. Similar conclusions were drawn for

295   Mg-(Fe)-pyriboles (jimthompsonite, chesterite and anthophyllite) and their mutual intergrowths in

296   Archean ultramafic rocks from the Isua Supracrustal Belt, West Greenland (Konishi et al. 2010).

297   In contrast, the presence of swells along the zippers (Fig. 10) supports the idea of hydration of

298   amphibole inclusions leading to their advanced pseudomorphic replacement by phyllosilicates (chlorite,

299   pyrophyllite, talc; Fig. 4) in the Wirrda Well specimen. The presence of gaps along non-coherent

300   boundaries between talc/pyrophyllite and amphibole (Fig. 10c) entail channels running parallel to the *c*

301   axis in pyribole. Such channels provide microstructures for fluid infiltration resulting in pyribole

302   hydration reactions, as first discussed for biopyriboles in the metamorphosed ultramafic body at Chester,

303   Vermont (Veblen and Buseck 1980). A wide range of microstructures have been reported and are intrinsic

304   to most polysomatic biopyribole sequences (see Bozhilov 2013 and references therein).

305   Documented occurrences from much larger, micron- to mm-scale pyribole sequences elsewhere

306   featuring polysomatic disorder include a dozen or so Mg-Fe-pyribole associations from ophiolites,

307   metamorphosed ultramafic complexes or other metamorphic terranes, as well as an extra-terrestrial

308   carbonaceous chondrite (see Bozhilov 2013). None of the reported occurrences include an Al-rich, calcic

309   amphibole, as shown here for Wirrda Well.

310   Chain-width disorder was, however, encountered as triple and quadruple chains in synthetic Al-rich

311   amphibole with X_{Tsk}=0.13 (X=mol.% tschermakite; 2.83 wt.% Al_2O_3) from the tremolite-tschermakite

312   solid solution (Najorka and Gottschalk 2003). These amphiboles were synthesized at 750 ºC and 500

313   MPa in 30-day runs, whereas defect-free structures with X_{Tsk}=0.39 (8 wt.% Al_2O_3) were obtained using

314   shorter (5-day) runs at slightly higher T (800 ºC) and far higher P (1,500 MPa) (Najorka and Gottschalk

315   2003). The formation conditions of triple-chain silicates were also assessed experimentally and

316   thermochemically showing that Na-Cjt is stable at metamorphic conditions of 2 kbar and 450 ºC, or could

317   form by reactions between igneous minerals (enstatite, forsterite) in oceanic harzburgite and seawater at

318   temperatures up to 300 ºC (Ams and Jenkins 2011). Na-free Cjt is estimated to be stable at comparable

319   conditions to Na-Cjt, with both NCP being postulated to occur in oceanic hydrothermal environments

320   and geothermal systems but not in serpentinized ultramafic rocks (Ams and Jenkins 2011).

321   *Genetic considerations*

322   Irrespective of the chain-width disorder, experimental runs showing a positive correlation between Al

323   content in amphibole and total pressure (e.g., Najorka and Gottschalk 2003) support the trend recognized

324   empirically from many petrological studies of igneous and metamorphic rocks. Hammarstrom and Zen

325   (1986) introduced the Al-in-hornblende geobarometer based on the dependance of the total Al content

326   (Al^{tot} a.p.f.u.) of igneous hornblende on pressure via the so-called "Tschermak exchange reactions" in

327   low variance granitoid systems at near solidus conditions. We can assume that Ftsk and plagioclase,

328   found within a few nm up to several μm from one another (Fig. 3a), are buffered by host magnetite and

329   thus the assemblage fulfils the textural equilibration criteria required for application of the barometer.

330   High pressure estimates (~11.5 kbar) are obtained for the Wirrda Well assemblage hosted in Donington

14

331   granite, giving a Al^{tot} value of 3.16 in ferro-tschermakite and using the formula P (kbar) = 0.5 +0.331(8)

332   x Al^{tot} + 0.995(4) x $(Al^{tot})^2$ for the revised Al-in-hornblende geobarometer (Mutch et al. 2016). Although

333   this revised geobarometer targeted low-pressure granitoids, amphibole compositions from earlier

334   experimental calibrations at pressures as high as 15 kbar (Schmidt 1992) were included in the Al^{tot} *vs.*

335   pressure plot (Fig. 10c in Mutch et al. 2016). Wirrda Well Ftsk lies within the range of synthetic

336   amphiboles with Al^{tot} of 3.042 and 3.349 a.p.f.u obtained at 11.5 and 13 kbar, respectively (Schmidt

337   1992).

338   Nevertheless, the silician magnetite with Ftsk inclusions most likely formed after intrusion

339   emplacement since the igneous accessory magnetite is Si-free (and associated with ilmenite), whereas

340   the amphibole is pargasitic in fresh Donington granite elsewhere in the Gawler Craton (Keyser et al.

341   2019). Of the two major geological events that affected the region after ~1.85 Ga (emplacement of

342   Donington granite and coeval dolerite dikes), the 1735–1690 Ma regional metamorphism is likely

343   responsible for formation of magnetite accumulations along granite-dyke contacts.

344   Regional metamorphism at amphibolite facies is supported not only by the pressure estimate of ~11.5

345   kbar from amphibole geobarometry but also by the observed assemblages which include plagioclase, the

346   latter forming as mineral clots at junctions between zones in magnetite with inclusions of different

347   orientation (Fig. 3a). Such intra-grain textures are also representative of syn-metamorphic mineral

348   growth under oriented stress. Thus, we consider magnetite accumulation via metamorphic segregation,

349   whereby impurities of Si, Al, Mg, Ca, etc., were likely provided by alteration of pre-existing lithologies,

350   particularly at granite-dolerite contacts (Fig. 2). Formation of Si-Fe-nanorods in magnetite promotes

351   preferential amphibole growth along these structures as the prograde metamorphism reaches its peak.

352   This interpretation is also supported by the linear trend observed on the ΣMe^{4+} *vs.* ΣFe plot for silician

353   magnetite (Fig. 2f). In detail, epitaxial growth of amphibole in magnetite can be explained by considering

354   the role of Si-rich <111> platelets acting as nucleation points. Cation diffusion is easily promoted within

15

355 the framework of oxygen packing along <111> directions in spinel group minerals, and matching (100)

356 planes of distorted oxygen arrays in inosilicates.

357 Retrograde reactions such as replacement of amphibole inclusions by chlorite/phyllosilicate (Fig. 10)

358 are associated with fractures affecting magnetite grain cores (Fig. 2c, d) and obliterating the amphibole

359 inclusions in foil # 2 (Fig. 3). Such an overprint is recorded at Wirrda Well by U-bearing hematite that

360 formed during the ~1.6 Ga IOCG event (Courtney-Davies et al. 2019). The host lithologies are largely

361 impacted by chloritization/sericitization that obliterates prograde metamorphic associations like those

362 preserved in silician magnetite.

363 The Wirrda Well silician magnetite differs from that observed at Olympic Dam in terms of the type

364 of silicate inclusions. Inclusion species also include calcic amphiboles and Al-rich silicates but these are

365 represented at Olympic Dam by (ferro)actinolite and (clino)zoisite rather than Ftsk (Ciobanu et al.

366 2019b). Such calc-silicate association was attributed to alkali-calcic alteration of the ~1.6 Ga Roxby

367 Downs granite, host to the Olympic Dam deposit (Ciobanu et al. 2019b; Verdugo-Ihl et al. 2020a).

368 Moreover, epidote is also present in early alteration of feldspars at Olympic Dam (Kontonikas-Charos et

369 al. 2018).

370 **IMPLICATIONS**

371 Although mineral association(s) can strongly impact the Al content in amphibole, as shown by

372 presence of high-Al hornblende (up to 3.3 a.p.f.u. Al) in low-pressure metacarbonates (Léger and Ferry

373 1991), P-T-X phase equilibria used for modelling such assemblages do not include magnetite. The role

374 played by magnetite in buffering reactions among biopyriboles or their polysomatic disorder has not yet

375 been tested experimentally. One example analogous to the case study here is the coherent nanoscale

376 intergrowths between spinel group minerals and aluminous, Ca-amphibole that are reported as lamellar

377 exsolutions in chromite from high-pressure terranes such as podiform chromitite from the Nakhl Massif,

378 Semail Ophiolite, Oman (Chen et al. 2019).

16

379   Unlike hematite, which is typified by a common U-W-Sn-Mo signature throughout the lifespan of

380   IOCG mineralizing systems in the Olympic Dam district (Verdugo-Ihl et al. 2017, 2019, 2020b;

381   Courtney-Davies et al. 2019, 2020a), magnetite records distinct geochemical/nanoinclusion signatures

382   dependent on the local geological setting. For example, at Acropolis, a prospect ~17 km west of Wirrda

383   Well that is hosted by volcanic sequences, magnetite is Ti-rich and typified by inclusions of spinel

384   (Verdugo-Ihl et al. 2021) analogous to those in igneous granite-hosted magnetite from Olympic Dam

385   (Ciobanu et al. 2019b; Verdugo-Ihl et al. 2020a). Uranium-Pb dating of silician magnetite from Olympic

386   Dam shows the likely presence of older Fe-rich protoliths and ~1760 Ma granitoids (Courtney-Davies et

387   al. 2020b). Elsewhere, actinolite is recognized among the otherwise wide range of nanomineral

388   inclusions in Fe-oxides from the Los Colorados IOCG deposit, Chilean Iron Belt (Deditius et al. 2018).

389   Proof of concept for the use of nanoscale Ftsk inclusions in magnetite as a mineral geobarometrer is

390   seen in the reliable application of ilmenite-magnetite nano-thermooxybarometry with estimated T-fO_2

391   values from compositions of mineral pairs measured at the nanoscale (Righter et al. 2014; Verdugo-Ihl

392   et al. 2021). The assemblage described here from Wirrda Well represents a ~1735–1690 Ma metamorphic

393   window preserved in magnetite that was inherited from ~1.85 Ga lithologies, and with a subsequent

394   IOCG-fluid overprint at ~1.6 Ga. Nanoscale studies of magnetite, if considered in an appropriate

395   petrological context, can provide valuable insights into the evolution of mineralizing systems within the

396   same district and, as more studies become available, also across distinct metallogenetic provinces

397   worldwide. Likewise, confirmation of nanomineral Ftsk pressure estimates by petrological studies show

398   the potential value of magnetite in recording and preserving evidence for discrete events in terranes with

399   protracted geological histories.

