Experimental synthesis of $ThSiO_4$ by fluid-induced alteration of chevkinite-(Ce)

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Experiments – hydrothermal lab

Experimental work has been carried out in the GeoForschungsZentrum Potsdam Hydrothermal laboratory

Hydrothermal line – cold seal autoclaves: 300-750°C; 100-500 MPa.

Noble metal tubing; laboratory facilities for the loading and sealing of noble metal capsules. Max. thermal gradient along the length of capsule is approx. 5°C. Accuracy of temp. ±3°C




Why chevkinite group minerals (CGM) have been selected as the main subject of experiments?

Chevkinite-group minerals:

- Often contain considerable amounts of REE (>50 wt.%) and other trace elements (Zr, Y, Nb, Sr, Cr)
- Total of 56 elements have been recorded in CGM, in amounts ranging from parts per million to tens of weight percent.There is, therefore, considerable compositional diversity, resulting in many substitution schemes and structural varieties.
- Can be a strong concentrator of such elements as Ga, Ge, Sb
- The considerable amounts of Th help to calculate time of mineral crystallization (i.e. Vazquez et al.. 2010)

- The frequency of occurrence of CGM is underappreciated because:
  - It is easy to confuse with other accessory phases
  - It is usually small (under 50 μm)
  - With our colleagues, we are showing that CGM are in fact widespread over an extensive range of igneous and metamorphic rocks and hydrothermal and ore deposits (over 20 papers published so far)

Some geochemical effects of CGM crystallization

- CGM strongly fractionate REE
  - The fractionation is very variable.
    - We have to determine how much of the variability is related to the nature of the coexisting accessory phases (e.g. in the U.K. Palaeogene granites CGM coexist with various combinations of REE rich epidotes, monazite, zircon, britholite and fergusonite), and by the composition of the fluids
    - In some rocks CGM are the dominant accessory and must therefore have the greatest effect on REE distribution
- CGM strongly fractionate Th from U.
  - The Th/U wt. ratio in CGM can exceed 100 (the typical mantle and crustal ratios are 3.5 to 4)
- CGM also fractionate Zr from Hf and Nb from Ta

Experimental details

24 different combinations

Main load
Chevkinite-(Ce)

Other components added (in proportions to vary the alkalinity)
Quartz, Albite, Apatite, Bytownite, An glass, Calcite, K feldspar, $Ca_3(PO_4)_2$

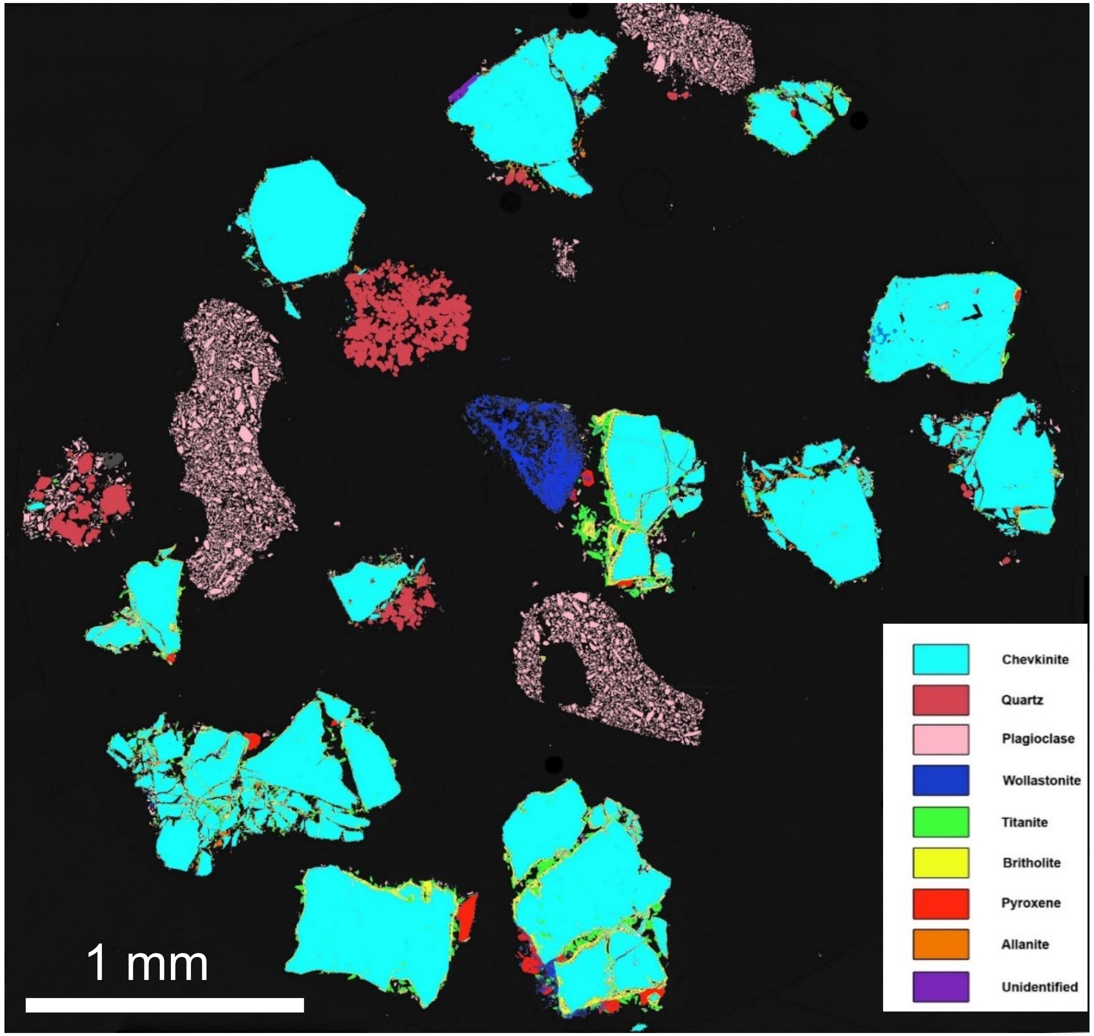
Hydrous fluid
$Ca(OH)_2$
Na(OH)
NaF
CaF_2

Temperature
500-600°C

Pressure
200 MPa

Time
from 21 to 84 days

BSE picture of the sample after the experiment



Mineral phases shown in artificial colours on the basis of the EDX hyperscan results

