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Ilmenite transformations in suevites from the Nördlinger Ries meteorite impact structure, Germany

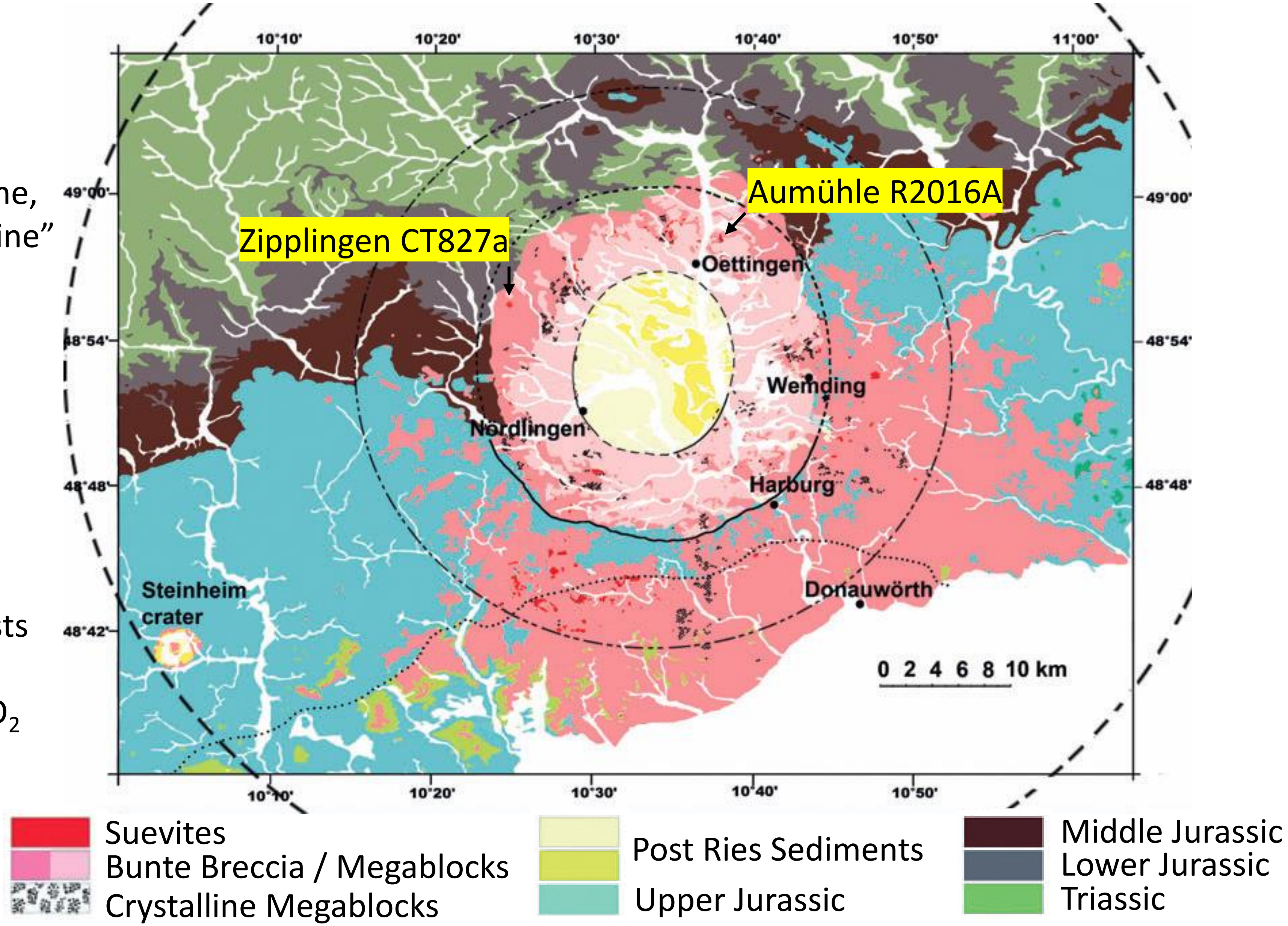
Dellefant, F., Trepmann, C. A., Gilder, S. A., Sleptsova, I. V., Schmahl, W. W., Kaliwoda, M.

Nördlinger Ries Impact Structure

Age ~15 Ma
Ø ~26 km
Target rock: Sedimentary cover (Limestone, sandstone, ~700m thick layer) + “crystalline” basement

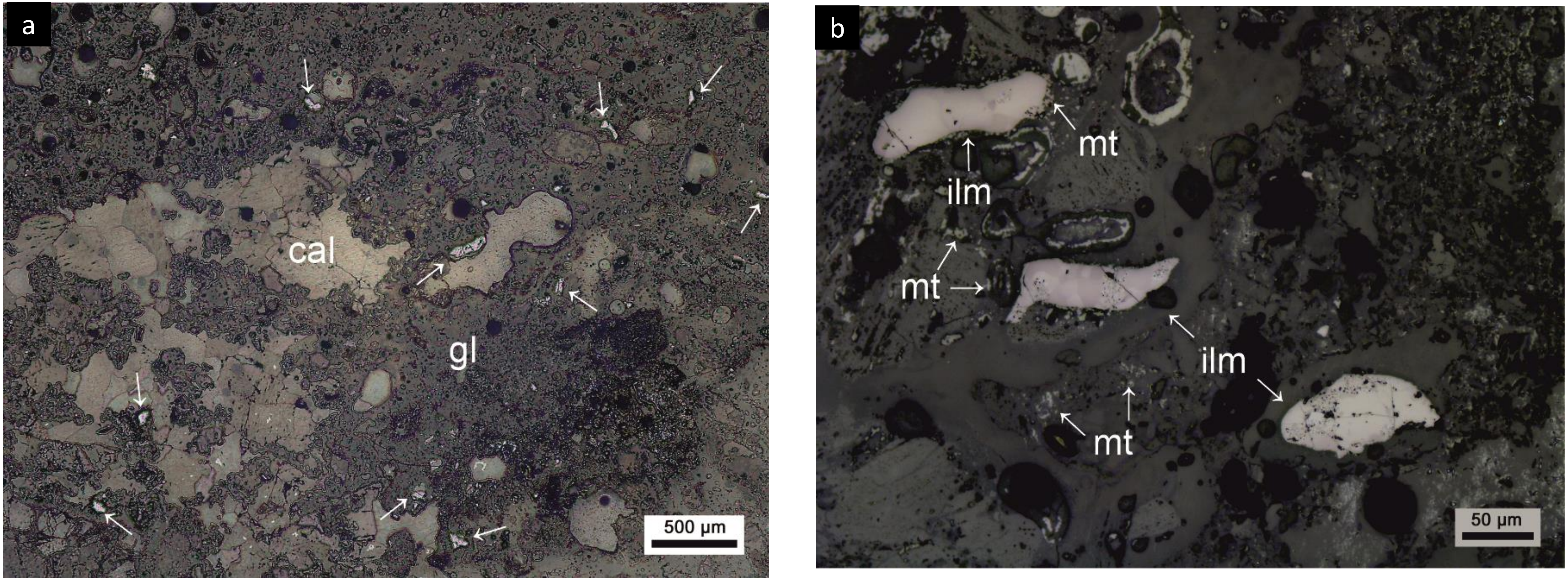
Sample location
Zipplingen (CT827a)
Aumühle (R2016A)