400   HAADF STEM imaging gives an improved visualization of pyribole structures and particularly the

401   distribution and topology of *A* cavities (Figs. 7-9), which are the sites with the greatest probability of

402   containing heterovalent SRO (Hawthorne et al. 2005). This type of imaging should provide further

17

403   insight into polysomes such as those between (cavity free) pyroxenes and amphiboles, as for example

404   the sequence '2111' reported from anthophyllite in ultramafic lenses (Lepontine Alps, Switzerland;

405   Grobety 1996) and subsequently the subject of debate as to whether these are artifacts or natural products

406   (Konishi et al. 2004).

407   The occurrence of chain-width disorder during pyribole crystallization is most likely the rule rather

408   than the exception in minerals that share crystal structural blocks. Recent HAADF STEM studies have

409   also revealed intergrowths of single units or individual sub-structural motifs relating to stacking disorder

410   recorded during crystallisation among members of diverse modular homologous series, e.g., REE-

411   fluorocarbonates (Ciobanu et al. 2017), mixed-layer chalcogenides (Cook et al. 2019), or Sb-Bi-sulfosalts

412   with chessboard structures (Li et al. 2019).

419   **REFERENCES CITED**

420   Abdu, Y.A., and Hawthorne, F.C. (2009) Crystal structure and Mössbauer spectroscopy of tschermakite from the

421   Ruby   locality   at   Fiskenaesset,   Greenland.   The   Canadian   Mineralogist,   47,   917–926.

422   https://doi.org/10.3749/canmin.47.4.917

423   Ams, B.E., and Jenkins, D.M. (2011) Formation conditions for triple-chain silicates. American Mineralogist, 96,

424   814–819. https://doi.org/10.2138/am.2011.3568

425   Bosi, F., Biagioni, C., and Pasero, M. (2019) Nomenclature and classification of the spinel supergroup. European

426   Journal of Mineralogy, 31, 183–192.

427 Bozhilov, K.N. (2013) Structures and microstructures of non-classical pyriboles. EMU Notes in Mineralogy, 14,

428   109–152.

429 Champness, P.E. (2002) Applications of Transmission Electron Microscopy. In: Advances in Imaging and

430   Electron Physics, vol. 121, p. 53–90, Academic Press. https://doi.org/10.1016/S1076-5670(02)80025-8

431 Chen, T., Jin, Z., Zhang, J., and Wang, L. (2019) Calcium amphibole exsolution lamellae in chromite from the

432   Semail   ophiolite: Evidence   for   a   high-pressure   origin.   Lithos,   334–335,   273–280.

433   https://doi.org/10.1016/j.lithos.2019.03.020

434 Ciobanu, C.L., Cook, N.J., Utsunomiya, S., Pring, A., and Green, L. (2011) Focussed ion beam–transmission

435   electron microscopy applications in ore mineralogy: Bridging micro- and nanoscale observations. Ore Geology

436   Reviews, 42, 6–31. https://doi.org/10.1016/j.oregeorev.2011.06.012

437 Ciobanu, C.L., Cook, N.J., Maunders, C., Wade, B.P., and Ehrig, K. (2016) Focused Ion Beam and Advanced

438   Electron Microscopy for Minerals: Insights and Outlook from Bismuth Sulphosalts. Minerals, 6, 112.

439   https://doi.org/10.3390/min6040112

440 Ciobanu, C.L., Kontonikas-Charos, A., Slattery, A., Cook, N.J., Ehrig. K., and Wade, B.P. (2017) Short-range

441   stacking disorder in mixed-layer compounds: a HAADF STEM study of bastnäsite-parisite intergrowths.

442   Minerals, 7, 227. https://doi.org/10.3390/min7110227

443 Ciobanu, C.L., Utsunomiya, S., Reich, M., Plümper, O., and Cook, N.J. (2019a) Editorial for Special Issue

444   "Minerals   Down   to   the   Nanoscale: A   Glimpse   at   Ore-Forming   Processes".   Minerals,   9,   692.

445   https://doi.org/10.3390/min9110692

446 Ciobanu, C.L., Verdugo-Ihl, M.R., Slattery, A., Cook, N.J., Ehrig, K., Courtney-Davies, L., and Wade, B.P.

447   (2019b) Silician Magnetite: Si–Fe-Nanoprecipitates and Other Mineral Inclusions in Magnetite from the

448   Olympic Dam Deposit, South Australia. Minerals, 9, 311. https://doi.org/10.3390/min9050311

449 Cook, N.J., Ciobanu, C.L., Liu, W.Y., Slattery, A., Wade, B.P., Mills, S., and Stanley, C.J. (2019) Polytypism and

450   polysomatism in mixed-layer chalcogenides: characterization of $PbBi_4Te_4S_3$ and inferences for ordered phases

451   in the aleksite series. Minerals, 9, 628. https://doi.org/10.3390/min9100628

452 Courtney-Davies, L., Ciobanu, C.L., Verdugo-Ihl, M.R., Dmitrijeva, M., Cook, N.J., Ehrig, K., and Wade, B.P.

453   (2019) Hematite geochemistry and geochronology resolve genetic and temporal links among iron-oxide copper

19

454   gold systems, Olympic Dam district, South Australia. Precambrian Research 335, 105480.

455   https://doi.org/10.1016/j.precamres.2019.105480

456   Courtney-Davies, L., Ciobanu, C.L., Tapster, S.R., Cook, N.J., Ehrig, K., Crowley, J.L., Verdugo-Ihl, M.R., Wade,

457   B.P., and Condon, D.J. (2020a) Opening the Magmatic-Hydrothermal Window: High-Precision U-Pb

458   Geochronology of the Mesoproterozoic Olympic Dam Cu-U-Au-Ag Deposit, South Australia. Economic

459   Geology, 115, 1855-1870, https://doi.org/10.5382/econgeo.4772.

460   Courtney-Davies, L., Ciobanu, C.L., Verdugo-Ihl, M.R., Cook, N.J., Ehrig, K., Wade, B.P., Zhu, Z.-Y., and

461   Kamenetsky, V.S. (2020b) ~1760 Ma magnetite-bearing protoliths in the Olympic Dam deposit, South

462   Australia: Implications for ore genesis and regional metallogeny. Ore Geology Reviews, 118, 103337.

463   https://doi.org/10.1016/j.oregeorev.2020.103337

464   Cressey, B.A., Whittaker, E.J.W., and Hutchison, J.L. (1982) Morphology and alteration of asbestiform grunerite

465   and anthophyllite. Mineralogical Magazine, 46, 77–87.

466   Deditius, A.P., Reich, M., Simon, A.C., Suvorova, A., Knipping, J., Roberts, M.P., Rubanov, S., Dodd, A., and

467   Saunders, M. (2018) Nanogeochemistry of hydrothermal magnetite. Contributions to Mineralogy and

468   Petrology, 173, 46. https://doi.org/10.1007/s00410-018-1474-1

469   Deer, W.A., Howie, R.A., and Zussman, J. (2013) An Introduction to the Rock-Forming Minerals, 3rd edition.

470   Mineralogical Society of Great Britain and Ireland, https://doi.org/10.1180/DHZ.

471   Drits, V.A., Guggenheim, S., Zviagina, B.B., and Kogure, T. (2012) Structures of the 2:1 layers of pyrophyllite

472   and talc. Clays and Clay Minerals, 60, 574-587. https://doi.org/10.1346/CCMN.2012.0600603

473   Fleet, M.E., Bilcox, G.A., and Barnett, R.L. (1980) Oriented magnetite inclusions in pyroxenes from the Grenville

474   Province. Canadian Mineralogist, 18, 89–99.

475   Gao, W., Ciobanu, C.L., Cook, N.J., Slattery, A., Huang, F., and Wang, D. (2019a) Nanoscale study of lamellar

476   exsolutions in clinopyroxene from olivine gabbro: Recording crystallization sequences in iron-rich layered

477   intrusions. American Mineralogist, 104, 244–261. https://doi.org/10.2138/am-2019-6764

478   Gao, W., Ciobanu, C.L., Cook, N.J., Slattery, A., Huang, F., and Song, D. (2019b) Nanoscale study of

479   titanomagnetite from the Panzhihua Layered Intrusion, Southwest China: Multistage exsolutions record ore

480   formation. Minerals, 9, 513. https://doi.org/10.3390/min9090513

481 Grobety, B.H. (1996) New short-range biopyribole polysomes from the Lepontine Alps, Switzerland. American

482 Mineralogist, 81, 404–417. https://doi.org/10.2138/am-1996-3-415

483 Grobéty, B.H. (1997) The replacement of anthophyllite by jimthompsonite: a model for hydration reactions in

484 biopyriboles. Contributions to Mineralogy and Petrology, 127, 237-247.

485 Hammarstrom, J.M., and Zen, E-an (1986) Aluminum in hornblende: An empirical igneous geobarometer.

486 American Mineralogist, 71, 1297–1313.

487 Hawthorne, F., and Grundy, H. (1973) The crystal chemistry of the amphiboles. I: Refinement of the Crystal

488 structure of ferrotschermakite. Mineralogical Magazine, 39, 36-48.

489 Hawthorne, F.C., Della Ventura, G., Oberti, R., Robert, J.-L., and Iezzi, G. (2005) Short-range order in minerals:

490 Amphiboles. The Canadian Mineralogist, 43, 1895–1920. https://doi.org/10.2113/gscanmin.43.6.1895

491 Hawthorne, F.C., Oberti, R., Harlow, G.E., Maresch, W.V., Martin, R.F., Schumacher, J.C., and Welch, M.D.

492 (2012) Nomenclature of the amphibole supergroup. American Mineralogist, 97, 2031–2048.

493 https://doi.org/10.2138/am.2012.4276

494 Keyser, W., Ciobanu, C.L., Cook, N.J., Courtney-Davies, L., Kennedy, A., Wade, B.P., Ehrig, K., Dmitrijeva, M.,

495 Kontonikas-Charos, A., Feltus, H., and Johnson, G. (2019) Petrographic and geochronological constraints on

496 the granitic basement to the Middleback Ranges, South Australia. Precambrian Research, 324, 170-193.