Chevkinite-(Ce) + $Ca(OH)_2$ + Quartz + Albite + H_2O →

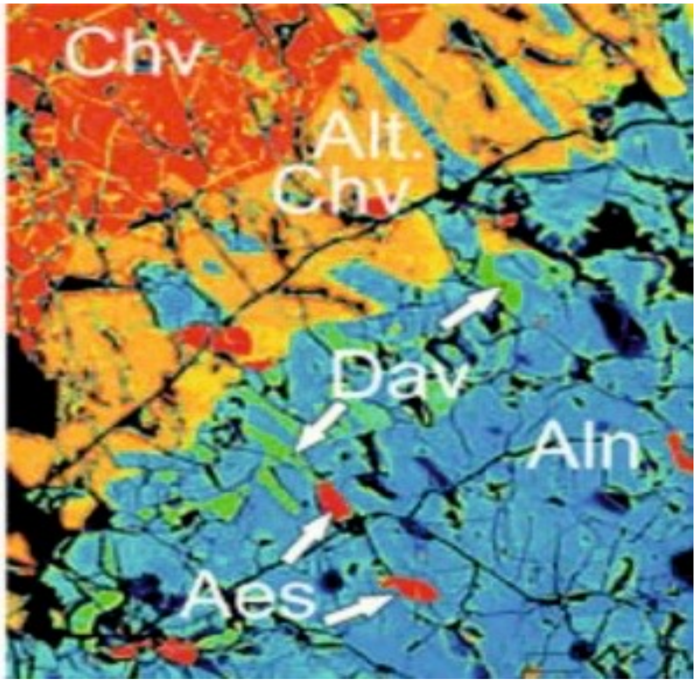
Britholite-(Ce) + **Titanite** + Pyroxene (Hedenbergite) + Wollastonite + Allanite-(Ce)

Alteration reactions

Our aim

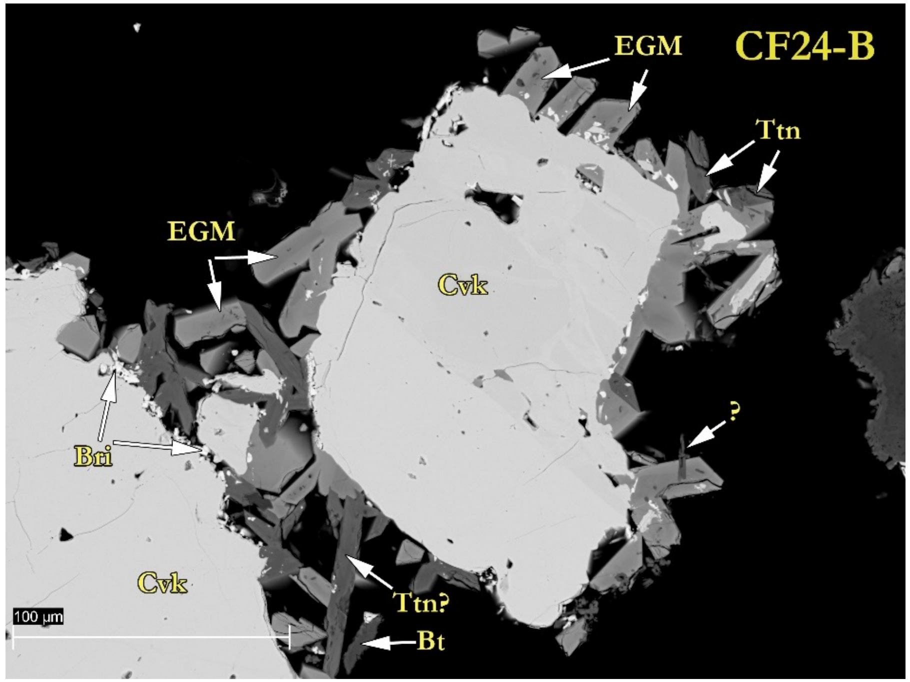
To synthesize the products of alteration close to what we observe in the nature

nature (metasomatite, Keivy)



BSE- false colour picture of altered chevkinite in metasomatite from Keivy Massif. Chv-chevkinite-(Ce), Aln-allanite, Aes- aeshinite-(Y), Dav – davidite-(La)

experiment



BSE picture of altered chevkinite, experiment CF 24. Cvk-chevkinite-(Ce), EGM – epidote group mineral, Ttn – titanite, Bri – britholite-(Ce), Bt - biotite

Chevkinite-(Ce) used in the experiment

Pristine crystal coming from pegmatite from Diamer district, Pakistan

It shows homogenous composition of most elements, except Th whose contents vary from 1.0 to 2.9 wt. % ThO_2

Specimen of chevkinite from from Diamer district, Pakistan

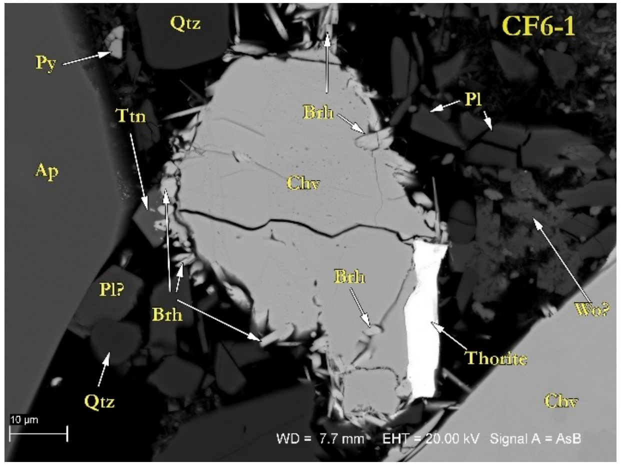
Details of experiments where $ThSiO_4$ was synthesized

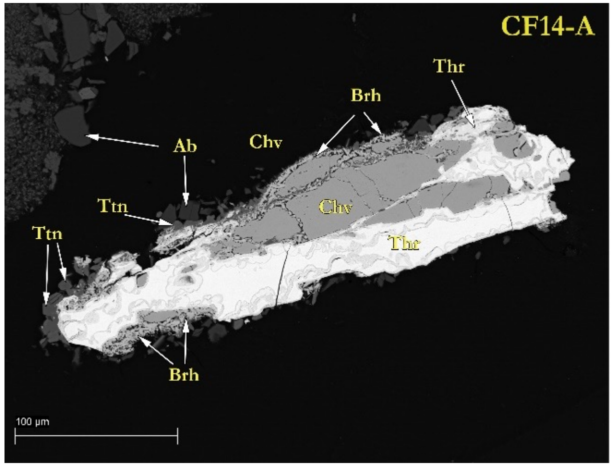
chevkinite, quartz, albite – always present in the load

