Fluid-induced alteration of chevkinite-(Ce) and structural orientation relations at the phase boundary

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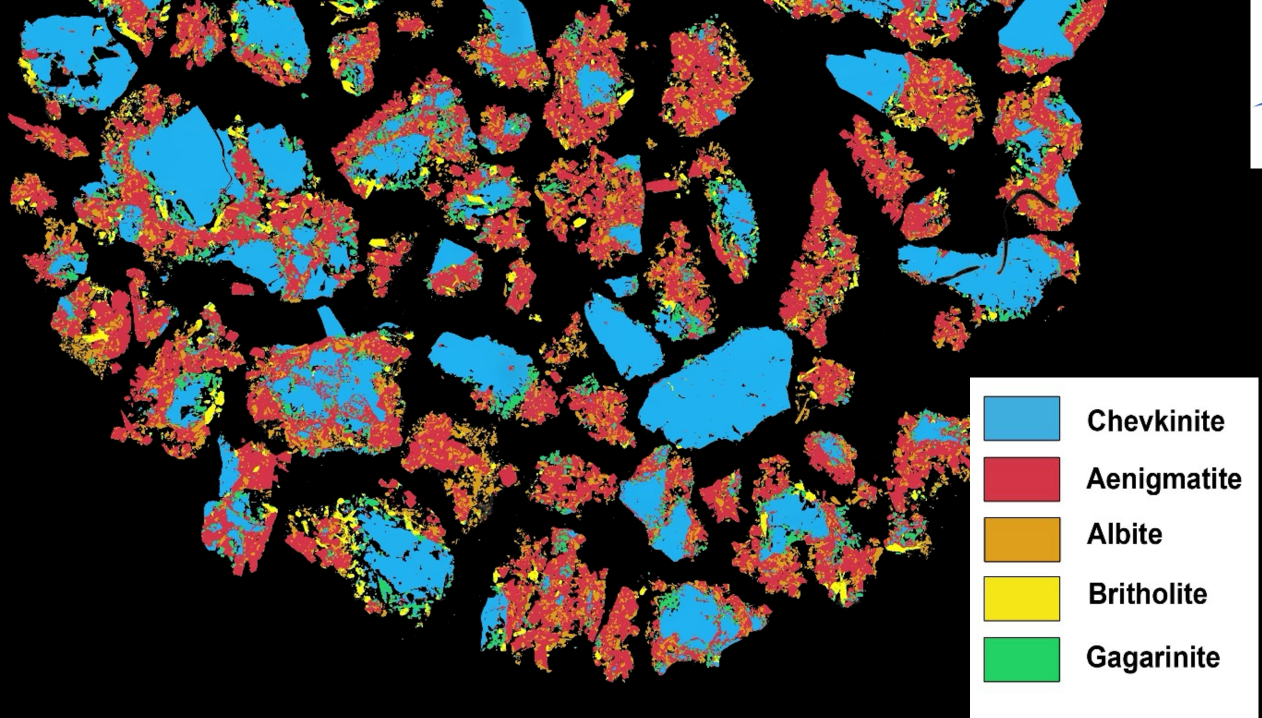
GFZ Helmholtz-Zentrum POTSDAM