497 https://doi.org/10.1016/j.precamres.2019.01.024

498 Konishi, H., Akai, J., Kurokawa, K. (1993) Calcic analog of clinojimthompsonite from the Oeyama ophiolite,

499 southwest Japan. Journal Geological Society Japan, 99, 679-682

500 Konishi, H., Alviola, R., and Buseck, P.R. (2004) 2111 biopyribole intermediate between pyroxene and amphibole:

501 Artifact or natural product? American Mineralogist, 89, 15-19. https://doi.org/10.2138/am-2004-0103

502 Konishi, H., Xu, H., and Dymek, R.F. (2010) High-resolution TEM study of jimthompsonite, chesterite, and chain-

503 width disorder in Archean ultramafic rocks from Isua, West Greenland. American Mineralogist, 95, 73–80.

504 https://doi.org/10.2138/am.2010.3212

505 Kontonikas-Charos, A., Ciobanu, C.L., Cook, N.J., Ehrig, K., Ismail, R., Krneta, S., and Basak, A. (2018) Feldspar

506 mineralogy and rare earth element (re)mobilization in iron-oxide copper gold systems from South Australia: a

507 nanoscale study. Mineralogical Magazine, 82(S1), S173–S197. https://doi.org/10.1180/minmag.2017.081.040

508 Léger, A., and Ferry, J.M. (1991) Highly aluminous hornblende from low-pressure metacarbonates and a preliminary thermodynamic model for the Al content of calcic amphibole. American Mineralogist, 76, 1002–1017.

511 Li, W., Ciobanu, C.L., Slattery, A., Cook, N.J., Liu, W., Wade, B.P., and Xie, G.Q. (2019) Chessboard structures: atom-scale imaging of homologues from the kobellite series. American Mineralogist, 104, 459–462.

513 Locock, A.J. (2014) An Excel spreadsheet to classify chemical analyses of amphiboles following the IMA2012 recommendations. Computers & Geosciences, 62, 1–11.

515 Medlin, D.L., Ramasse, Q.M., Spataru, C.D., and Yang, N.Y.C. (2010) Structure of the (0001) basal twin boundary in Bi_2Te_3. Journal of Applied Physics, 108, 043517. https://doi.org/10.1063/1.3457902

517 Medlin, D.L., and Snyder, G.J. (2013) Atomic-scale interfacial structure in rock salt and tetradymite chalcogenide thermoelectric materials. JOM, 65, 390–400. https://doi.org/10.1007/s11837-012-0530-y

519 Medlin, D., Erickson, K., Limmer, S., Yelton, W., and Siegal, M.P. (2014) Dissociated 1/3 <0111> dislocations in Bi_2Te_3 and their relationship to seven-layer Bi_3Te_4 defects. Journal of Materials Science, 49, 3970–3979.

521 Medlin, D.L., Yang, N., Spataru, C.D., Hale, L.M., and Mishin, Y. (2019) Unraveling the dislocation core structure at a van der Waals gap in bismuth telluride. Nature Communications, 10, 1820. https://doi.org/10.1038/s41467-019-09815-5

524 Mutch, E.J.F., Blundy, J.D., Tattitch, B.C., Cooper, F.J., and Brooker, R.A. (2016) An experimental study of amphibole stability in low-pressure granitic magmas and a revised Al-in-hornblende geobarometer. Contributions to Mineralogy and Petrology, 171, 85. https://doi.org/10.1007/s00410-016-1298-9

527 Najorka, J., and Gottschalk, M. (2003) Crystal chemistry of tremolite–tschermakite solid solutions. Physics and Chemistry of Minerals, 30, 108–124. https://doi.org/10.1007/s00269-002-0291-1

529 Oberti, R., Boiocchi, M., Hawthorne, F.C., and Ciriotti, M.E. (2018) Ferro-tschermakite from the Ploumanac'h granitic complex, Brittany, France: mineral description. European Journal of Mineralogy, 30, 171–176. https://doi.org/10.1127/ejm/2018/0030-2700

532 Papike, J.J., and Ross, M. (1970) Gedrites – crystal structures and intracrystalline cation distributions. American Mineralogist, 55, 1945–1972.

534 Reid, A. (2019) The Olympic Cu-Au Province, Gawler Craton: A Review of the Lithospheric Architecture,

535   Geodynamic Setting, Alteration Systems, Cover Successions and Prospectivity. Minerals, 9, 371.

536   https://doi.org/10.3390/min9060371

537 Righter, K., Keller, L.P., Rahman, Z., and Christoffersen, R. (2014) Redox-driven exsolution of iron titanium

538   oxides in magnetite in Miller Range (MIL) 03346 nakhlite: Evidence for post crystallization oxidation in the

539   nakhlite cumulate pile? American Mineralogist, 99, 2313–2319. https://doi.org/10.2138/am-2014-4926

540 Schmidt, M.W. (1992) Amphibole composition in tonalite as a function of pressure: an experimental calibration

541   of the Al-in-hornblende barometer. Contributions to Mineralogy and Petrology, 110, 304-310.

542 Thompson Jr., J.B. (1978) Biopyriboles and polysomatic series. American Mineralogist, 63, 239–249.

543 Utsunomiya, S., and Ewing, R.C. (2003) Application of high-angle annular dark field scanning transmission

544   electron microscopy, scanning transmission electron microscopy-energy dispersive X-ray spectrometry, and

545   the energy-filtered transmission electron microscopy to the characterization of nanoparticles in the

546   environment. Environmental Science and Technology, 37, 786–791.

547 Van Tendeloo, G., Bals, S., Van Aert, S., Verbeeck, J., and Van Dyck, D. (2012) Advanced electron microscopy

548   for advanced materials. Advanced Materials, 24, 5655–5675. https://doi.org/10.1002/adma.201202107

549 Veblen, D.R. (1981) Non-classical pyriboles and polysomatic reactions in biopyriboles. In D.R. Veblen, Ed.,

550   Amphiboles and Other Hydrous Pyriboles—Mineralogy, 9A, p. 189–234. Reviews in Mineralogy,

551   Mineralogical Society of America, Chantilly, Virginia.

552 Veblen, D.R. (1992) Electron microscopy applied to nonstoichiometry, polysomatism, and replacement reactions

553   in minerals. Reviews in Mineralogy and Geochemistry, 27, 181-229.

554 Veblen, D.R., and Burnham, C.W. (1978) New biopyriboles from Chester, Vermont: II. The crystal chemistry of

555   jimthompsonite, clinojimthompsonite, and chesterite, and the amphibole-mica reaction. American

556   Mineralogist, 63, 1053–1073.

557 Veblen, D.R., and Buseck, E.R. (1979) Chain-width order and disorder in biopyriboles. American Mineralogist,

558   64, 687–700.

559 Veblen, D.R. and Buseck, P.R. (1980) Microstructures and reaction mechanisms in biopyriboles. American

560   Mineralogist, 65, 599–623.

561   Veblen, D.R. and Buseck, P.R. (1981) Hydrous pyriboles and sheet silicates in pyroxenes and uralites; intergrowth

562   microstructures and reaction mechanisms. American Mineralogist, 66, 1107–1134.

563   Veblen, D.R., Buseck, P.R., and Burnham, C.W. (1977) Asbestiform chain silicates: New minerals and structural

564   groups. Science, 198, 359–365.

565   Veblen, D.R., Banfield, J.F., Guthrie, G.D., Heaney, P.J., Ilton, E.S., Livi, K.J.T., and Smelik, E.A. (1993) High-

566   resolution and analytical transmission electron microscopy of mineral disorder and reactions. Science, 260,

567   1465-1472.

568   Verdugo-Ihl, M.R., Ciobanu, C.L., Cook, N.J., Ehrig, K.J., Courtney-Davies, L., and Gilbert, S. (2017) Textures

569   and U-W-Sn-Mo signatures in hematite from the Olympic Dam Cu-U-Au-Ag deposit, South Australia:

570   Defining   the   archetype   for   IOCG   deposits.   Ore   Geology   Reviews,   91,   173–195.

571   https://doi.org/10.1016/j.oregeorev.2017.10.007

572   Verdugo-Ihl, M.R., Ciobanu, C.L., Slattery, A., Cook, N.J., Ehrig, K., and Courtney-Davies, L. (2019). Copper-

573   arsenic   nanoparticles   in   hematite: fingerprinting   fluid-mineral   interaction.   Minerals,   9,   388.

574   https://doi.org/10.3390/min9070388

575   Verdugo-Ihl, M.R., Ciobanu, C.L., Cook, N.J., Ehrig, K.J., and Courtney-Davies, L. (2020a) Defining early stages

576   of IOCG systems: evidence from iron oxides in the outer shell of the Olympic Dam deposit, South Australia.

577   Mineralium Deposita, 55, 429–452. https://doi.org/10.1007/s00126-019-00896-2

578   Verdugo-Ihl, M., Ciobanu, C.L., Cook, N.J., Ehrig, K., Slattery, A., and Courtney-Davies, L. (2020b) Trace-

579   element remobilisation from W–Sn–U–Pb zoned hematite: Nanoscale insights into a mineral geochronometer

580   behaviour   during   interaction   with   fluids.   Mineralogical   Magazine   84,   502-516.

581   https://doi.org/10.1180/mgm.2020.49

582   Verdugo-Ihl, M.R., Ciobanu, C.L., Cook, N.J., Ehrig, K.J., Slattery A., Courtney-Davies, L and Dmitrijeva M.

583   (2021) Nanomineralogy of hydrothermal magnetite from Acropolis, South Australia: Genetic implications for

584   iron-oxide copper gold mineralization. American Mineralogist, in press, https://doi.org/10.2138/am-2020-

585   7557.

586   Xu, H., Shen, Z., and Konishi, H. (2014) Si-magnetite nano-precipitates in silician magnetite from banded iron

587   formation: Z-contrast imaging and ab initio study. American Mineralogist, 99, 2196–2202.