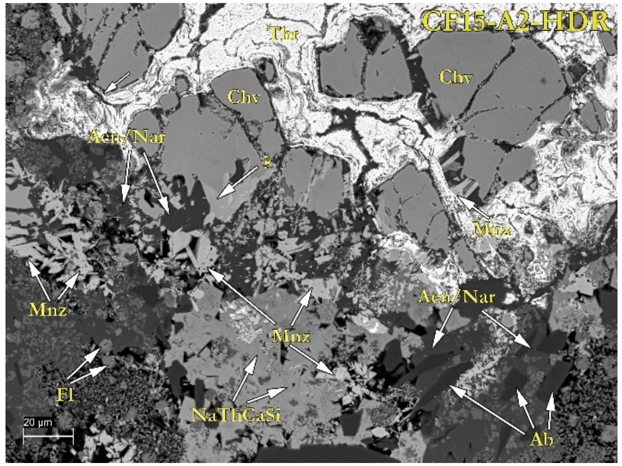
experiment	added components	conditions	fluid
CF 6 –	bytownite, fluorapatite, FeS_2, $CaCO_3$	200MPa, 600°C, 26 days	$Ca(OH)_2$
CF 14 -	**-**	**200MPa, 550°C, 84 days**	**$Ca(OH)_2$**
CF 15 -	**$Ca_3(PO4)_2$**	**200MPa, 550°C, 84 days**	**NaF**
CF 18 -	Al_2O_3	200MPa, 600°C, 42 days	$Ca(OH)_2$
CF 23 -	An glass, K felds., FeO, $Mg(OH)_2$	200MPa, 600°C, 32 days	$Ca(OH)_2$ + CaF_2
CF 24 -	bytownite, K felds., FeO, $MgOH)_2$	200MPa, 600°C, 32 days	$Ca(OH)_2$ + CaF_2

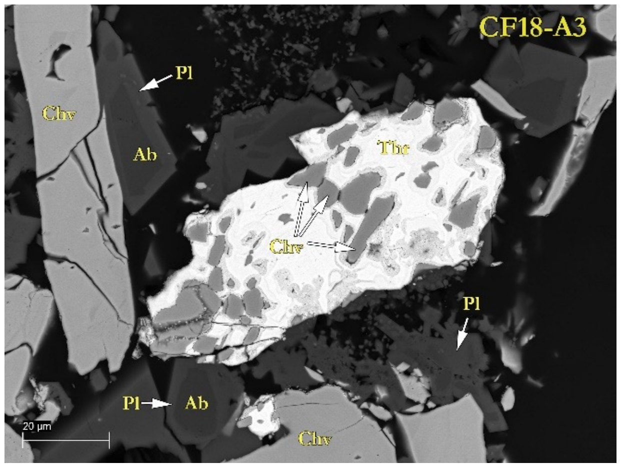
$ThSiO_4$ case

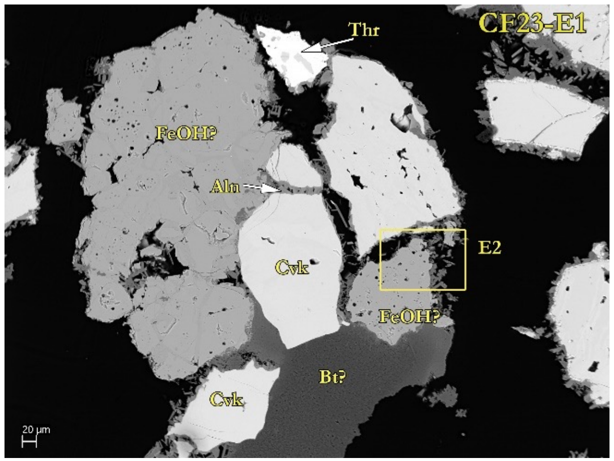
As a result in several of 24 experiments $ThSiO_4$ as a separate phase has appeared