Scope
Investigation of ilmenites within:
Glass fragments (CT827a) and gneiss clasts (R2016A) within suevites to elucidate characteristic microfabrics for T, P, and fO_2 conditions



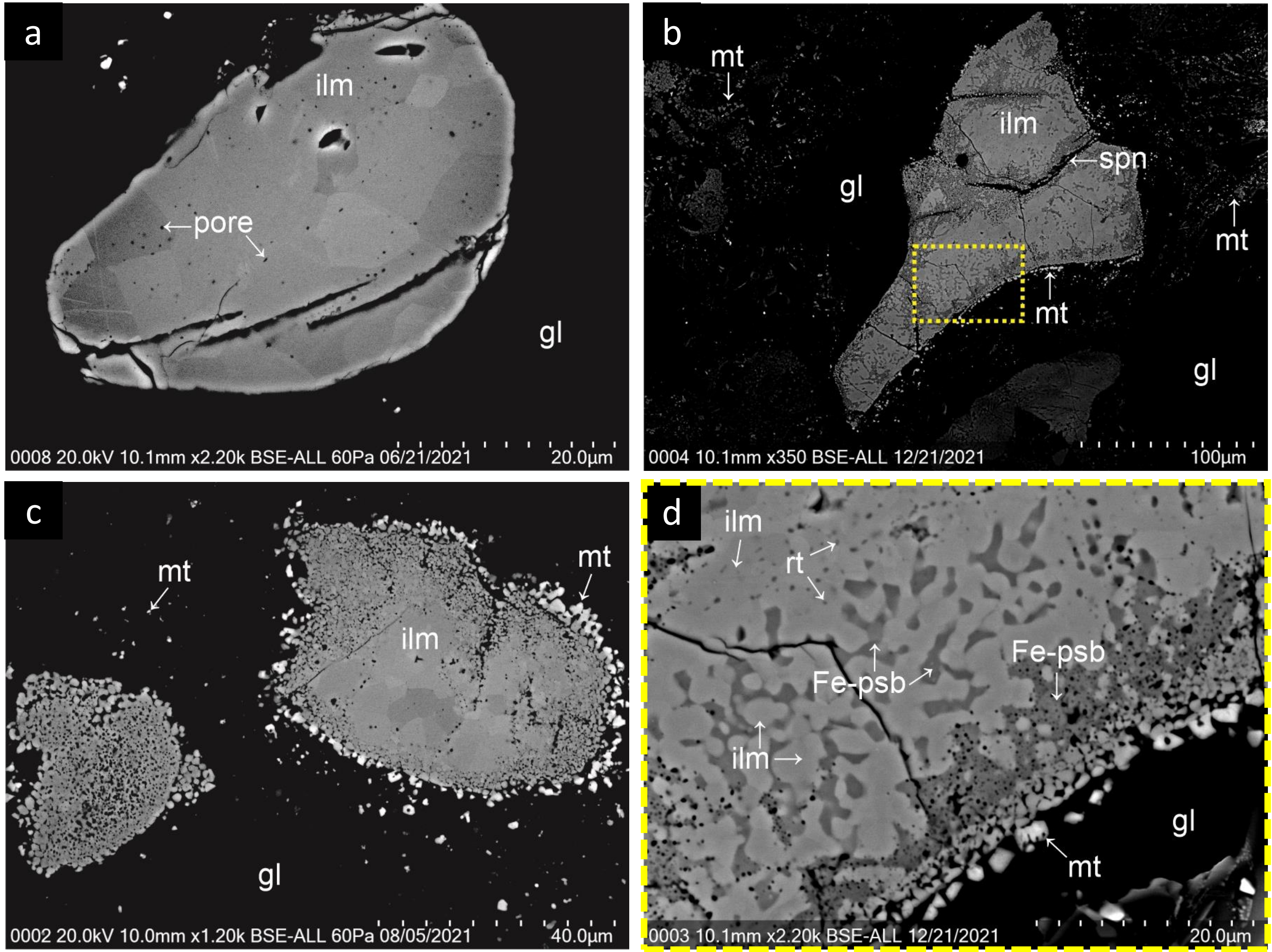
(Modified after Stöffler et al. 2013)

Suevite Zipplingen (sample CT827)



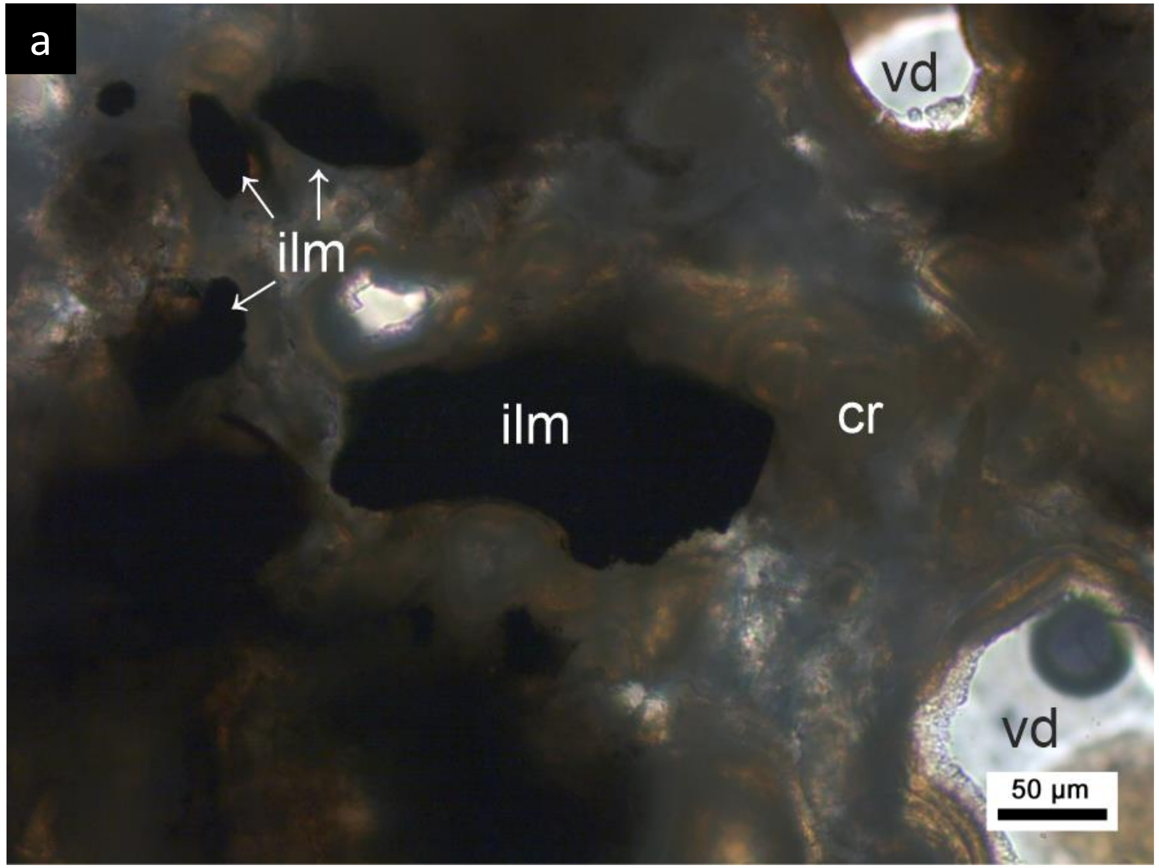
Reflected light micrographs showing the matrix representing mostly devitrified glass (gl, ca. 85%). Calcite (cal, ca. 15%) occurs as up to cm-sized aggregates. Ilmenite (ilm) grains, with diameters ranging from ten to up to few hundreds of µm, are homogeneously distributed in the matrix (white arrows) and cover less than 1% of the sample*)*. Ilmenite locally shows a rim of magnetite (mt). Within the matrix, close to the ilmenites, finely dispersed magnetite grains occur *(b)*.