588   https://doi.org/10.2138/am-2014-4964

589   Yin, S., Wirth, R., Ma, C.Q., and Xu, J.N. (2019) The role of mineral nanoparticles at a fluid-magnetite interface:

590   Implications for trace-element uptake in hydrothermal systems. American Mineralogist, 104, 1180–1188.

591   Zanazzi, P.F., Montagnoli, M., Nazzareni, S., and Comodi, P. (2007) Structural effects of pressure on monoclinic

592   chlorite: A single-crystal study. American Mineralogist, 92, 655-661.

593   **FIGURE CAPTIONS**

594   **Figure 1.** (a, b) Atom filling models for crystal structures of ferro-tschermakite and clinojimthompsonite projected

595   onto [001] showing occupancy of cation sites as marked. Crystallographic information data from Hawthorne

596   and Grundy (1973) and Veblen and Burnham (1978). The two building blocks, 'mica (**M**)' and 'pyroxene (**p,**

597   **q**)', each of ~4.5 Å length, are also marked and separated by dashed lines. Yellow and green overlays show the

598   2- and 3-*I beam* configurations for the double and triple chain silicate, in this case, ferro-tschermakite and

599   clinojimthompsonite, respectively. Note that these can be also formalized as '**pMqM**' and '**pMMqMM**'

600   sequences across one-unit cell whereby the *b* length corresponds to 4.5 Å x 4 (~18 Å) and 4.5 Å x 6 (~27 Å)

601   for the double and triple chain silicate, respectively.

602   **Figure 2.** (a) Photograph of drill core sample from which the studied sample was cut. Magnetite (Mt) forms a band

603   at the contact between altered granite and dolerite (?). (b, c) Reflected light images showing details of magnetite

604   grains. Note trails of sulfides crosscutting the magnetite band in (b). Crystal zoning with respect to fine, dusty

605   inclusions in magnetite can be seen in (c). Back scatter electron (BSE) image showing location of the two FIB

606   cuts from which S/TEM foils were prepared. Abbreviations: Cp=chalcopyrite; Py=pyrite. (e) Plot of Si (a.p.f.u.)

607   *vs*. ΣFe (a.p.f.u.) showing three types of magnetite substitution involving Si versus Fe exchange. The end-

608   member phases are marked with stoichiometry calculated on the basis of 32 oxygen atoms. Substitution (1) is

609   towards fayalite and preserves full metal occupancy, whereas the other two substitutions involve Fe vacancies

610   ($\square$). Substitution (3) depicts cation exchange with metal vacancies in the octahedral Fe^{2+} sites coupled with Si

611   replacement of Fe^{3+} in tetrahedral sites of the magnetite structure, leading to the $\gamma\text{-}\square_4Fe^{2+}_4Fe^{3+}_8Si_8O_{32}$ (or γ-

25

612    $Fe_{1.5}SiO_4$) phase with $P4_332$ symmetry if vacancy ordering is encountered (Xu et al. 2014). (f) Plot ΣMe^{4+}

613   (Si+Ti±U; a.p.f.u.) *vs.* ΣFe (a.p.f.u.) for analyzed magnetite using stoichiometry on a 32 O atom basis

614   (Supplemental[1] Table A1). The data plot close to substitution line (3), albeit with an offset due to the presence

615   of other silicate inclusions. The linear trend suggests, nonetheless, that inclusion nucleation is preferentially

616   controlled by the magnetite structure.

617   **Figure 3.** Overview of the studied S/TEM foils, also indicating mapped areas and locations of inclusions and Si-

618   Fe-nanorods discussed in the text. Growth zones in magnetite with changes in orientation of inclusions are

619   marked by dashed lines in (a). Also note inclusion clots in both foils. Abbreviations: Chl-chlorite, Plag–

620   plagioclase, Qz–quartz, Rt–rutile, Ser–sericite, Ftsk–ferro-tschermakite.

621   **Figure 4.** Images of inclusions in magnetite from foil # 1 representing aspects as written in the headings for each

622   panel. Note high density of amphibole (circled in red) relative to chlorite (circled in yellow) as shown in (b).

623   Triple-chain silicate in amphibole marked by arrowheads on (d-f). Abbreviations: BF-Bright Field; Chl-

624   chlorite; Ftsk–ferro-tschermakite; Mt=magnetite; P=pyrophyllite; Phyl=phyllosilicate; T=talc.

625   **Figure 5**. HAADF STEM images (a, b, d, e) and Fast Fourier Transform (FFT) pattern (c) for ferro-tschermakite

626   (Ftsk) inclusions in silician magnetite. (a) Ferro-tschermakite and Si-Fe-rods oriented along <111> in magnetite

627   (Mt). Note chlorite (Chl) replacing the amphibole. (b) Image and FFT pattern (inset) of Si-Fe-rod in magnetite.

628   (c) FFT pattern of amphibole inclusion in magnetite showing epitaxial intergrowths between the two minerals

629   sharing orientations as marked. White and yellow rectangles correspond to ferro-tschermakite and magnetite,

630   respectively. Note strong disorder along the b^* axis in the amphibole due to the presence of triple-chain silicate

631   zippers. (d) Ferro-tschermakite grain with single rows of triple-chain silicate along the entire length of the

632   grain. (e) High resolution image of the boundary between magnetite and ferro-tschermakite inclusions showing

633   epitaxial relationships along directions as marked.

634   **Figure 6**. (a) HAADF STEM image and superimposed Si element map showing Si-Fe rods and plagioclase (Plag)

635   inclusion. (b) STEM EDX profile through magnetite and across Si-Fe rods indicated in (a). (c) HAADF STEM

636   image and STEM EDX element maps of ferro-tschermakite inclusion for selected elements. (d) Integrated

637   STEM EDX spectrum for ferro-tschermakite inclusion in (c). (e) EDX signals for Al, Ca and Mg across the

638   inclusion in (c). Abbreviations: Ftsk–ferro-tschermakite; Mt–magnetite.

26

639 **Figure 7.** Comparison between high resolution HAADF STEM images, simulations (shown for slice # 10 and

640   probe size 1; see Supplemental[1] Fig. A4 for additional explanation) and crystal structure models for ferro-

641   tschermakite (Ftsk) and clinojimthompsonite (Cjt) on [001] zone axis. (a) Defect-free amphibole and (b) double

642   rows of 3-chain silicate (dashed lines) occurring in amphibole. Both images show patterns with arrays of 7-

643   and 10-brightest dots (yellow circles) flanked by 2- and 3-pairs of less bright dots (blue circles). (c) Simulation

644   of Ftsk reproduces the acquired image whereby the cations along the octahedron strip and the double-pairs of

645   Si cations (*T* sites) correspond to the yellow and blue circles in (a). Note the intensity variation along the

646   octahedron strip on the image fits perfectly the simulation, in concordance with the compositional similarity

647   between the analyzed amphibole and the Ftsk used for simulation (Hawthorne and Grundy 1973). (d)

648   Simulation of Cjt showing the 10-atoms along the octahedron strip flanked by 3-pairs of Si atoms (*T* sites),

649   topology typical of the 3-chain silicate. Note these features are readily recognizable on the image in (b).

650   However, the variation of signal intensity along the octahedron strip differs between the simulation and image,

651   indicating that the imaged 3-chain silicate differs compositionally (a Ca-, Fe-richer variety?) from the Mg-rich

652   Cjt specimen used for simulation (Veblen and Burnham 1978). (e, f) Simulation and (g, h) atom filling structure

653   models showing the unit cell of Ftsk and Cjt with cation sites as marked (letters in legend correspond to those

654   used in Figure 1). The sites corresponding to *A* cavities in the amphibole are well-marked on the images and

655   simulations as the darkest, diamond-shaped motifs separating the octahedron strips. Paired-*A* cavities are

656   inferred for the triple-chain silicate considering the perfect fit between the simulation and the image in (b).

657   Likewise, the cations at the edges of the octahedron strip are attributable to '*B*' sites.

658 **Figure 8.** *I-beam* models (digits refer to the number of chains in the silicate) as overlays on simulation (a) and

659   image (b) of amphibole with chain-width disorder displayed on [001] zone axis. Note the HAADF STEM

660   simulations and imaging provide a direct visualization of the intergrown structures since they show the main

661   building modules formed by the cations (compare with Figure 1 for the crystal models). (a) The single and

662   double zippers of triple-chain silicate within amphibole show coherent terminations along the zig-zag arrays of

663   cations at the edges of the octahedron strips. (b) The zippers are also readily depicted on the HAADF STEM

664   image by the longer octahedron strip and double-diamond shaped motifs typical of the triple-chain silicate.

27

665 **Figure 9.** HAADF STEM simulations (a, b) and images (c, d) showing relationships between *I-beam* models

666   (digits corresponding to the number of chains) and unit cells of ferro-tschermakite and clinojimthompsonite

667   projected/imaged on [001] zone axis. (a, b) Two rows of *I-beam* stacks for the double- and triple-chain silicate

668   correspond to 1-, and 1.5-unit cells (white overlays), respectively. (c, d) Chain-width disorder in the Wirrda

669   Well amphibole is defined by single- and double-rows of triple-chain silicate. Note the mentioned 1- and 1.5-

670   unit cells correspond to lengths of ~27 Å and ~41 Å along the *b* axis, distances that include edges of ½ unit

671   cells shared between the two pyriboles.

672 **Figure 10.** HAADF STEM images (a, b, d, e) and models (c, f, g) showing replacement of amphibole by

673   phyllosilicates and their intergrowths. (a) Irregular swells along the 3-chain silicate zippers in amphibole

674   (dashed line) imaged on [001] zone axis. (b) Detail of image in (a) showing the stepwise termination of a zipper

675   (arrowed). The distance of ~9.2 Å between alternating brighter and darker strips corresponds to the *c* parameter

676   of phyllosilicates such as a 2:1 mixture of pyrophyllite (P) and talc (T). (c) Replacement of 3-chain silicate by

677   phyllosilicates within the swell interpreted in terms of *I-beam* models whereby the (010) boundary between

678   phyllosilicates and amphibole (orientation in the inset) is coherent along the '**p** or **q**' type slabs and gaps occur

679   at the zipper termination. (d) Chlorite (Chl) imaged on [100] zone axis displaying intergrowths with other

680   phyllosilicates. The FFT pattern (inset) shows the intergrowths are highly disordered along the *c** axis. (e)

681   Detail of image in (d; arrowed location) showing stacking disorder in chlorite. (f, g) Projection on [100] for

682   phyllosilicates used for interpreting the assemblages in (b) and (d). Crystal structure models from: [1]=Drits et

683   al. (2012); [2]=Zanazzi et al. (2007).