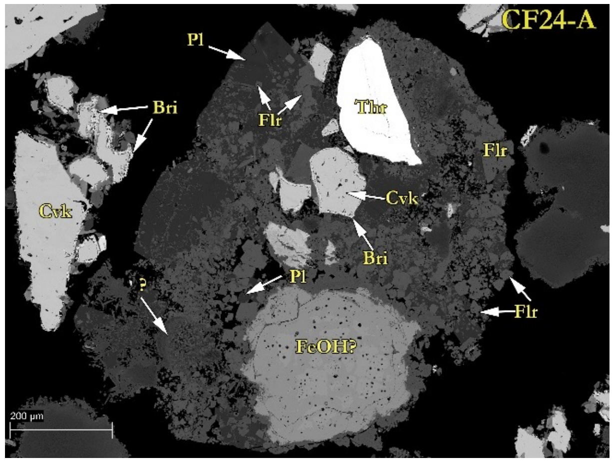




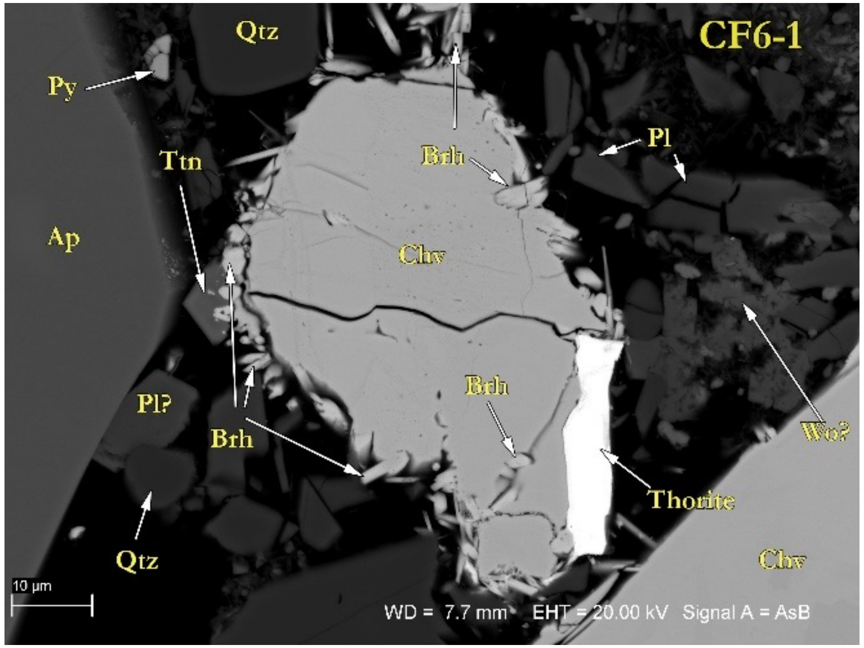


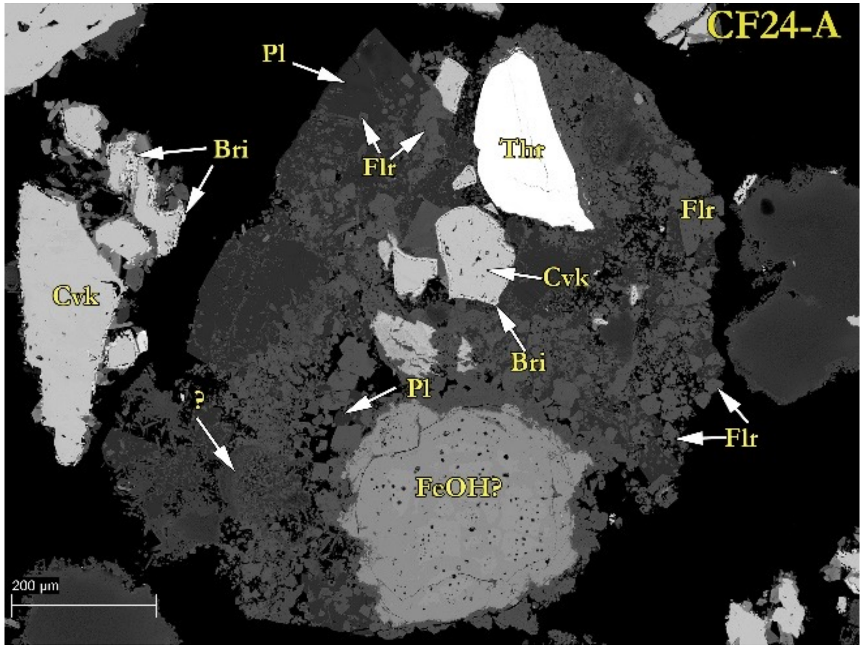






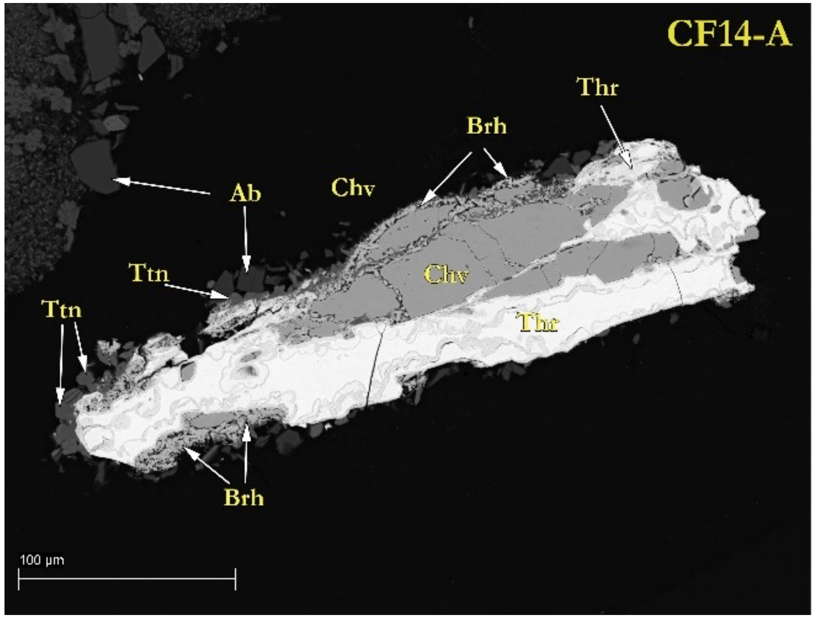
Textural features

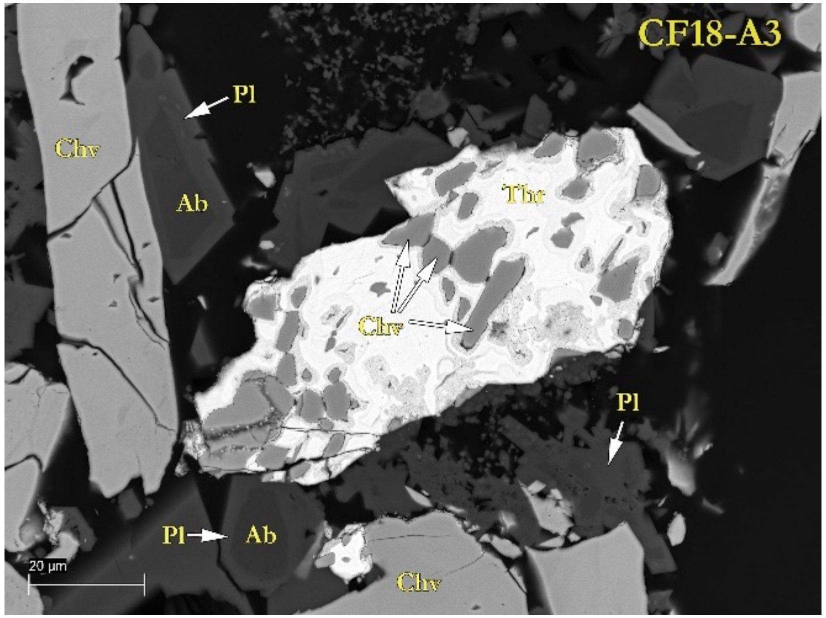


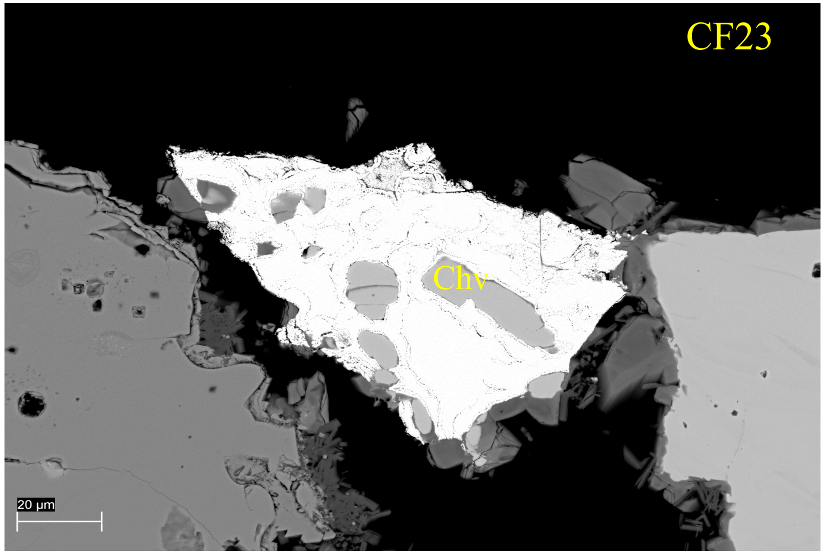


Solid, uniform $ThSiO_4$ not showing any obvious variation in texture. Position of the phase is variable (bordering chevkinite or isolated)