“Standard” formula of chevkinite-group of minerals $A_4BC_2D_2(Si_2O_7)_2O_8$

where

A = REE, Ca, Sr

B = Fe^{2+}

C = Fe^{2+}, Fe^{3+}, Ti, Al

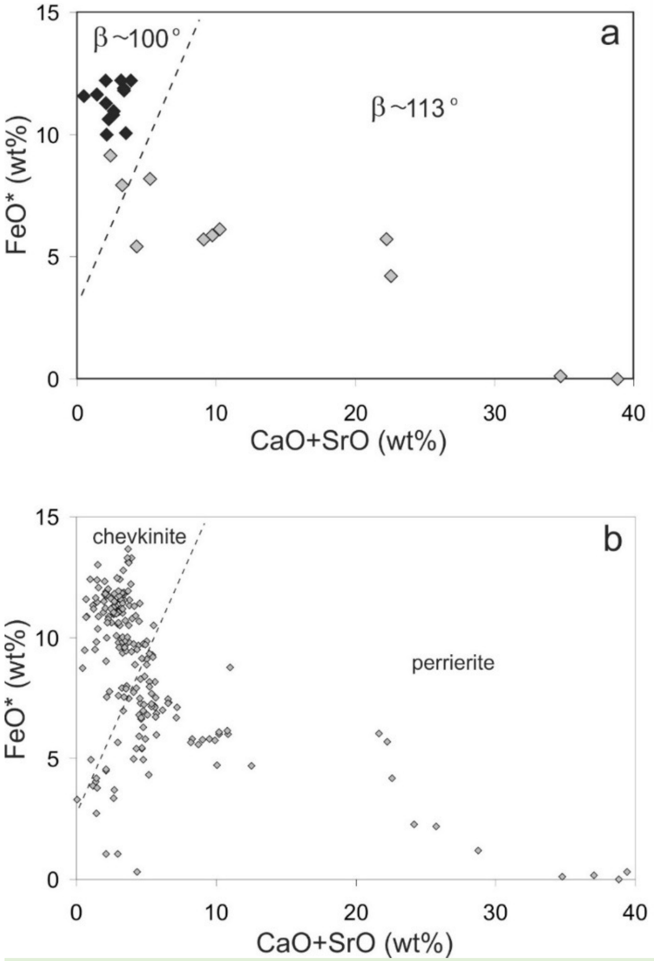
D = Ti

But **56** elements recorded at ppm to percent level (16 at % level)

Members of the chevkinite group,

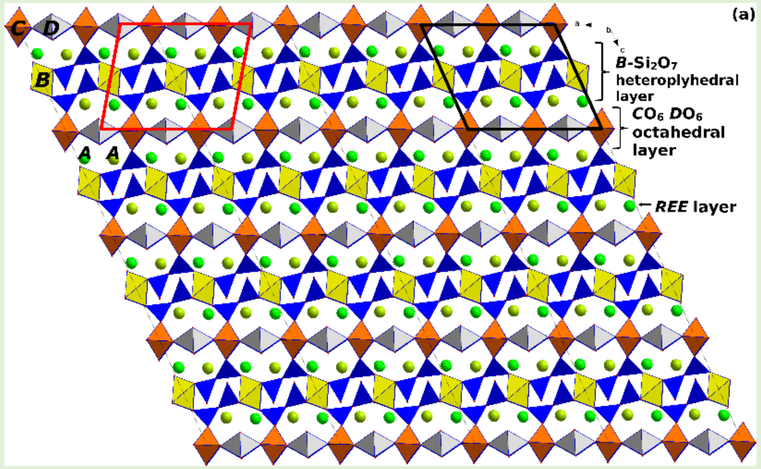
(accepted by the CNMNC-IMA)

Mineral	Formula	Reference
Chevkinite subgroup		
Chevkinite-(Ce)	$(REE,Ca)_4Fe^{2+}(Ti,Fe^{3+},Fe^{2+},Al)_2Ti_2Si_4O_{22}$	Ito, Arem (1971)
Polyakovite-(Ce)	$(REE,Ca)_4(Mg,Fe^{2+})(Cr, Fe^{3+})_2(Ti,Nb)_2Si_4O_{22}$	Sokolova et al. (2001)
Maoniupingite-(Ce)	$(REE,Ca)_4(Fe^{3+},Ti,Fe^{2+},\square)(Fe^{3+},Fe^{2+},Nb,Ti)_2Ti_2Si_4O_2$	Shen et al. (2005)
Dingdaohengite-(Ce)	$Ce_4Fe^{2+}Ti_2Ti_2(Si_2O_7)_2O_8$	Xu et al. (2008)
Christofschäferite-(Ce)	$(Ce,La,Ca)_4Mn(Ti,Fe^{3+})_3(Fe^{3+},Fe^{2+},Ti)(Si_2O_7)_2O_8$	Chukanov et al. (2012)
Delhuyarite-(Ce)	$Ce_4Mg(Fe^{3+}{}_2W)\square(Si_2O_7)_2O_6(OH)_2$	Holstam et al. (2017)
Perrierite subgroup		
Perrierite-(Ce)	$(REE,Ca)_4Fe^{2+}(Ti,Fe^{3+},Fe^{2+},Al)_2Ti_2Si_4O_{22}$	Ito, Arem (1971)
Strontiochevkinite	$(Sr_2[La,Ce]_{1.5}Ca_{0.5})_4Fe^{2+}{}_{0.5}Fe^{3+}{}_{0.5}(Ti,Zr)_4Si_4O_{22}$	Haggerty, Mariano (1983)
Rengeite	$Sr_4ZrTi_4Si_4O_{22}$	Miyajima et al. (2001)
Matsubaraite	$Sr_4Ti_5(Si_2O_7)_2O_8$	Miyajima et al. (2002)
Hezuolinite	$(Sr,REE)_4Zr(Ti,Fe^{3+},Fe^{2+})_2Ti_2O_8(Si_2O_7)_2$	Yang et al. (2012)
Perrierite-(La)	$(La,Ce,Ca)_4(Fe^{2+},Mn)(Ti,Fe^{3+},Al)_4(Si_2O_7)_2O_8$	Chukanov et al. (2011)