28

Table 1. Compositional data for tschermakite and ferro-tschermakite.

Conc.	Tsk (Mg-Hb)	Ferro-tschermakite		
wt. %	[1]	[2]	[3]	*[4]
SiO_2	45.90	40.12	41.32	44.28
TiO_2	0.44	0.87	0.37	0.57
Al_2O_3	14.43	18.67	18.13	18.33
V_2O_3			0.05	
Cr_2O_3	1.73		0.02	
MnO	0.25	0.27	0.20	0.33
FeO	2.79	16.75	17.55	
Fe_2O_3	0.82	2.64		19.13
NiO			0.01	
ZnO			0.02	
MgO	17.50	5.48	6.94	5.28
CaO	11.98	11.65	10.58	10.50
Na_2O	1.70	0.80	1.61	1.26
K_2O	0.25	0.75	0.45	0.31
H_2O^+	2.09	1.61	1.96	
F	0.10	0.07	0.12	
O=F,Cl (calc)	-0.04	-0.03	-0.05	0.00
Total	99.94	99.65	99.28	100.0
Recalculated wt.%				
FeO	1.02	17.16	14.72	16.91
Fe_2O_3	2.79	2.19	3.14	0.34
H_2O^+	2.10	1.97	1.97	2.05
Total	100.15	99.97	99.60	100.17

a.p.f.u. calculated for 22 O atoms
[calculations by spreadsheet of Locock et al. (2014)]

_T_	Si	6.40	6.01	6.14	6.48
	Al	1.60	1.99	1.87	1.52
	∑T	8.00	8.00	8.00	8.00
	Ti	0.05	0.10	0.04	0.06
	Al	0.77	1.31	1.31	1.64
	V			0.01	
	Cr	0.19		0.00	
_C_	Fe^{3+}	0.29	0.25	0.35	0.04
	Ni			0.00	
	Zn			0.00	
	Mn^{2+}				0.04
	Fe^{2+}	0.06	2.12	1.75	2.07
	Mg	3.64	1.22	1.54	1.15
	∑C	5	5	5	5
	Mn^{2+}	0.03	0.03	0.03	0.00
_B_	Fe^{2+}	0.06	0.03	0.08	0.00
	Ca	1.79	1.87	1.68	1.65
	Na	0.13	0.07	0.22	0.35
	∑B	2	2	2	2
_A_	Na	0.34	0.16	0.25	0.01
	K	0.04	0.14	0.09	0.06
	∑A	0.38	0.31	0.33	0.07
	∑T,C,B,A	15.38	15.31	15.33	15.07
_W_	OH	1.96	1.97	1.94	2
	F	0.04	0.03	0.06	
	∑W	2	2	2	2

Abbreviations: Tsk=tschermakite; (Mg-Hb=magnesiohornblende. [1] Abdu and Hawthorne (2009); [2] Hawthorne and Grundy (1973); [3] Oberti et al. (2018); [4] Wirrda Well, present study. *= mean of integrated area using Schreiber-Wims and Brown-Powell methods.
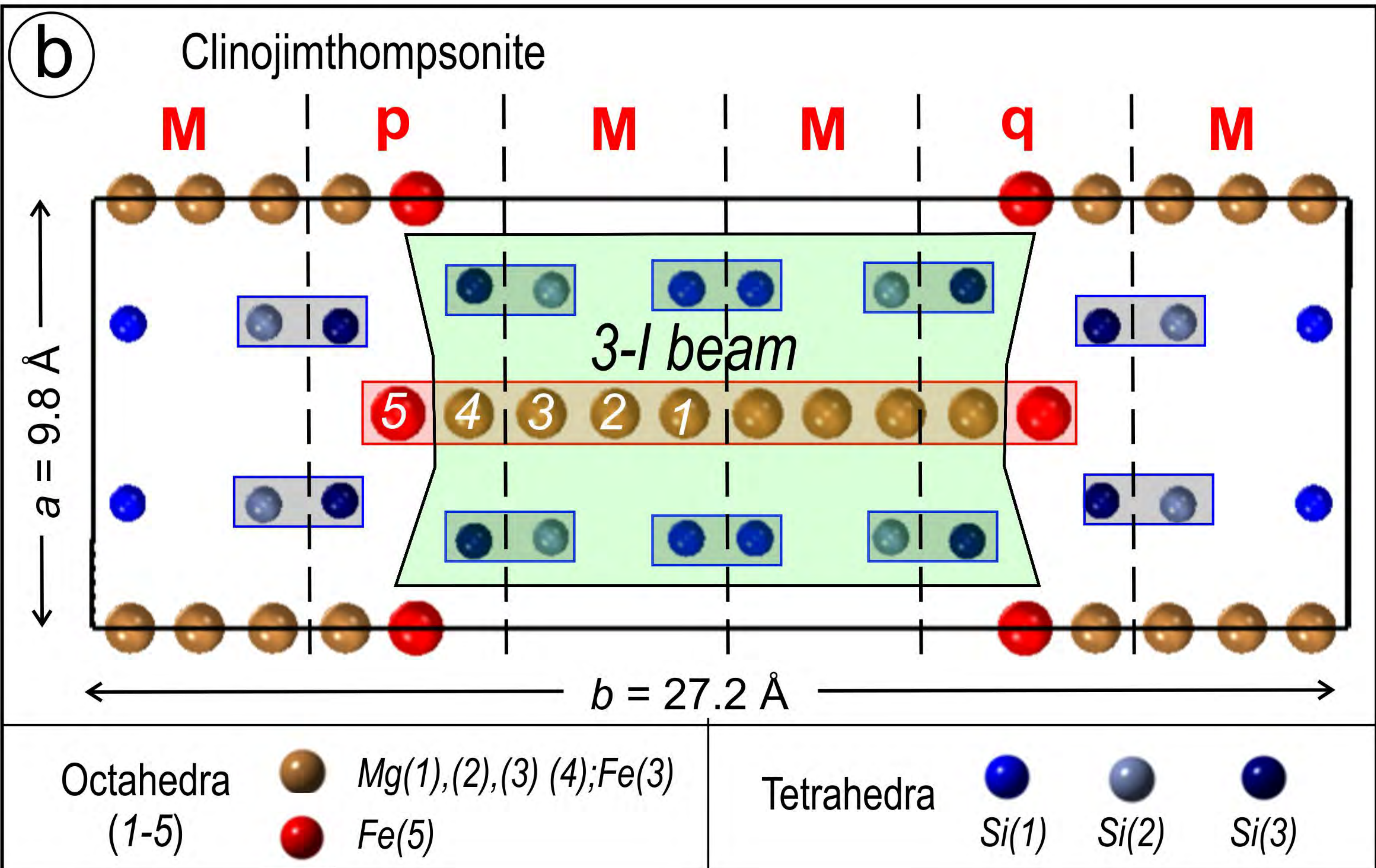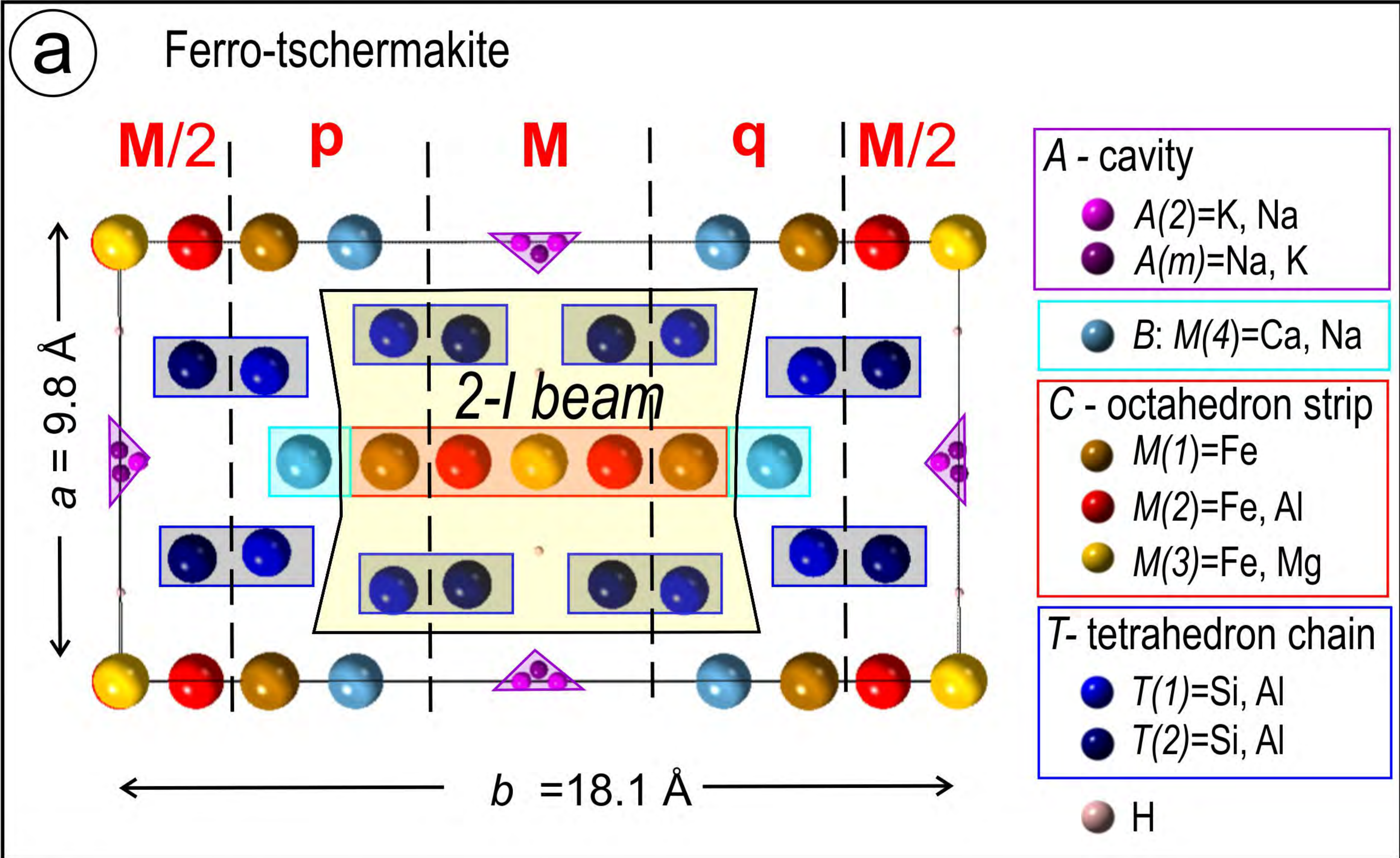
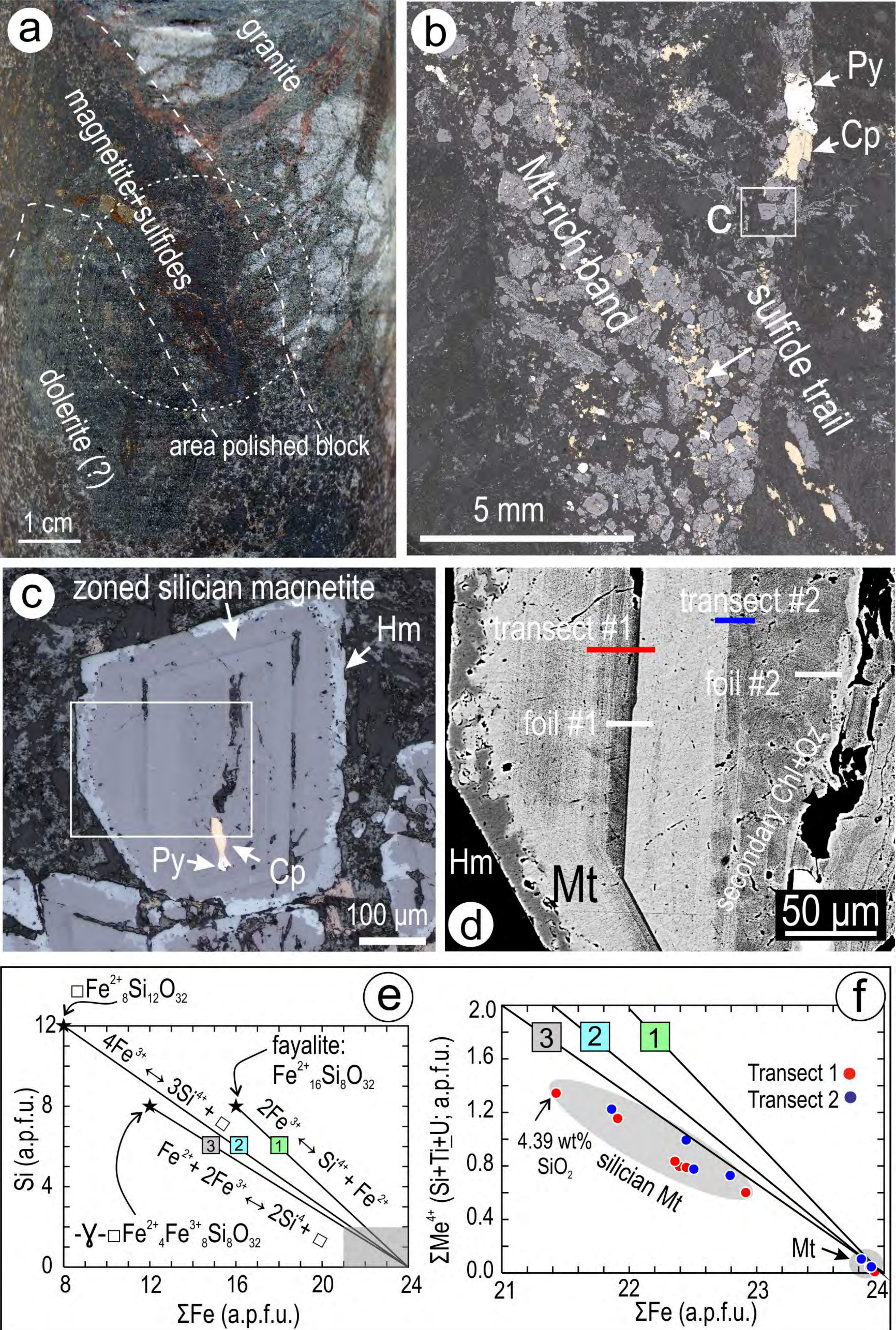**(a)** Ferro-tschermakite