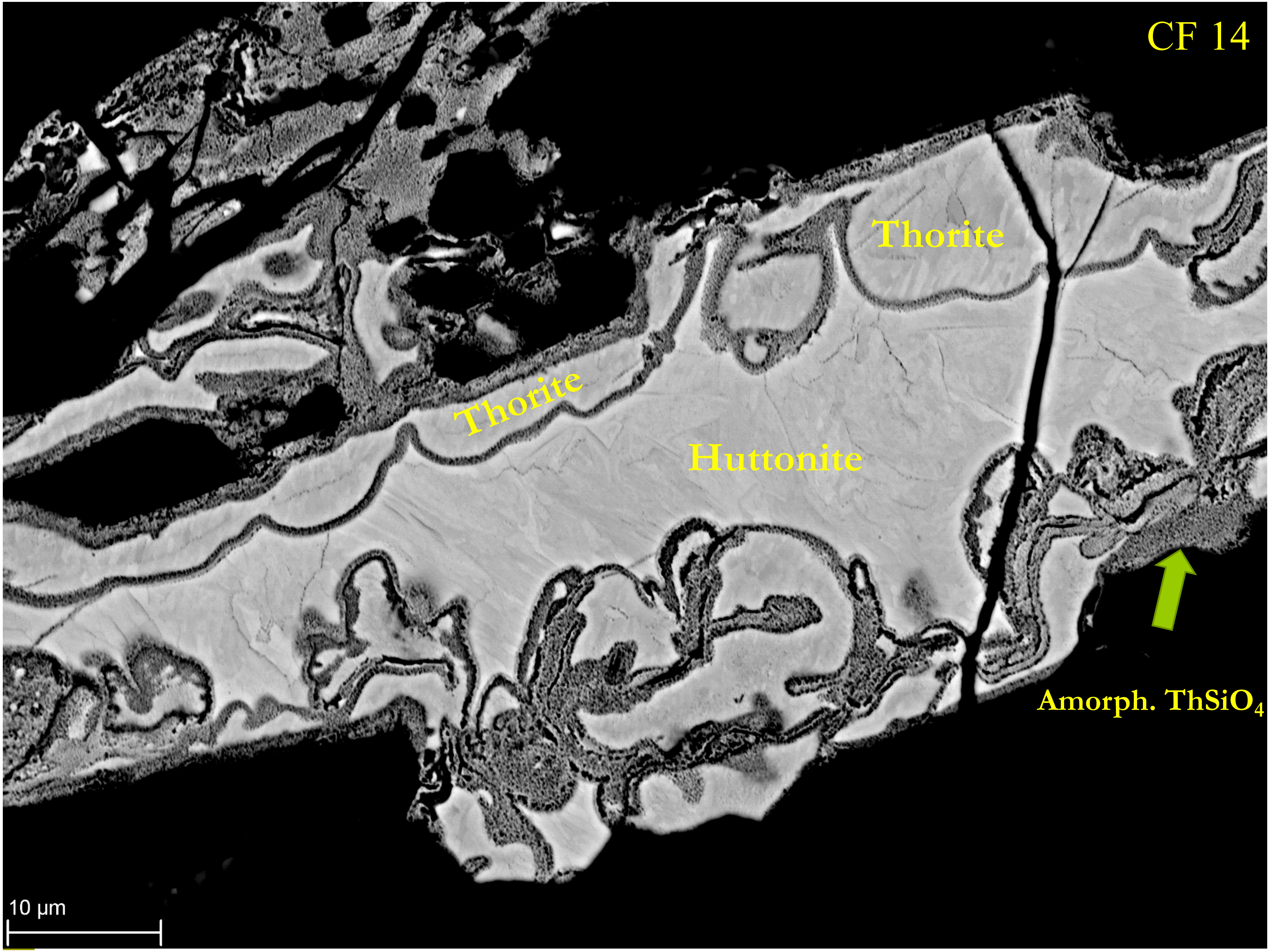
Textural features





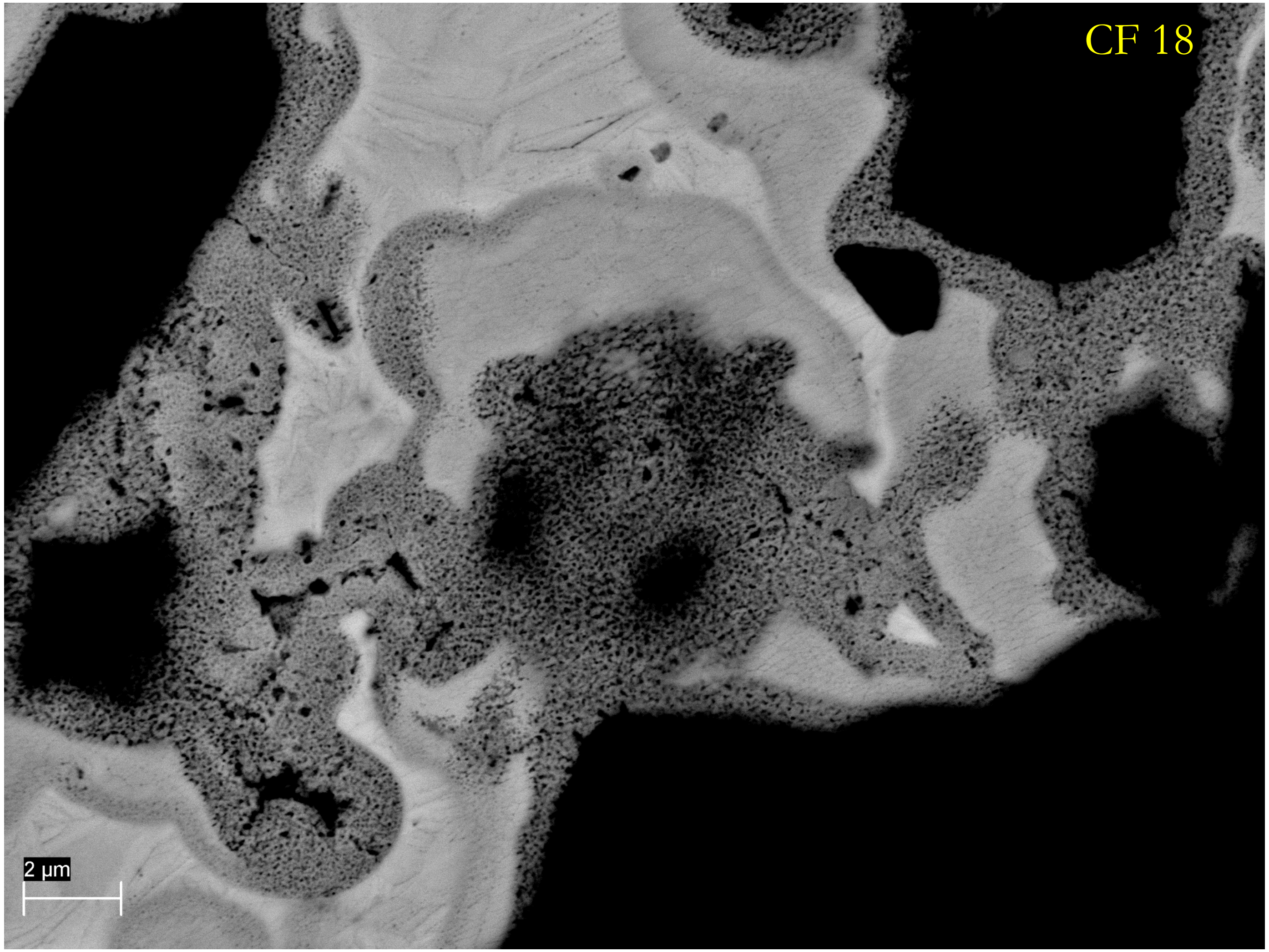


Fairly big $ThSiO_4$ replacing chevkinite.
„Islands” of chevkinite display the same orientation
3 different $ThSiO_4$ phases are present. We can observe
Progressive “swamping” of chevkinite


CF 14
Thorite
Thorite
Huttonite
Amorph. ThSiO4
10 µm

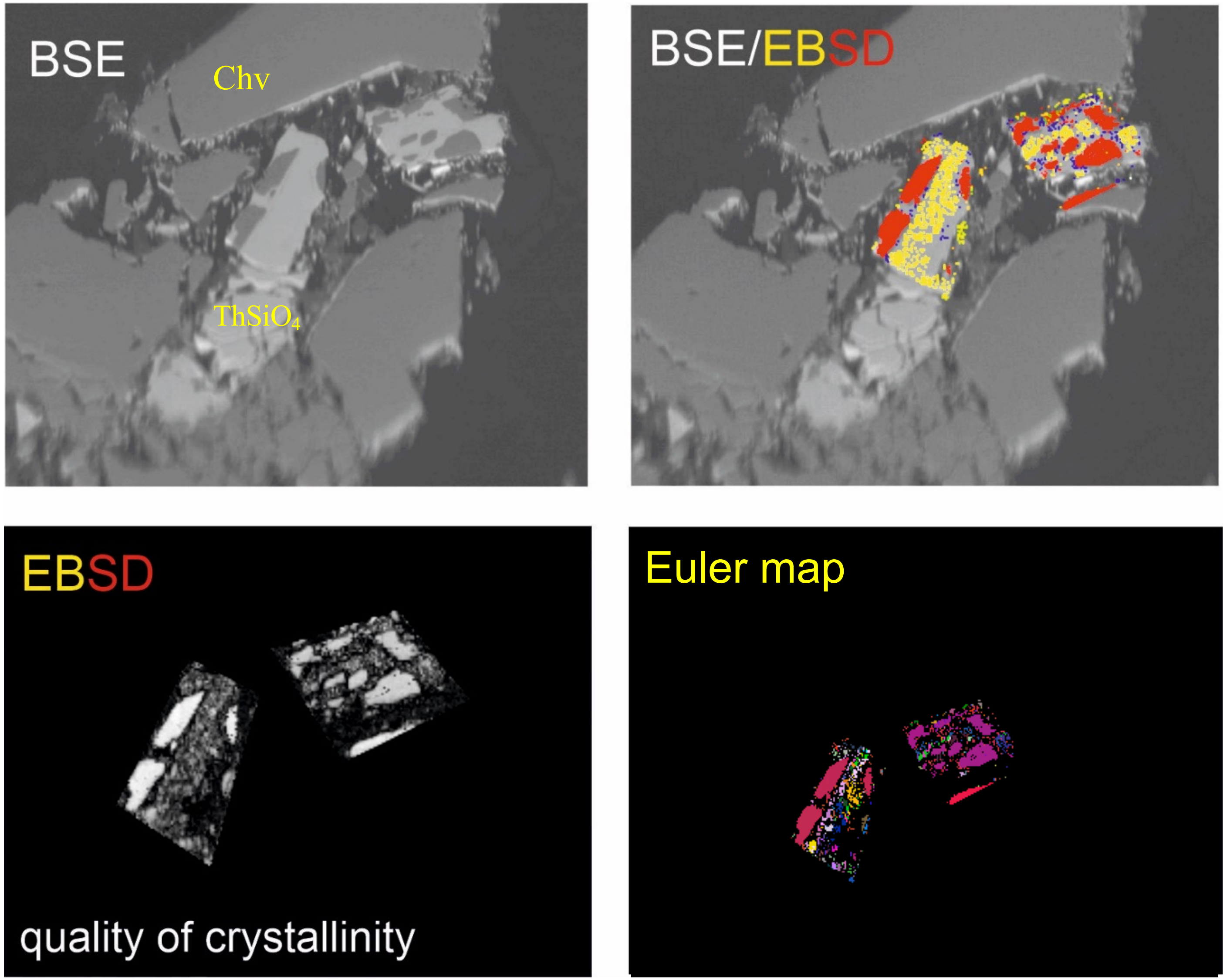
Nano-bubbles formation due to accumulation of helium

(Ewing *et al.*, 2000, Seydoux-Guillaume *et al.*, 2007)



Helium is a product of Th and U disintegration.
It is has been suggested (Seydoux-Guillaume et al., 2007) that $ThSiO_4$ is composed of an amorphous matrix with He-bubbles inclusions. Due to the very high amount of helium produced during α-decay of U and Th in $ThSiO_4$, and due to the amorphous state of this phase, helium is not incorporated in the $ThSiO_4$ phase but is segregated into bubbles, because of the presence of cracks and due to the amorphous structure of $ThSiO_4$, it is improbable that helium accumulates within the $ThSiO_4$ inclusion but diffuses out of this phase and out the sample.