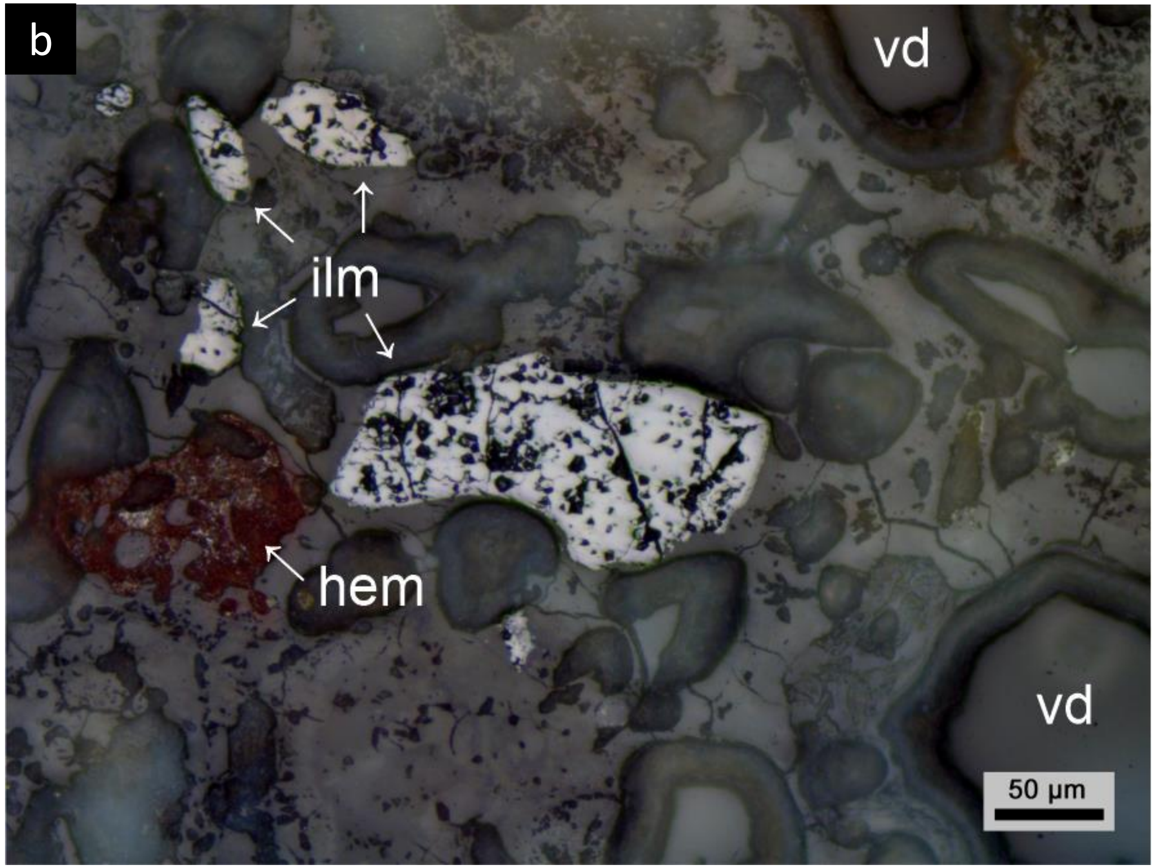
Ilmenite microfabrics, suevite Zippling (Sample CT827)



BSE images show ilmenite crystals with diameters ranging from ten to few hundreds of µm. The polycrystalline aggregates show a foam-structure, characterized by smoothly curved grain boundaries and 120° angles at triple junctions *(a)*. Fractures can be filled by sphene ($CaTi[O|SiO_4]$) (spn) *(b)*. Euhedral magnetite <2 µm in diameter occur within the matrix and at the aggregates rim *(c,d)*. Ferropseudobrookite ($FeTi_2O_5$) associated with a high porosity occurs at the aggregates boundary towards the glass matrix and along fractures *(b, d)*. The porosity correlates with the magnetite rim surrounding the aggregate at the contact to the matrix *(b)*. Further within the grain, a symplectitic zone of intergrown ferropseudo-brookite and ilmenite occurs. Rutile <0.5 µm in diameter is located at the grain boundaries within the polycrystalline ilmenite center of the aggregates *(d)*.

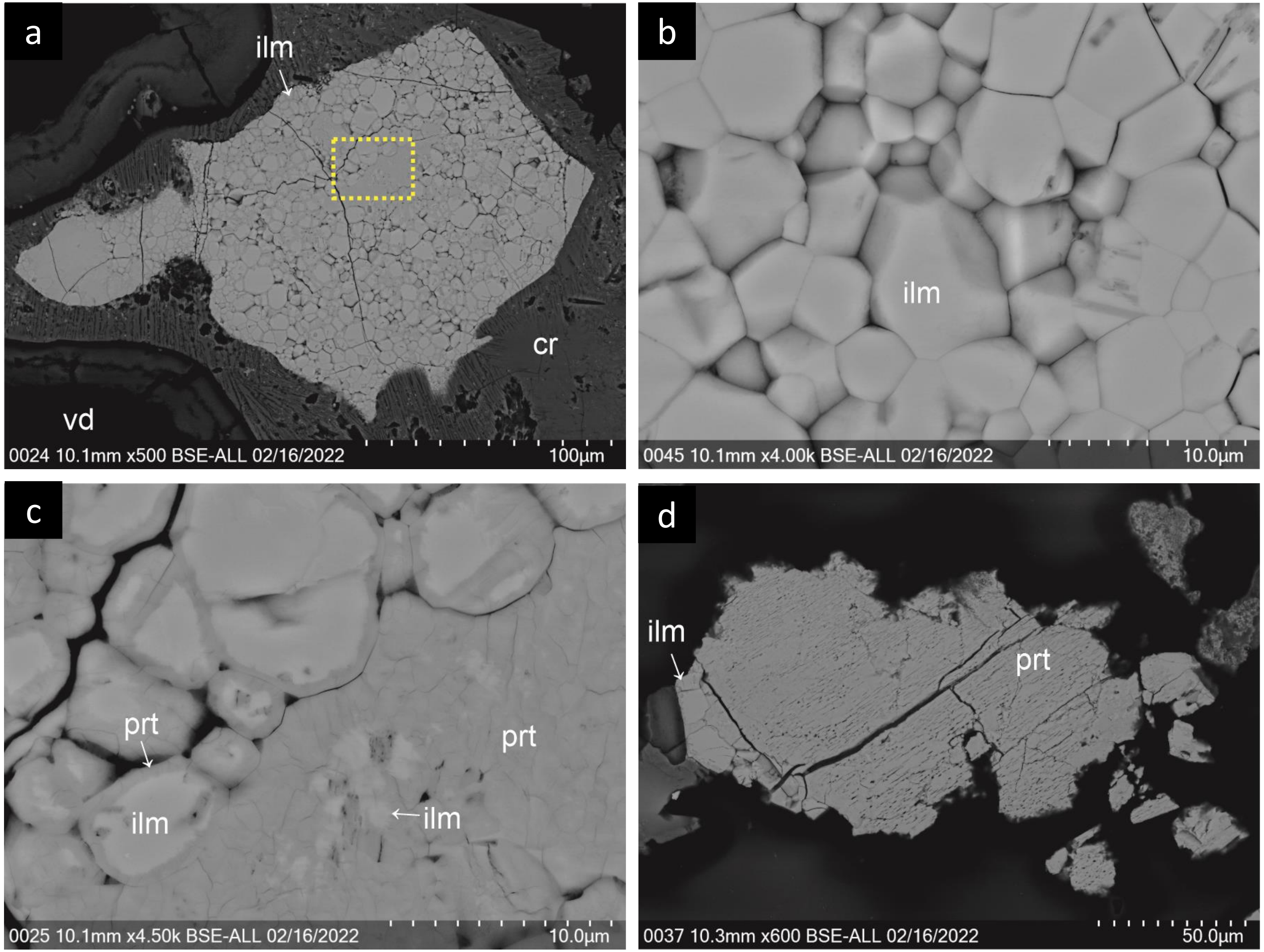
Gneiss clast in suevite, Aumühle (Sample R2016A)