M/2   p   M   q   M/2

a = 9.8 Å

b = 18.1 Å

2-I beam

A - cavity
- *A(2)*=K, Na
- *A(m)*=Na, K

B: *M(4)*=Ca, Na

C - octahedron strip
- *M(1)*=Fe
- *M(2)*=Fe, Al
- *M(3)*=Fe, Mg

T- tetrahedron chain
- *T(1)*=Si, Al
- *T(2)*=Si, Al

H

(b) Clinojimthompsonite

M   p   M   M   q   M

a = 9.8 Å

b = 27.2 Å

3-I beam

5 4 3 2 1

Octahedra (1-5)   *Mg(1),(2),(3) (4);Fe(3)*   *Fe(5)*

Tetrahedra   *Si(1)*   *Si(2)*   *Si(3)*

Figure 1

Figure 2

a — foil #1

map1
Rt+Chl+Fl
Si-Fe-rods & Ftsk
Plag→
oriented Ftsk inclusions & Si-Fe-rods
Fig. 6c □
1 μm

b — foil #2

map 2
clot of Ch+Rt+Ser+Qz
map 3
Rt
map 4
Plag
1 μm

Figure 3

BF (a) and HAADF STEM (b, c) images of the boundary between inclusion-rich and -free zones in magnetite

a

500 nm

b

200 nm

c

100 nm

inclusion-free magnetite

d

Ftsk
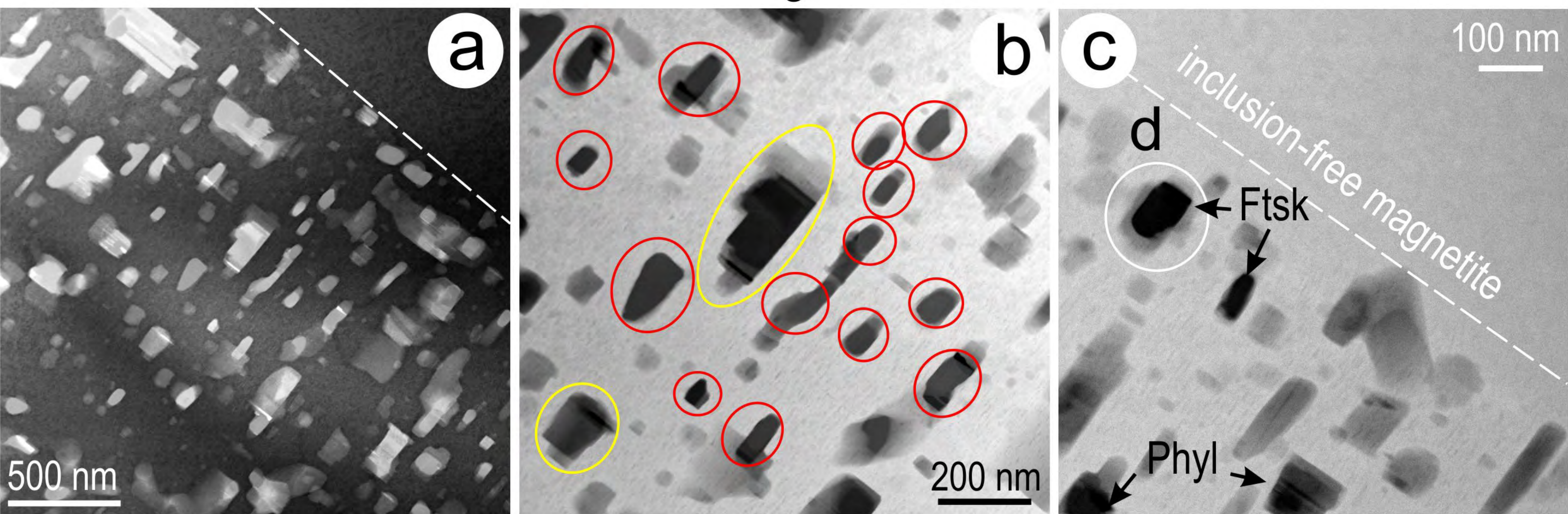
Phyl

BF(d) and HAADF STEM (e, f) images of ferro-tschermakite grains in magnetite tilted on $[11\bar{2}]$ zone axis

d

10 nm

e

grain mapped in Fig. 6c

10 nm

f

Phyl alt. (Fig. 10a,b)

20 nm
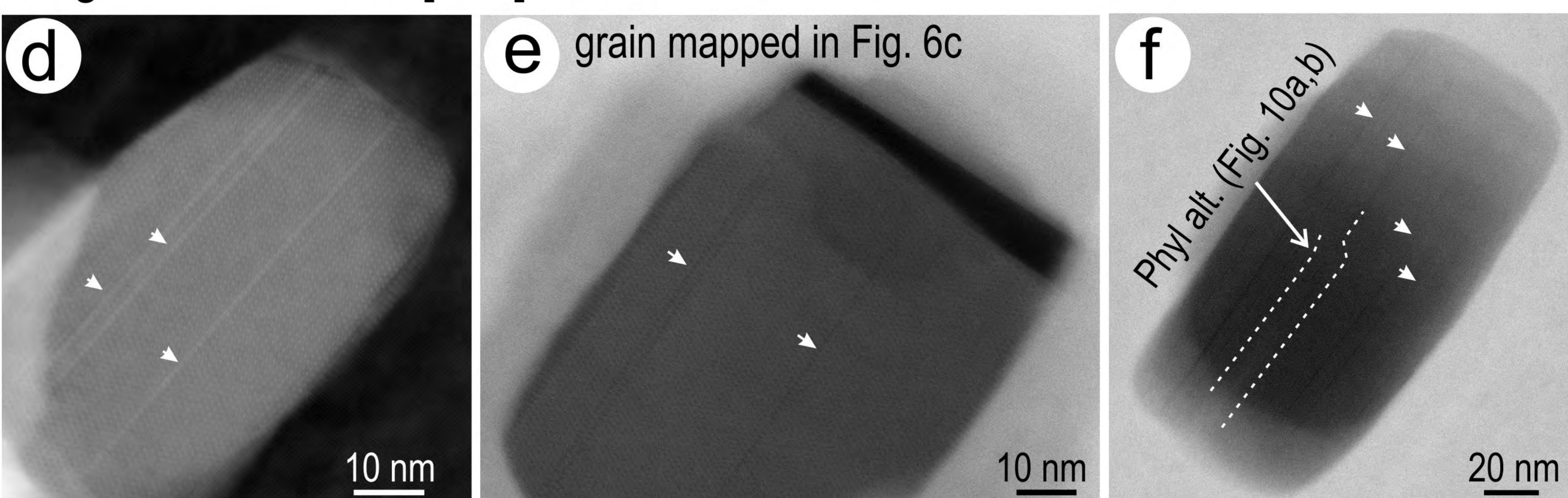
HAADF STEM images of phyllosilicate lamellar aggregates in magnetite

g

P/T

Chl

Fig.10d

20 nm

Mt $[11\bar{2}]$

h

Mt $[11\bar{2}]$

Chl & P/T

50 nm

i

Mt [110]