Crystallinity and orientation of $ThSiO_4$

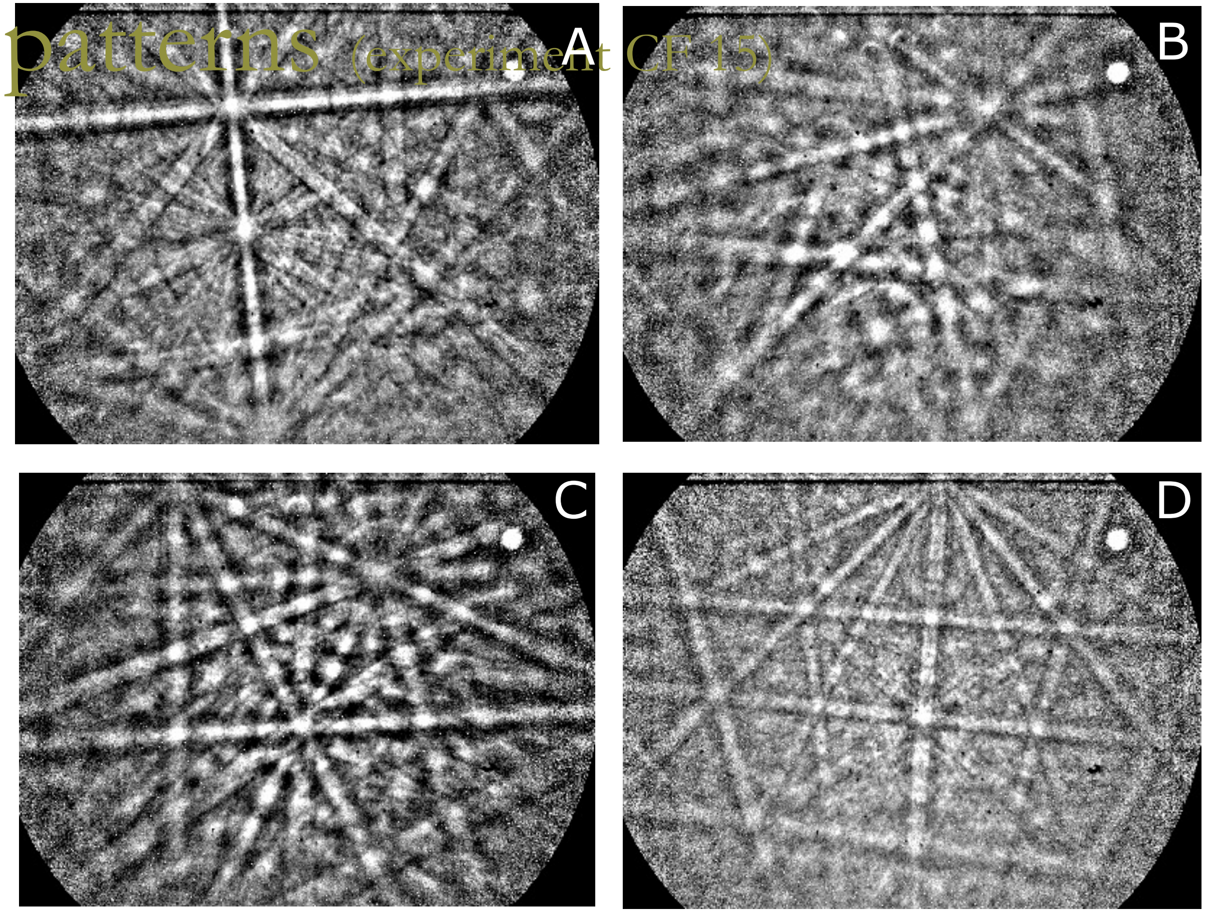


Experiment CF 14
an example

- huttonite
- chevkinite
- thorite

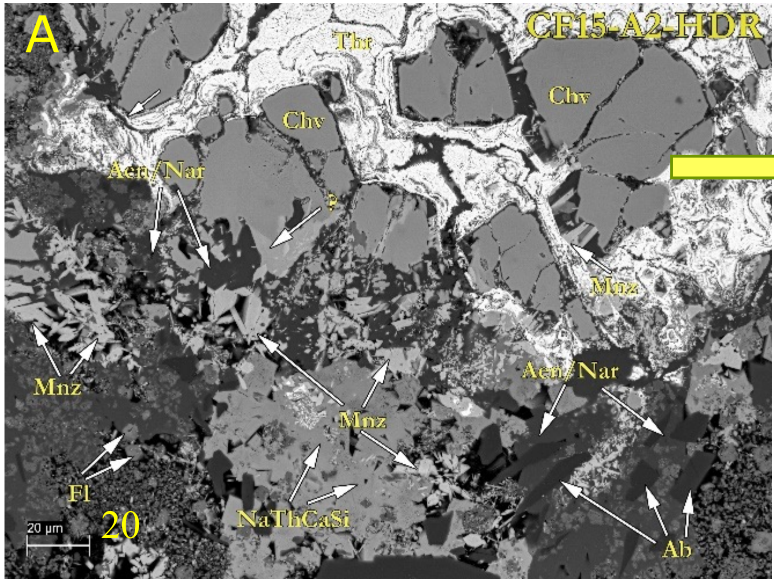
Experimental electron backscatter diffraction (EBSD) patterns

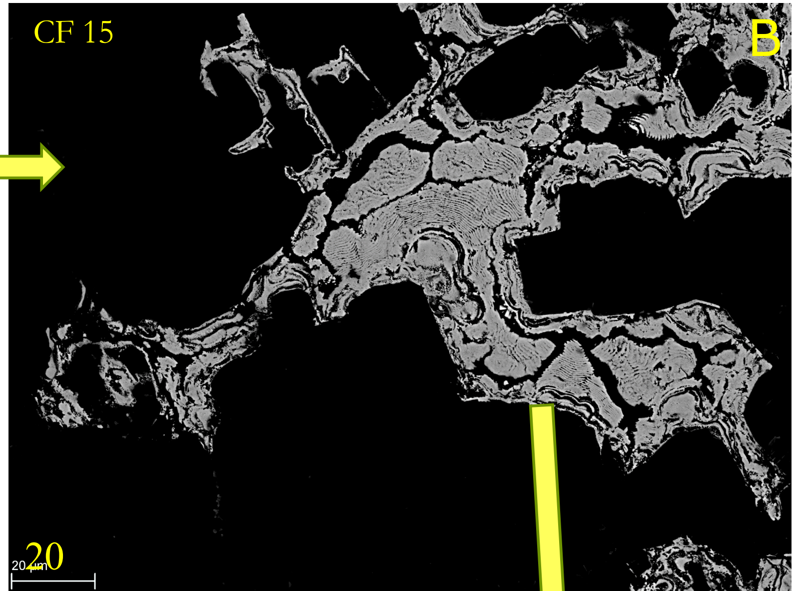
patterns (experiment CF 15)