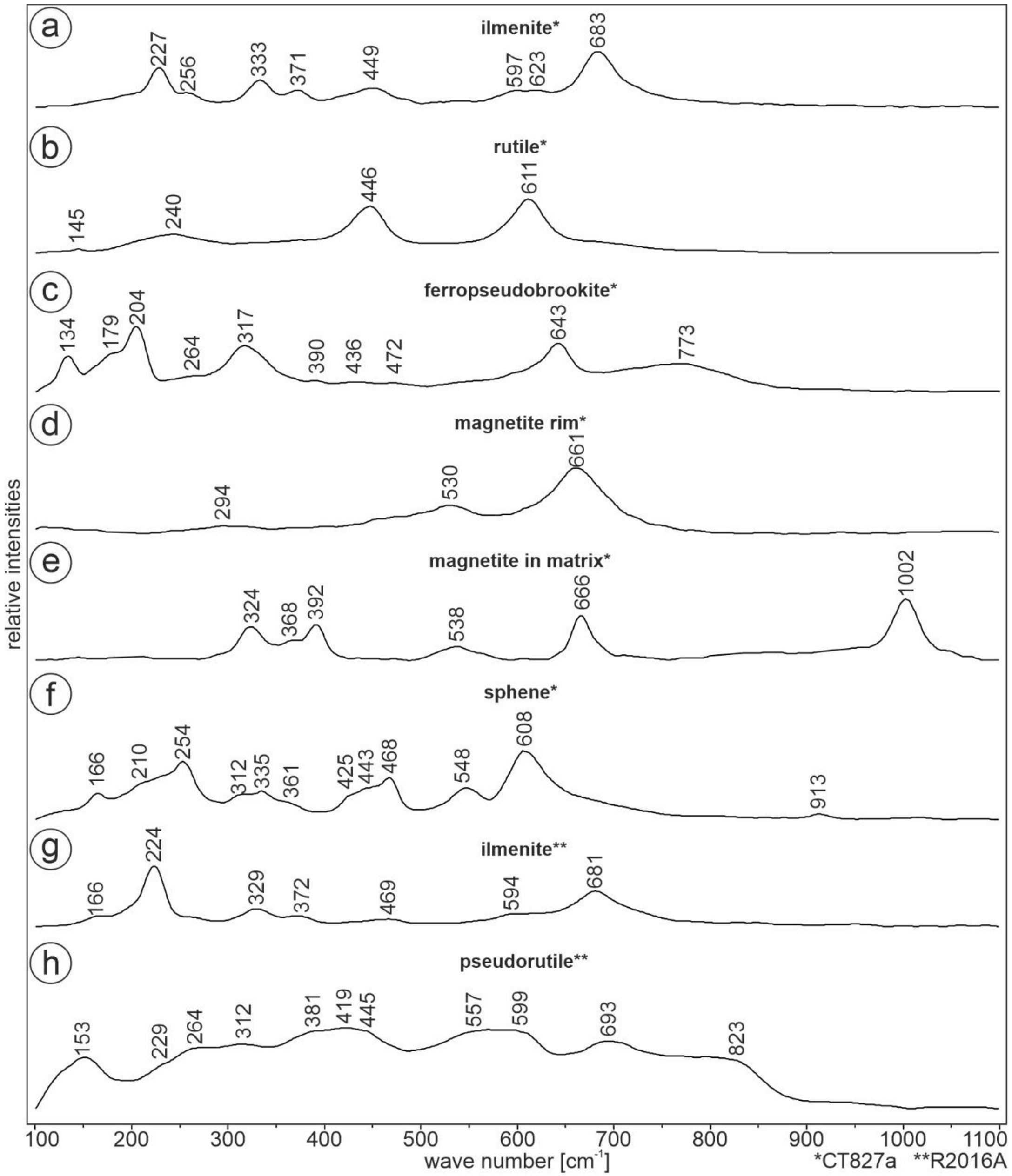
Reflected light micrographs from the gneiss clast within suevite close to the underlying bunte breccia, Aumühle quarry. The cryptocrystalline matrix (cr) with only few larger crystals show many voids (vd) *(a)*. Ilmenite (ilm) and secondary hematite (hem) occur homogeneously distributed with diameters ranging from ten to up to few hundreds of µm *(b)* in minor amounts.

Ilmenite microfabrics, gneiss clast in suevite, Aumühle



BSE images, sample R2016A: Ilmenite (ilm) (diameters 10-100s of µm) are distributed homogeneously throughout the void-rich cryptocrystalline to glassy matrix. Ilmenite displays a polycrystalline microfabric with foam structure *(a,b)* characterized of µm-size grains with four to six smoothly curved grain boundaries and 120° angles at triple junctions. Pseudorutile (prt) can occur as rim surrounding ilmenite or as larger crystals with some ilmenite remnants being present in the centre *(c)* or completley replacing ilmenite with elongated pores displaying a preferred orientation *(d)*.