Chl & P/T

50 nm

Figure 4

Figure 5

a — HAADF Si: Plag, Si-Fe rods, profile, 1 μm

b — Si: atom fraction vs Position (nm), 0–300

c — Ftsk, Mt, profile, 50 nm; Si, Al, Ca maps

d — intensity (a.u.) vs energy (keV): C, O, Na-Kα, Mg-Kα, Al-Kα, Si-Kα, Ca-Kα, Fe-Kα, ferro-tschermakite

e — atom fraction vs Position (nm): Al, Ca, Mg

Figure 6

Ferro-tschermakite

Clinojimthompsonite

HAADF STEM

image

simulation

Crystal struct. model

A
B
C
T
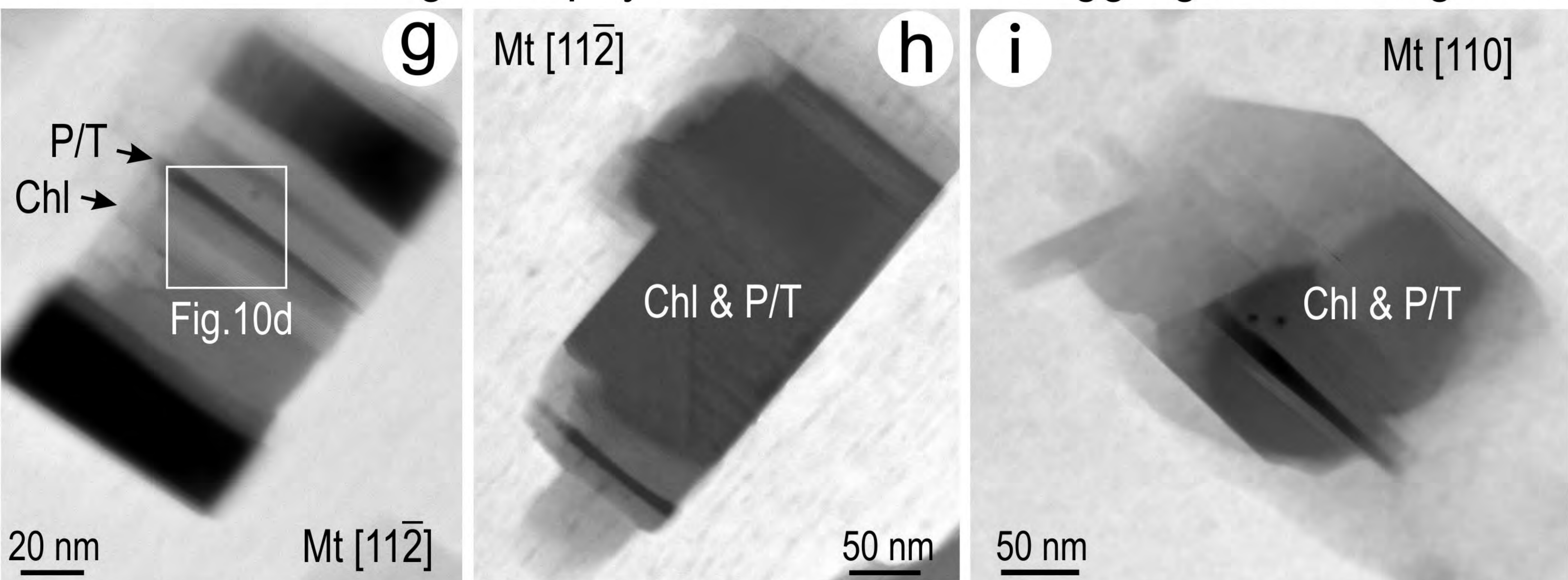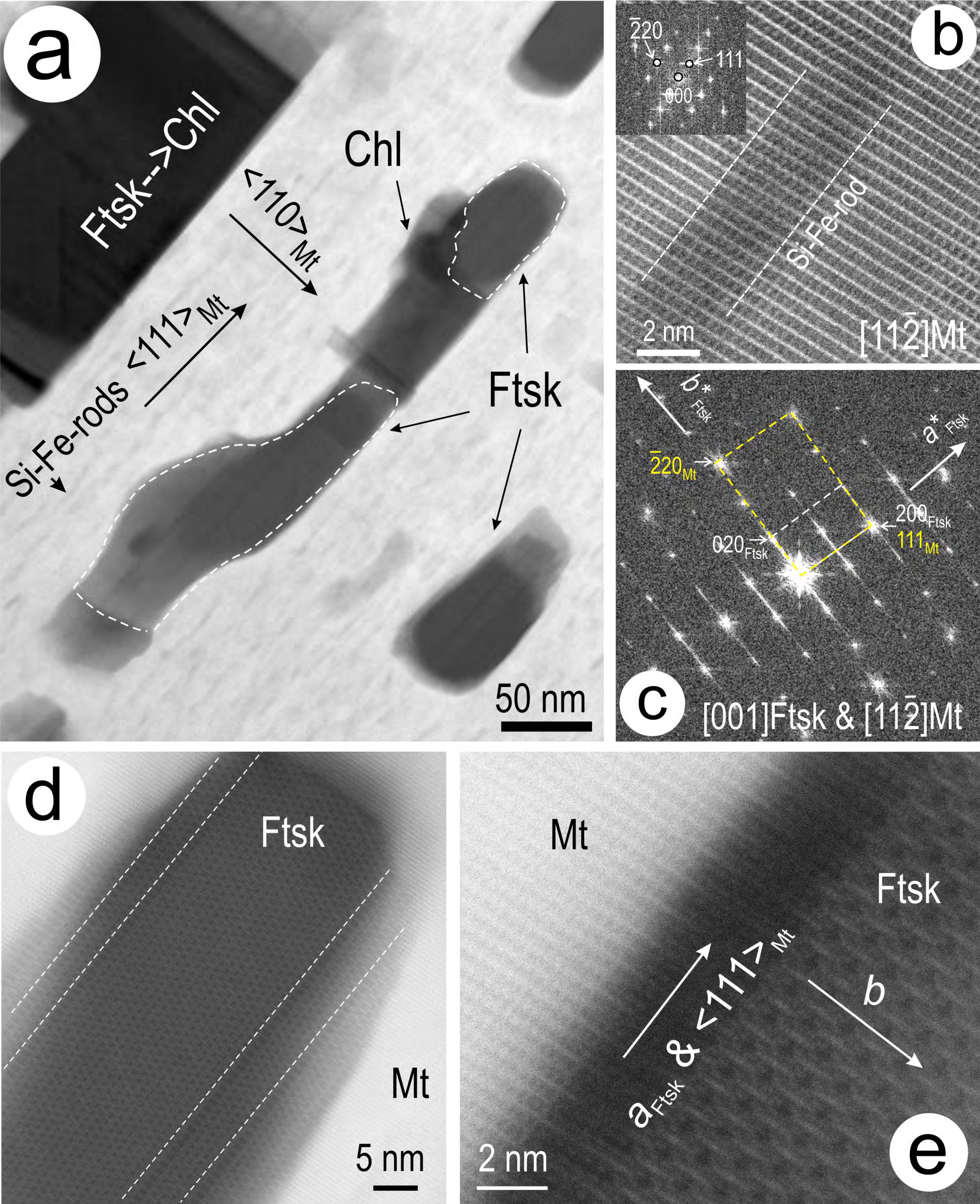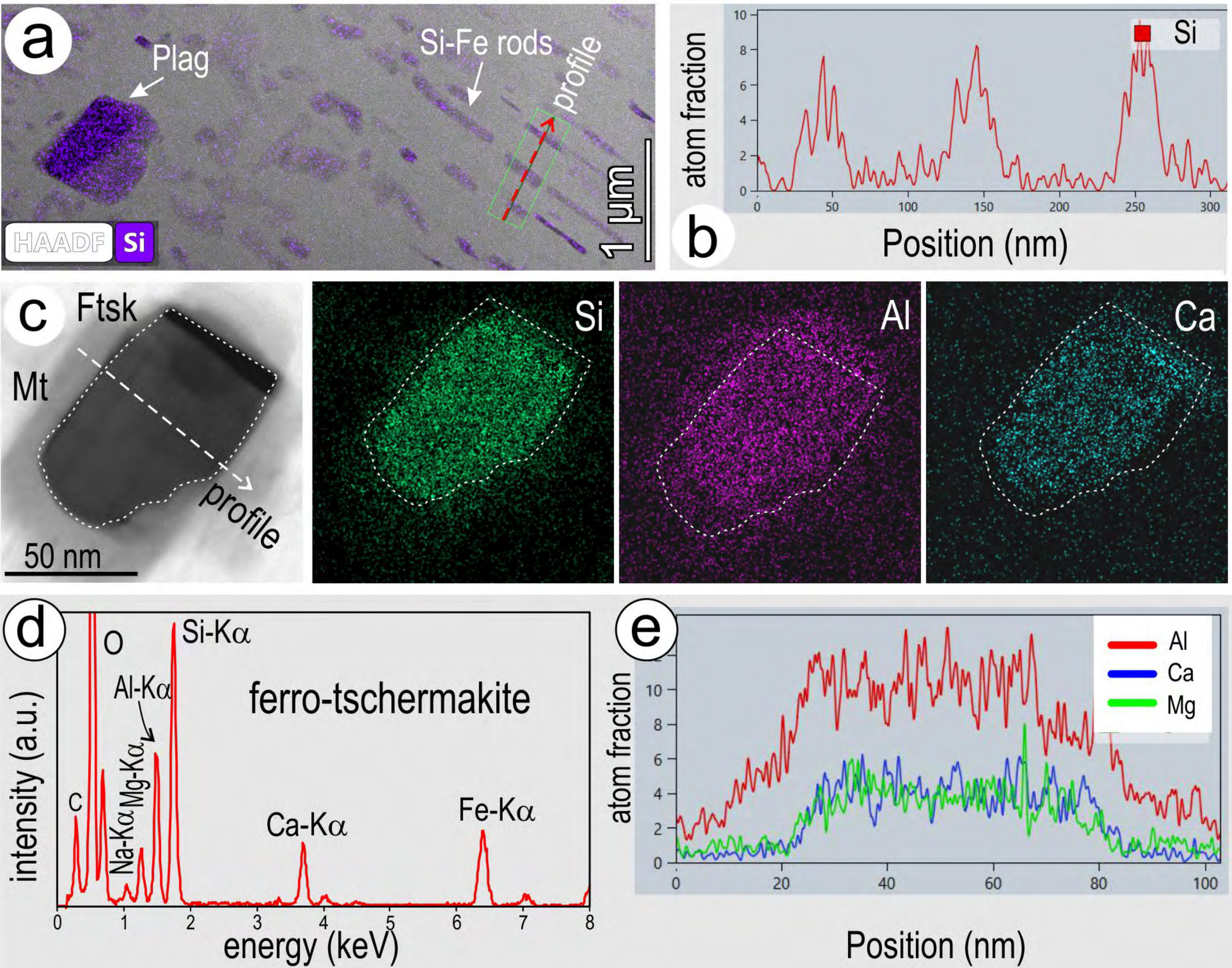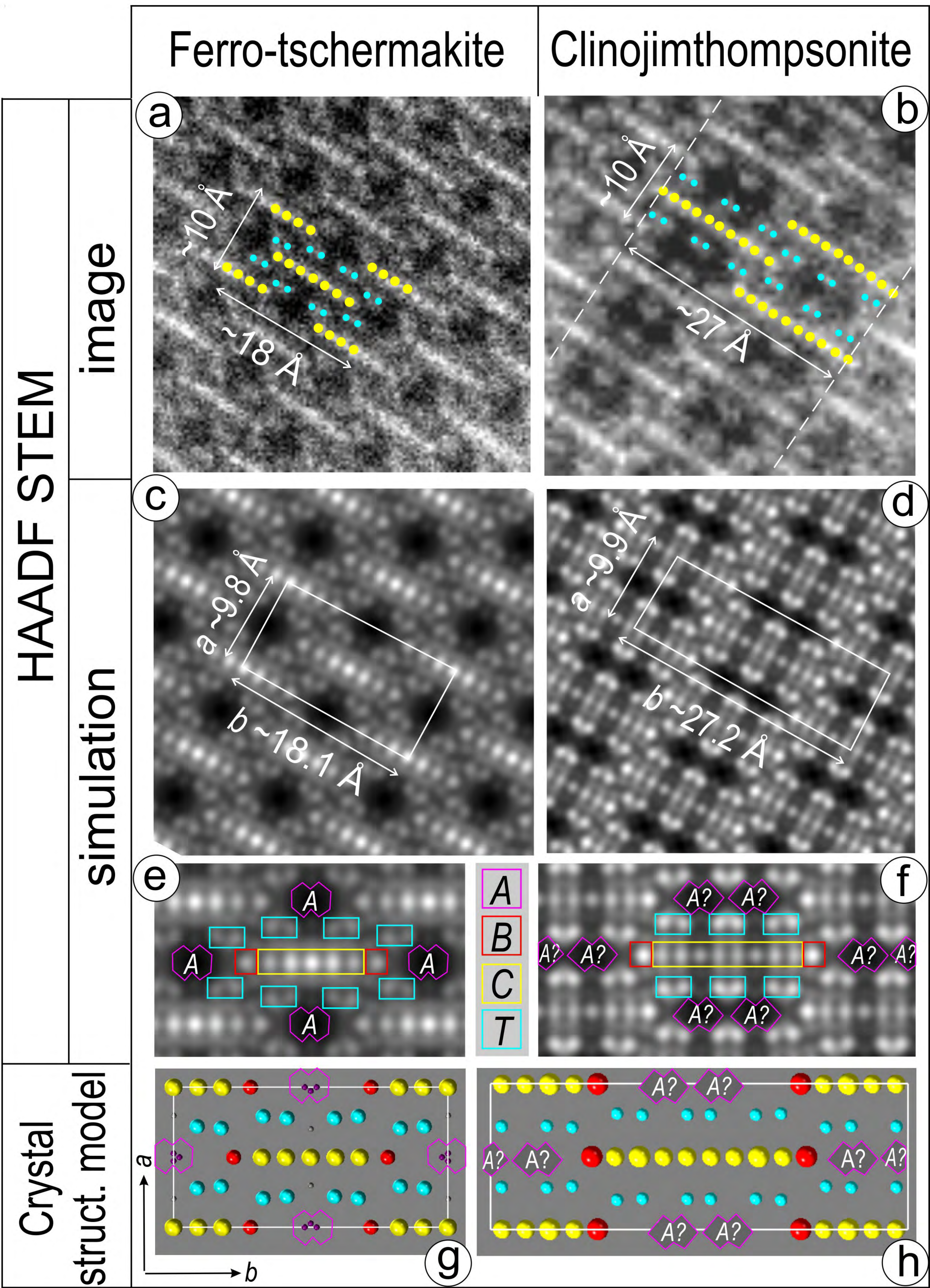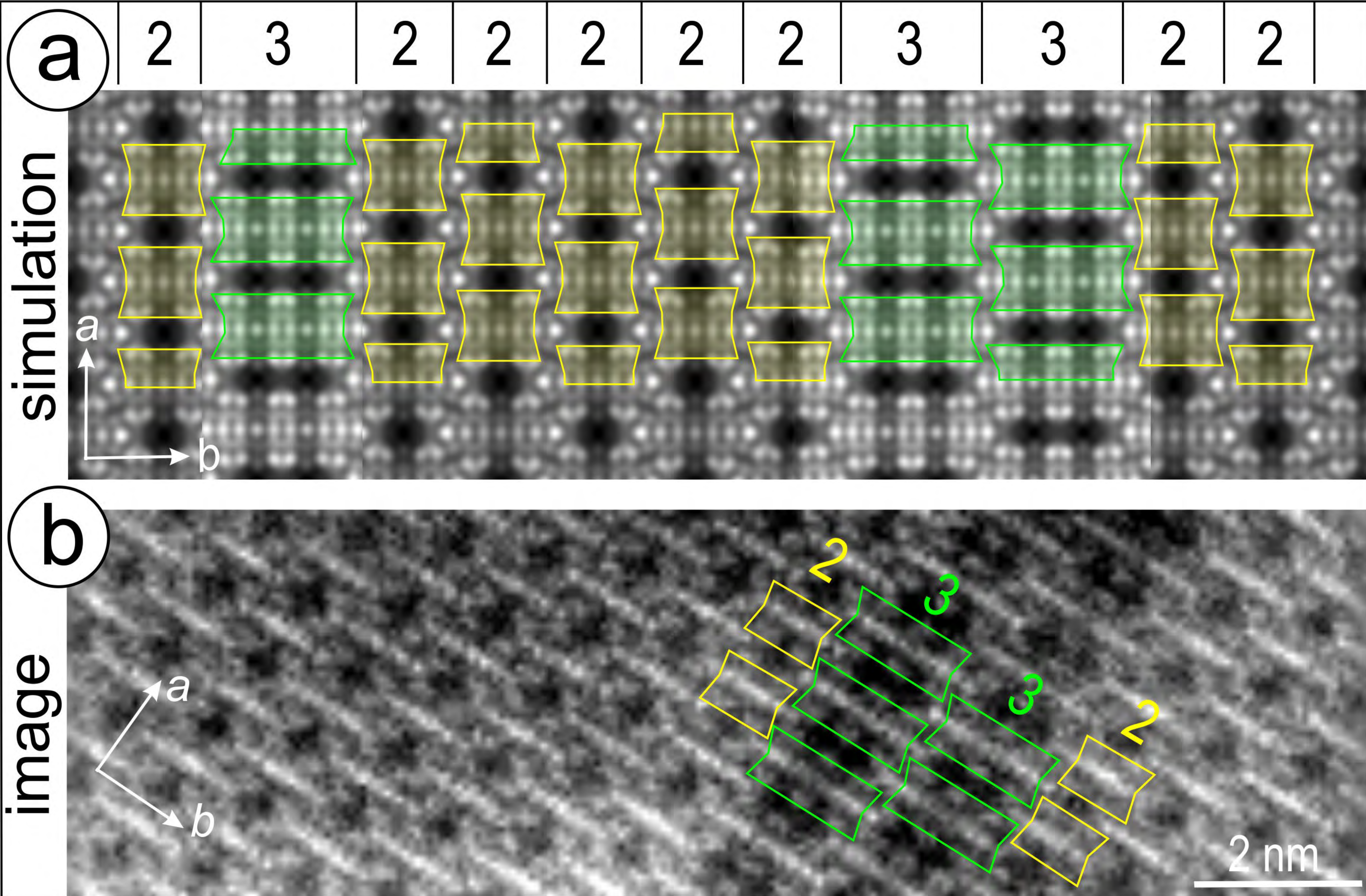
Figure 7

Figure 8

a Ferro-tschermakite

2
2

$b = 18.1$ Å

b Clinojimthompsonite

$1.5\ b = 40.8$ Å

3
3

$b = 27.2$ Å

c

2
2
3
2
2

~18 Å
~27 Å

d

2 2
3 3
2 2

~18 Å
~41 Å

Figure 9

Figure 10