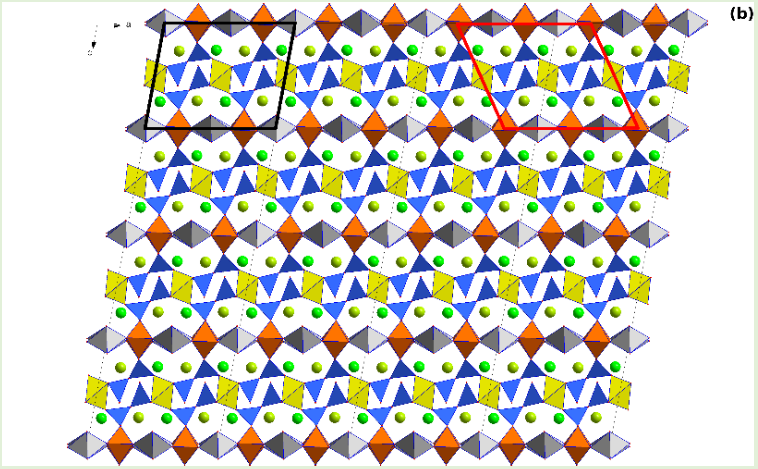


chevkinite vs perrierite

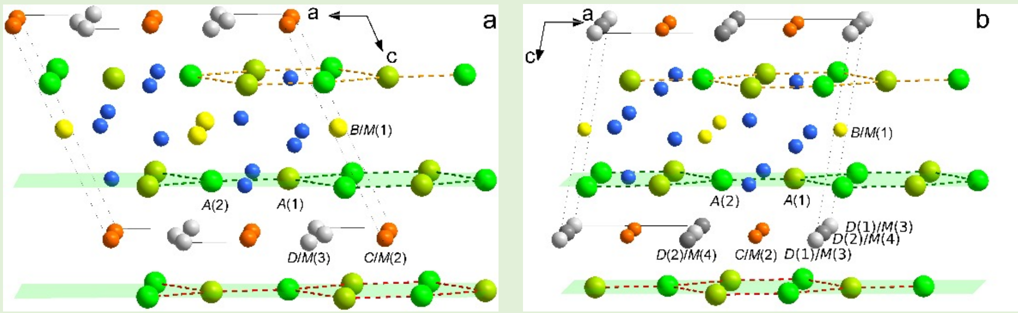
The (CaO+SrO) – FeO* (all Fe as Fe^{2+}) plot used as an empirical discriminant between the chevkinite and perrierite subgroups by Macdonald and Belkin (2002) and modified by Macdonald et al. (2009). Data plotted are for crystals that have had the b angle determined, updated with post-2009 data.



The crystal structure of perrierite along y (a)



The crystal structure of chevkinite along y (b)



Difference in stacking order of REE

Chevkinite group of minerals, conditions of formation

Pressure	≥50 to ≤1 kbar
Temperature	~1200 to 350°C (both rather poorly constrained)
$\boldsymbol{f}$**O_2**	ΔFMQ -2 to +5
$\boldsymbol{p}$**H_2O**	from “dry” to water-saturated

Experimental approach

- Natural chevkinite in a granitic system + reactive fluids ($Ca(OH)_2$, NaF, H_2O)
- Charge loaded into 3 mm diameter, 1 cm long Au capsules arc-welded shut
- Au capsules loaded into cold-seal autoclaves on a hydrothermal line.