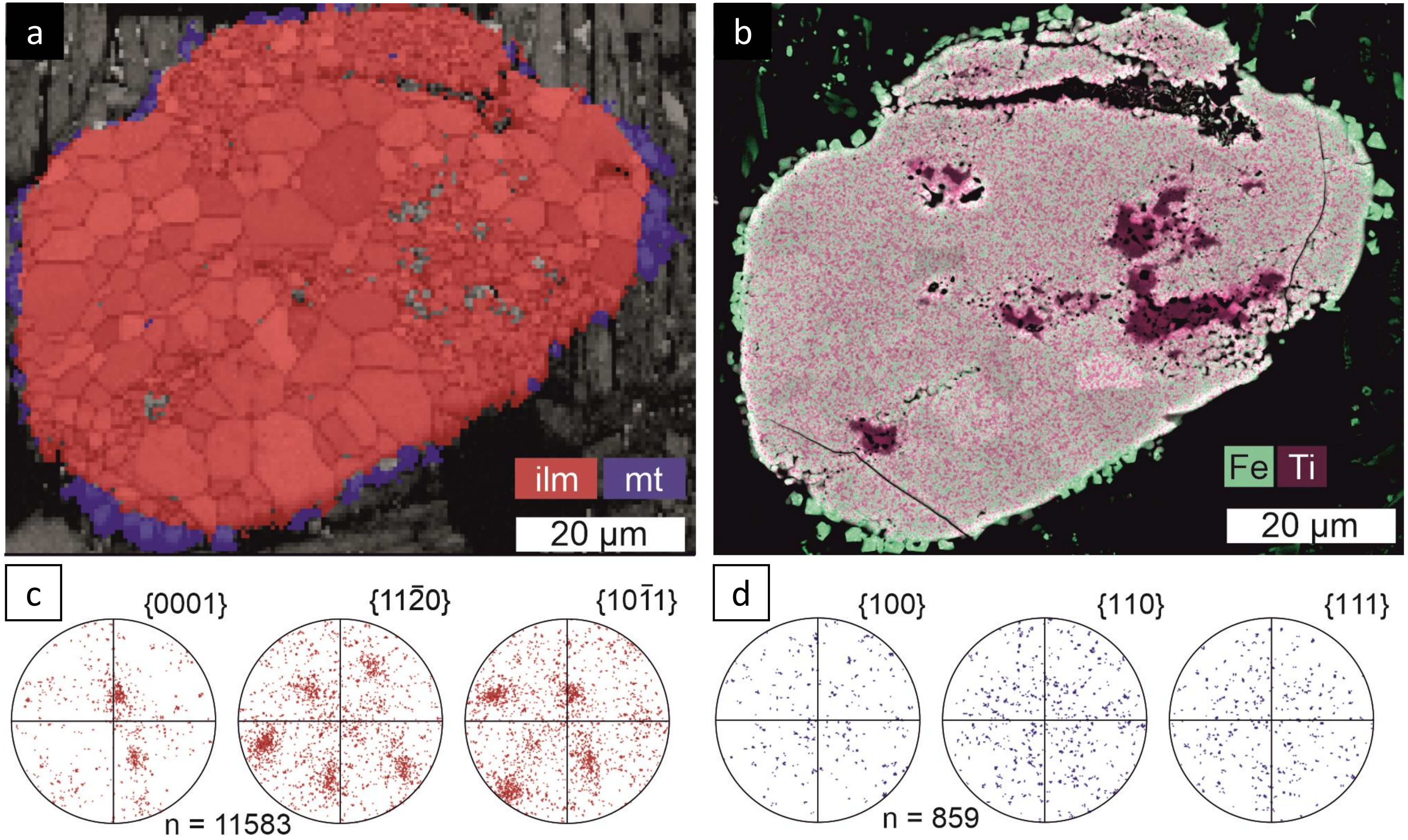
Phase Determination



The phases were determined using the ratios of Fe and Ti concentrations based on electron dispersive X-ray spectroscopy (EDS) in combination with reflected light microscopy, Raman spectroscopy *(a-h)*, and electron backscatter diffraction (EBSD).

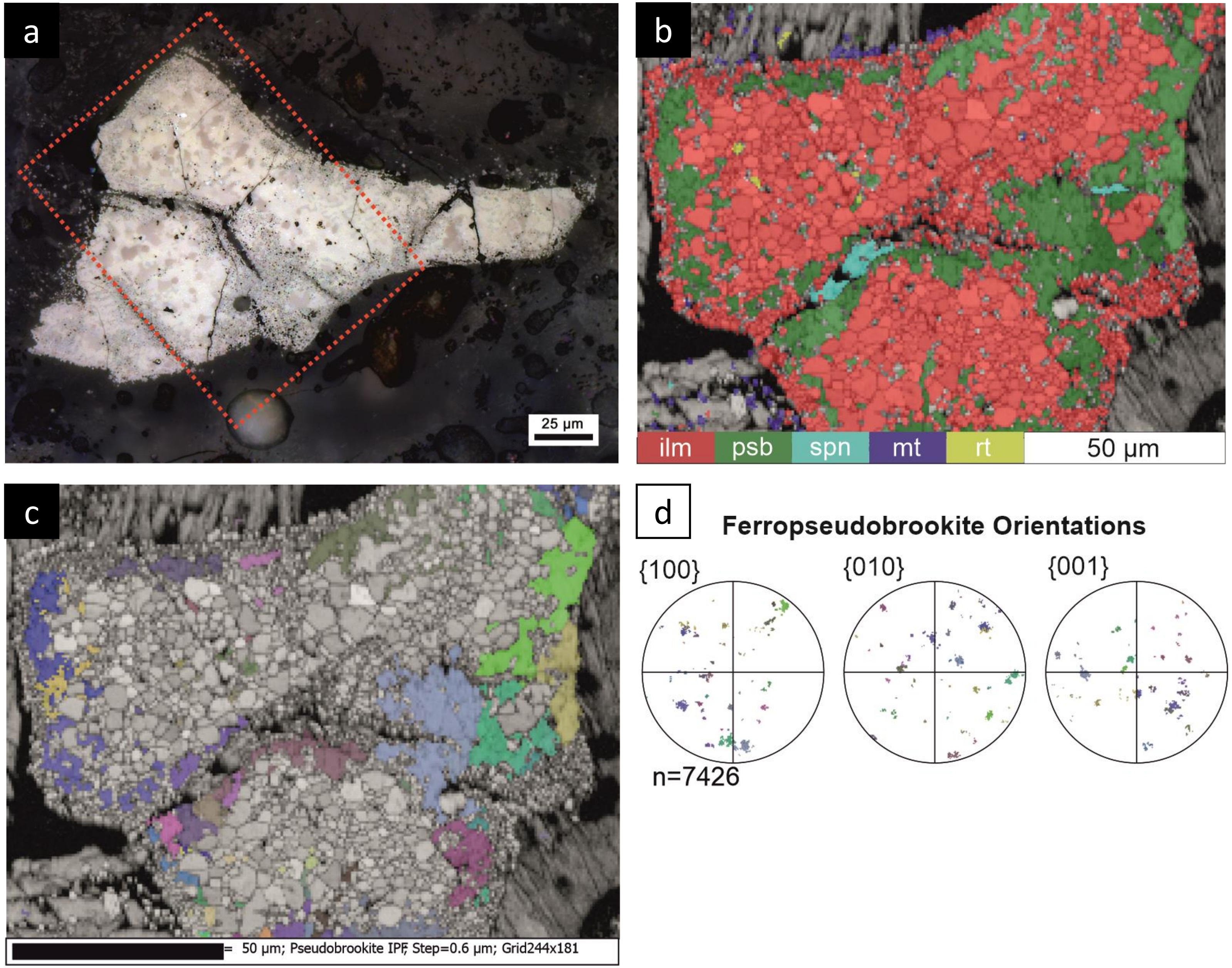
Phase	**Chemical Formula**	**Fe Valence state**	**Fe/Ti ratio**
ilmenite	$FeTiO_3$	2+	1
ferropseudobrookite	$FeTi_2O_5$	2+	0.5
Magnetite	Fe_3O_4	2+/3+	0.75
pseudorutile	$Fe_2Ti_3O_9$	3+	0.4
sphene/titanite	$CaTi[O\|SiO_4]$	-	-
Rutile	TiO_2	-	-