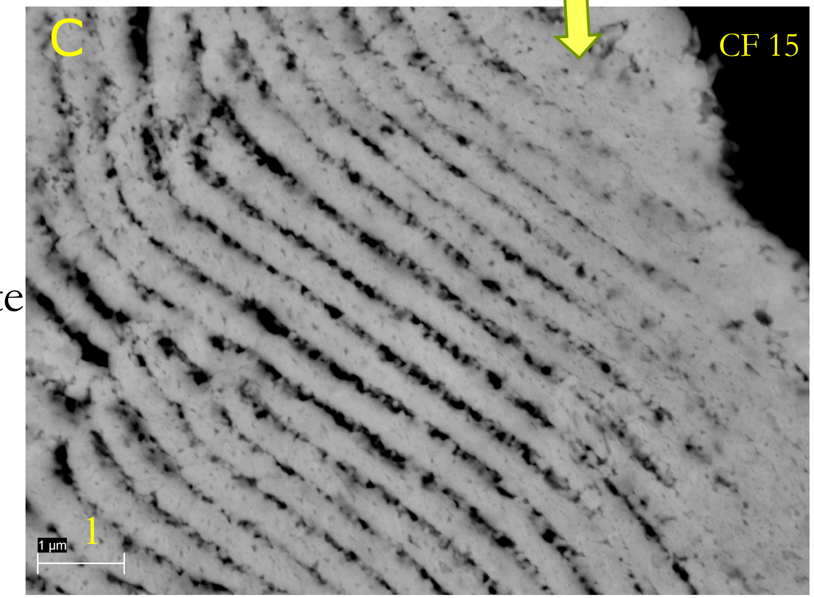


A – chevkinite-(Ce)
B - thorite
C - huttonite
D - turkestanite

Textural features







Vein-like body (A) of amorphous $ThSiO_4$ partially replacing chevkinite. Blocky structure present in central area (B). In detail laminar structure of $ThSiO_4$ (C). Black streaks are narsarsukite and turkestanite

Microchemical characteristics

	huttonite			thorite			amorphic?	amorphic?	amorphic?	Thr?	Thr?	Thr?
Sample	CF14-Th-5	CF14-Th-6	CF14-Th-8	CF14-Th-25	CF14-Th-26	CF14-Th-34	CF15-Th-12	CF15-Th-13	CF15-Th-19	CF15-Th-14	CF15-Th-16	CF15-Th-17
P_2O_5	0,07	0,1	0,07	bdl	0,04	0,06	**1,47**	**1,9**	**0,71**	0,27	0,3	0,58
SiO_2	18,43	18,55	18,88	18,42	18,38	17,5	17,77	17,83	18,16	18,56	18,54	18,3
ThO_2	74,67	74,58	75,05	75,15	75,73	74,08	69,74	70,98	72,47	73,54	73,74	72,96
UO_2	4,67	4,24	4,39	3,89	4,15	3,91	3,92	3,7	4,06	4,51	4,62	3,72
Sc_2O_3	0,03	0,04	0,04	0,03	0,04	0,04	0,03	0,04	0,04	0,04	0,04	0,04
Y_2O_3	bdl	0,19	0,11	0,15	0,13	0,19	0,09	0,11	bdl	0,17	bdl	bdl
La_2O_3	bdl	0,22	bdl	bdl	bdl	bdl	**0,93**	**0,96**	**0,42**	bdl	bdl	0,35
Ce_2O_3	0,23	0,65	0,23	bdl	0,22	bdl	**2,13**	**2,1**	**1,05**	0,58	0,58	0,86
Pr_2O_3	bdl	bdl	bdl	bdl	bdl	bdl	**0,31**	**0,23**	**0,18**	bdl	bdl	0,13
Nd_2O_3	bdl	0,39	bdl	bdl	bdl	bdl	**0,79**	**0,9**	**0,4**	0,36	0,28	0,36
Sm_2O_3	bdl	bdl	bdl	bdl	bdl	bdl	bdl	0,16	bdl	0,17	bdl	bdl
Gd_2O_3	bdl	bdl	bdl	bdl	bdl	bdl	0,14	0,15	bdl	bdl	bdl	bdl
CaO	0,06	bdl	bdl	bdl	bdl	bdl	0,11	0,08	bdl	bdl	bdl	bdl
FeO	0,15	0,23	0,16	0,14	bdl	bdl	bdl	bdl	bdl	0,16	bdl	bdl
PbO	0,08	0,25	0,09	0,08	0,07	0,09	0,05	0,16	0,11	bdl	0,09	0,12
Na_2O	0,35	0,24	0,28	bdl	bdl	bdl	bdl	0,45	0,28	bdl	0,55	0,63
Total	98,84	99,96	99,3	97,86	98,76	95,92	97,57	99,8	97,93	98,52	98,82	98,13

Other relevant information

- Most of experiments did not produce $ThSiO_4$ phase. Th released from chevkinite-(Ce) is located in low concentration in other products (i.e. britholite contains up to 1,8 wt.% of ThO_2).
- Turkestanite $(Ca,Na,\square)_2ThSi_8O_{20}\cdot nH_2O$ is another Th-bearing phase that appears in one experiment only (CF 15)
- Chevkinite-(Ce) shows distinct depletion in Th contents on the rim where the alteration takes place
- We do not see fluorine present in any $ThSiO_4$ analysis, perhaps suggesting that the Th was transported as a hydroxide

Preliminary conclusions

Alteration of chevkinite-(Ce) results in $ThSiO_4$ production at temperatures range 550-600°C and at pressure of 200 MPa

3 types of ThSiO4 have grown
-thorite
-huttonite
-amorphous ThSiO4

Longer time of experiment has supported production of

Experimental Thorite=>Huttonite phase transition reported in literature (Mazeina et al., 2005) is much higher (above 800°C) than observed in our experiments (550°C)

Experiments are contributing to our knowledge of Th solubility, transport mechanisms, and controls of structure (appearance of thorite, huttonite or amorphous phase)

MUCH REMAINS TO BE DONE

Thank you for your attention

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