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

Experiment	P(MPa)	T(°C)	Time (days)	Chevkinite	Quartz	Albite	NaF	H_2O
CF-4	400	600	21	15.82	3.4	3.06	0.88	5.68
CF-13	200	550	64	15.58	5.21	5.51	2.4	5
CF-22	200	600	42	21	5.59	5.6	4.3	5

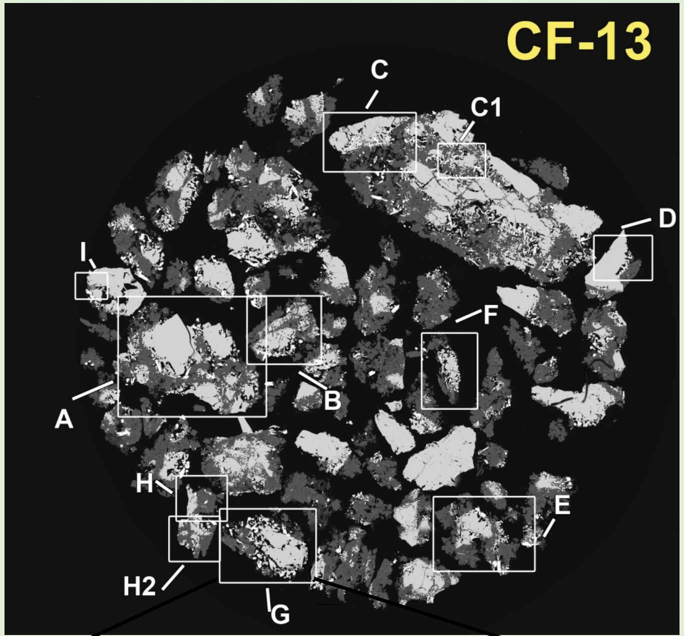
Experiment the results

One of reaction products is a very rare Na, REE fluoride,

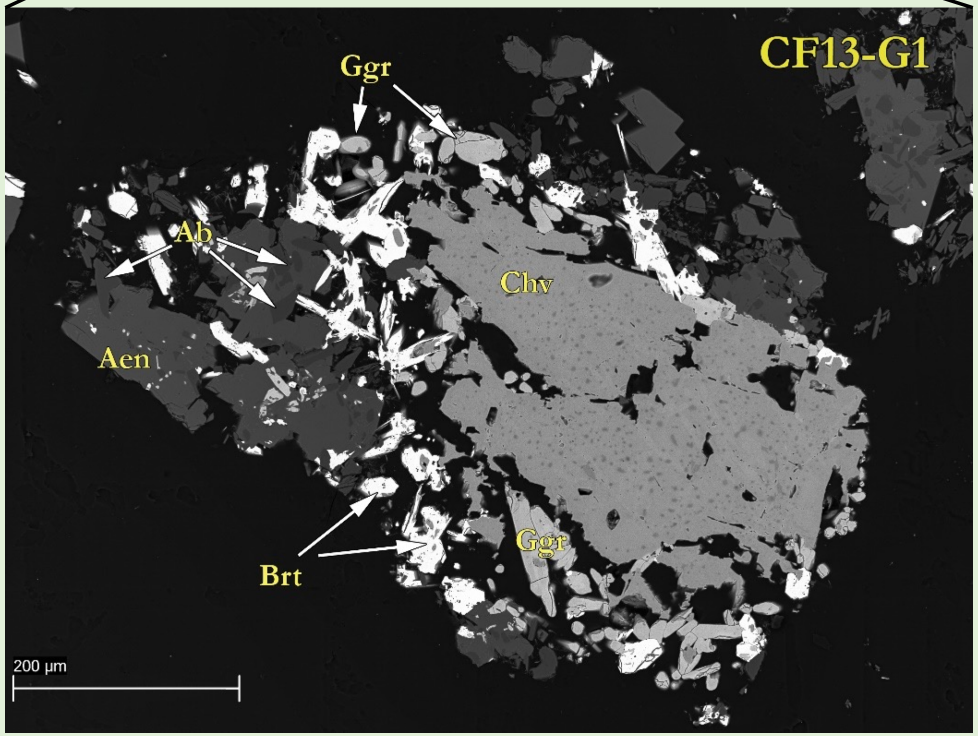
Gagarinite-(Ce) (Ggr) $Na(REE_xCa_{1-x})(REE_yCa_{1-y})F_6$