Ilmenite and Magnetite crystallographic orientations



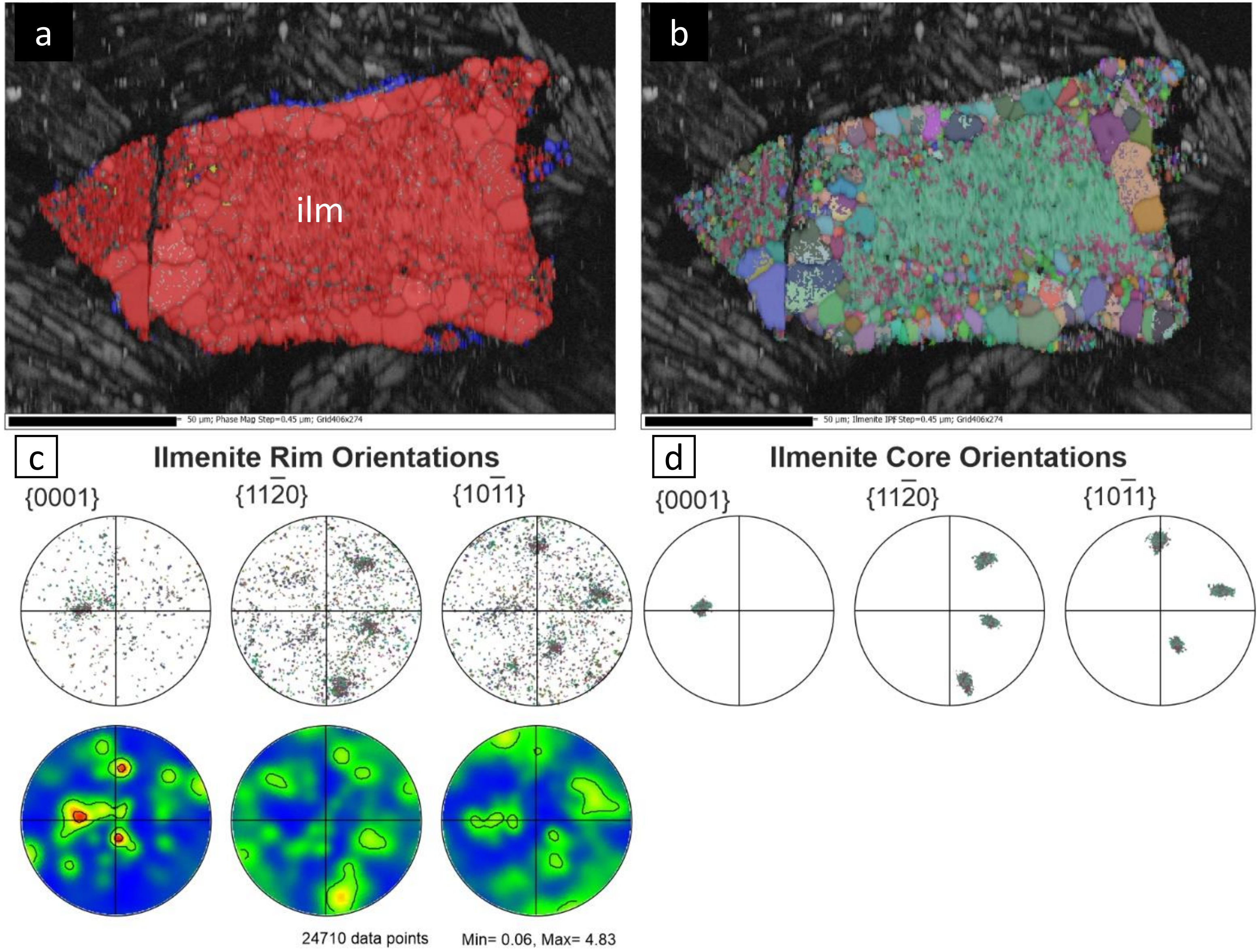
EBSD data of ilmenite aggregates (a) occur with areas of pure TiO_2 within the grain core (b). Euhedral µm-size magnetite grains are frequently located at the rim of the aggregates (a, b). Ilmenite grains show a weak crystallographic preferred orientation (c), whereas magnetite grains at the rim (a,b) display a random orientation (d).

Ilmenite and Ferropseudobrookite crystallographic Orientations



Within sample CT827a, polycrystalline ilmenite (ilm) occurs with ferropseudobrookite (psb), independent of the assemblage size, which can range from tens of µm to few hundreds of µm in diameter (a). Ferropseudobrookite occurs predominantly at the boundary of the aggregate to the glass matrix or along cracks (b), where also sphene (spn) can be identified. The ferropseudobrookite grains show irregular phase and grain boundaries with sizes of tens of µm (c) and a random orientation (d).

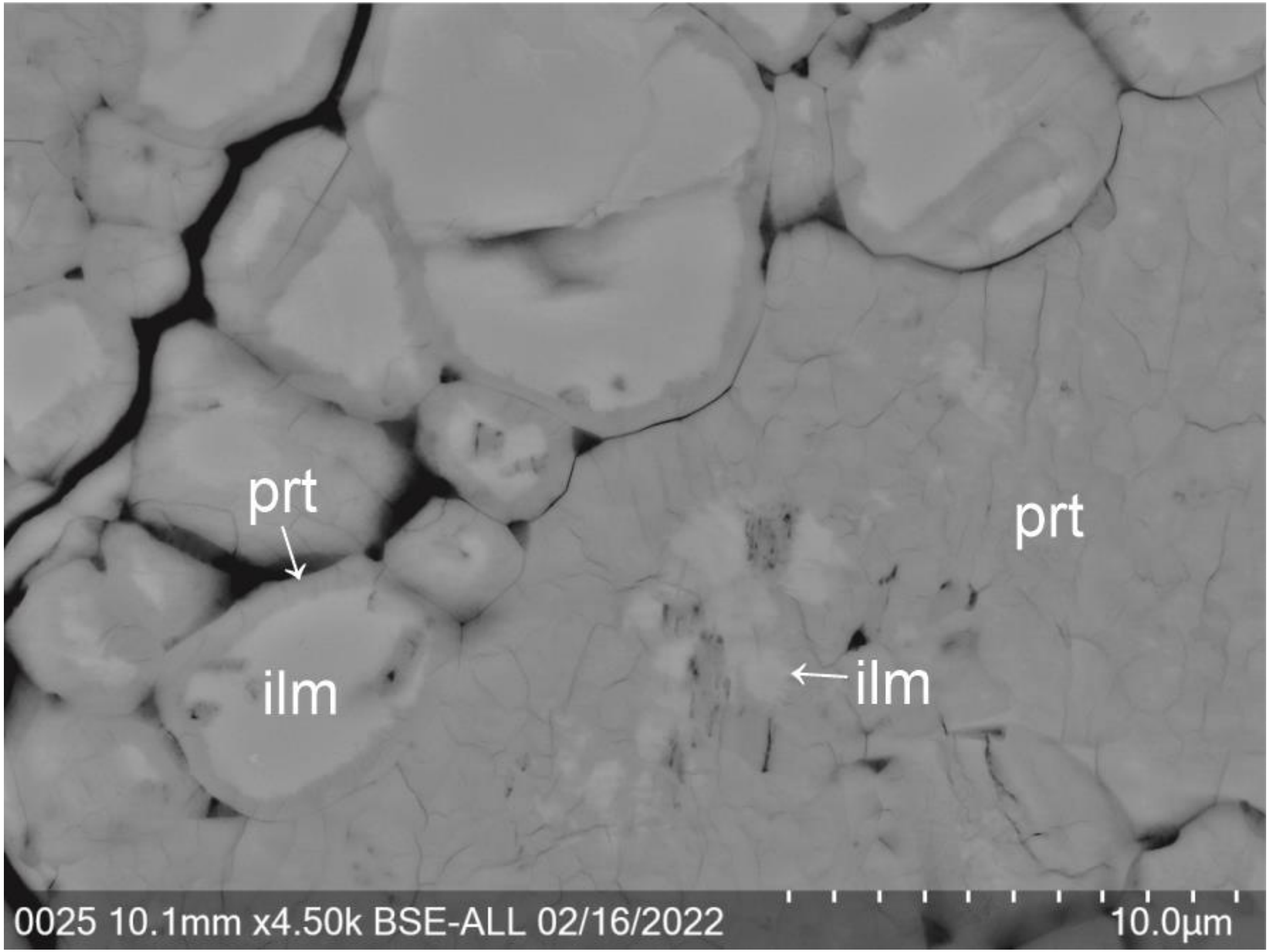
High Pressure Phase Transition of Ilmenite



EBSD data (sample CT827a) showing a rare case of a coarse ilmenite core surrounded by a poly-crystalline rim *(a,b)*. The rim grains display a weak crystallographic preferred orientation *(c)*, which is controlled by the orientation of the core orientation *(d)*. Whereas the coarse ilmenite shows an internal misorientation, the grain aggregate is showing a foam structure.

This foam structure is interpreted as the result of the transformation from a high pressure phase formed at >16 GPa (Leinenweber et al. 1991) upon shock compression during the subsequent decompression.

High Temperature Phase Transition of Ilmenite



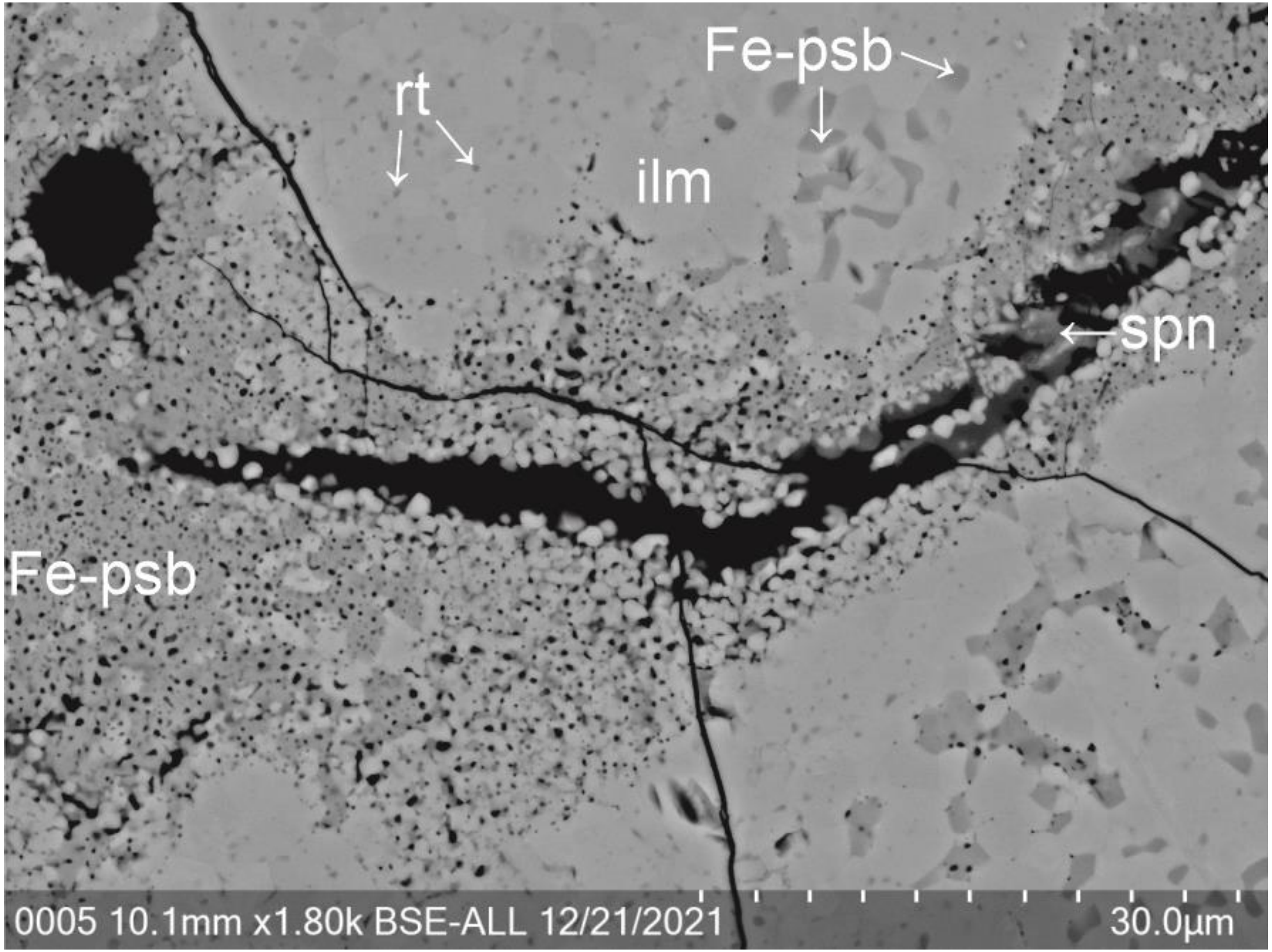
(Gupta et al. 1991; Mücke and Chaudhuri 1991)

BSE image (sample R2016A) of ilmenite aggregates with a foam structure, where grains are rimmed by pseudorutile, indicating the formation of pseudorutile after pressure release. The transformation from ilmenite to pseudorutile occurs with temperatures less than 700°C and a high oxygen fugacity to transfer Fe^{2+} to Fe^{3+}.

Pseudorutile formation:

$3FeTiO_3 \rightarrow Fe_2Ti_3O_9$ + leached Fe

High Temperature Phase Transition of Ilmenite cont'd



BSE image (sample CT827a), ferropseudobrookite predominantly occurs at the Fe-Ti-oxide aggregate boundary and along fractures displaying a high porosity. The formation requires temperatures >1140°C and a low oxygen fugacity. Further inward towards the aggregate core, often a symplectitic intergrowth of ilmenite and ferropseudobrookite can be observed, as well as small (<µm) rutile along ilmenite boundaries. The reaction of ilmenite to form ferropseudobrookite also generates FeO, which migrates to the aggregate rim, where a change in redox condition and an increase in the oxygen fugacity leads to the formation of magnetite.

Ferropseudobrookite formation:

$2FeTiO_3 \rightarrow FeO + FeTi_2O_5$

Magnetite formation:

$3FeO + ½O_2 \rightarrow Fe_3O_4$

(Lindsley 1965; El Goresy & Chao 1976)

Ilmenite transformations

Pre-Ries	Pressure ↑	Pressure ↓
Ilmenite	Ilmenite (perowskite) >16 GPa (Leinenweber et al. 1991)	Polycrystalline Ilmenite

Aumühle (R2016A)

Temperature ↑	Temperature ↓
Pseudorutile + Ilmenite	Pseudorutile + Ilmenite

Pseudorutile formation:

$3FeTiO_3 \rightarrow Fe_2Ti_3O_9$ + leached Fe

(Mücke & Chaudhuri 1991)

(Gupta et al. 1991)

fO_2 high

$T_{max} < 700°C$

Zipplingen (CT827a)

Temperature ↑	Temperature ↓
Ferropseudobrookite + FeO migration	Ferropseudobrookite + Ilmenite + Rutile

Ferropseudobrookite formation:

$2FeTiO_3 \rightarrow FeO + FeTi_2O_5$

Back reaction

$FeTi_2O_5 \rightarrow FeTiO_3 + TiO_2$

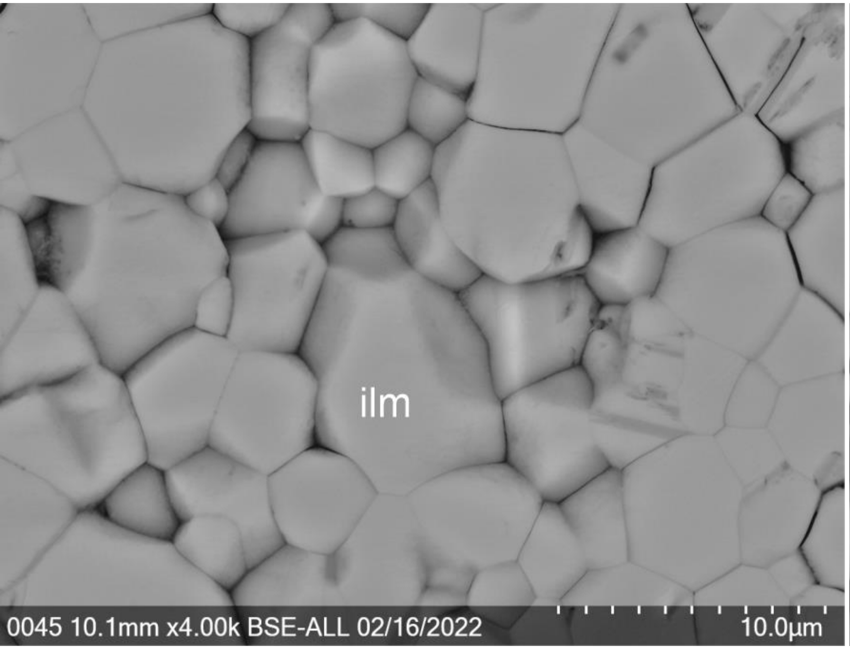
(Lindsley 1965; El Goresy & Chao 1976)

fO_2 low

$T_{max} > 1140°C$

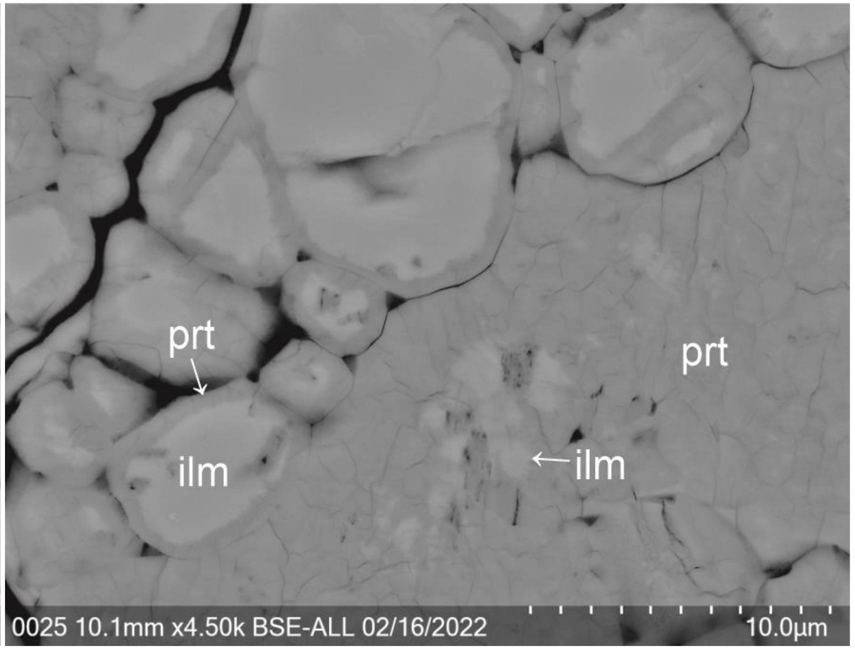
Summary

1. Foam-structure of ilmenite aggregate



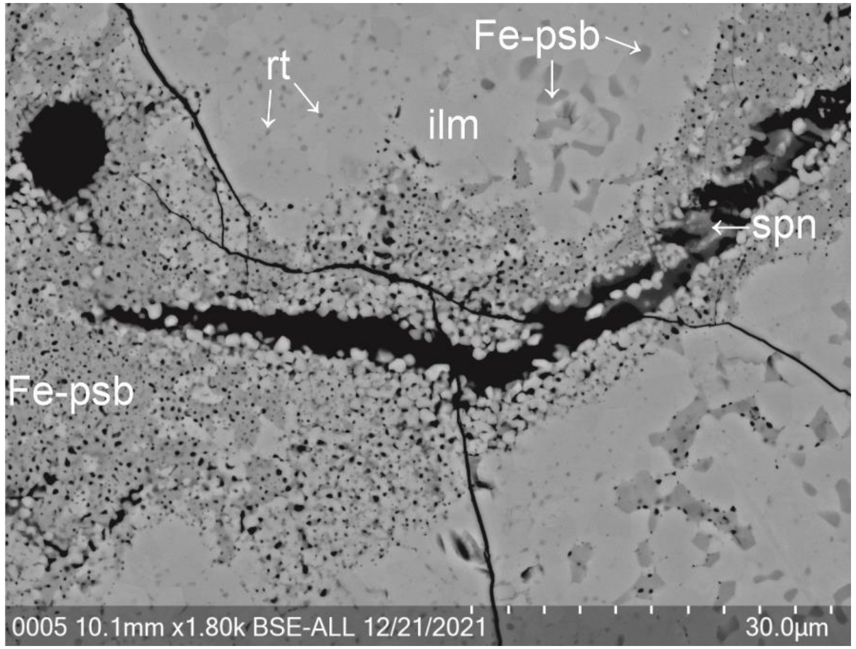
> 16 GPa

2. Pseudorutile surrounding ilmenite



T < 700°C and high fO_2

3. Ferropseudobrookite intergrowth



T > 1140°C and low fO_2

Ilmenite from shocked basement rocks provides a high potential to record HP-HT shock conditions by specific microstructures

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