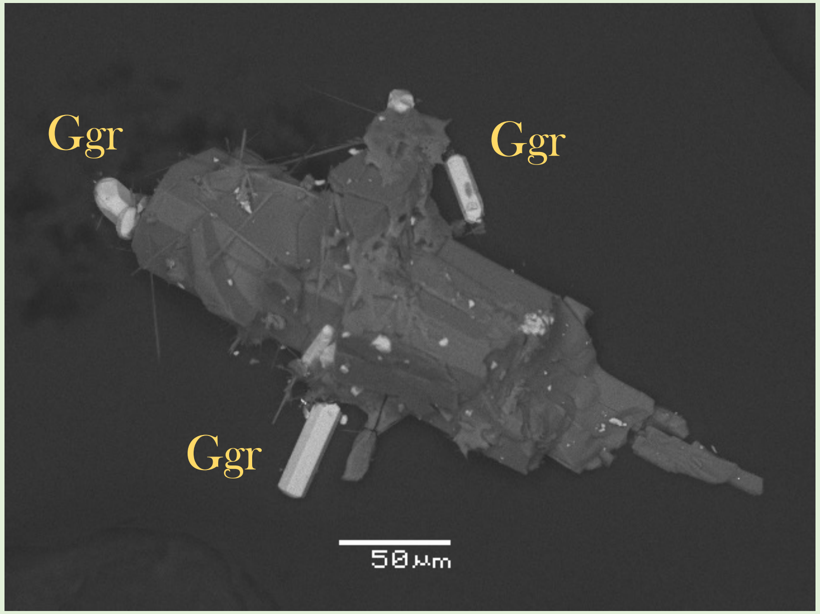
The formula of zajacite-(Ce) (now gagarinite-(Ce)) was given by Jambor et al. (1996) as $Na_{0.9}[(REE)_{1.2}Ca_{0.92}]_{2.04}F_6$. The experimental phases of this study by EPMA are, on the basis of 6 F, compositionally variable and not stoichiometric: $[Na_{0.87-1.36}(Ca+Sr+REE)_{2.23-2.73}]F_6$, with the sum of cations ranging from 3.29 to 3.77 apfu.

High escape of Na during EPMA – inaccuracy in composition deterination



BSE image of polished cut





BSE image of gagarinite-(Ce) single crystals placed on a carbon tape

Composition, multiple EDS analyses:

		Gagarinite_CF13		Gagarinite_CF4	
	F	6.079	± 0.11	6.102	± 0.094
anions:		6.079		6.102	
	Na	1.120	± 0.09	1.060	± 0.087
	Mg	0.000	± 0.01	0.000	± 0.007
	Ca	0.235	± 0.00	0.423	± 0.005
	Ti	0.007	± 0.00	0.000	± 0.004
	Fe	0.008	± 0.01	0.000	± 0.006
	Sr	0.019	± 0.00	0.027	± 0.003
	Y	0.000	± 0.00	0.000	± 0.005
	La	0.366	± 0.03	0.248	± 0.019
	Ce	0.768	± 0.02	0.667	± 0.018
	Pr	0.085	± 0.02	0.119	± 0.014
	Nd	0.278	± 0.02	0.297	± 0.014
	Sm	0.022	± 0.02	0.042	± 0.011
	Gd	0.009	± 0.01	0.013	± 0.008
	Dy	0.004	± 0.02	0.000	± 0.020
cations:		2.92	0.27365	2.90	

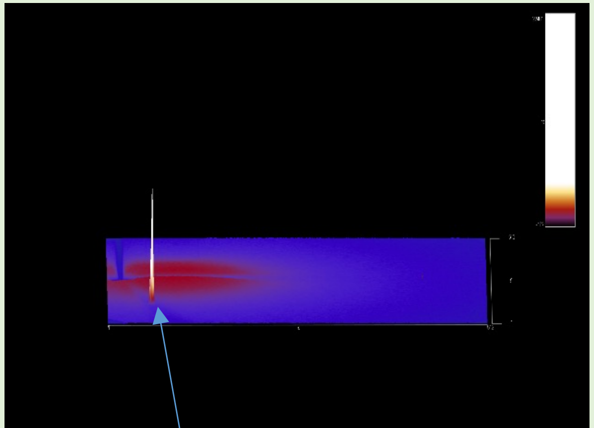
Single crystal x-ray diffraction

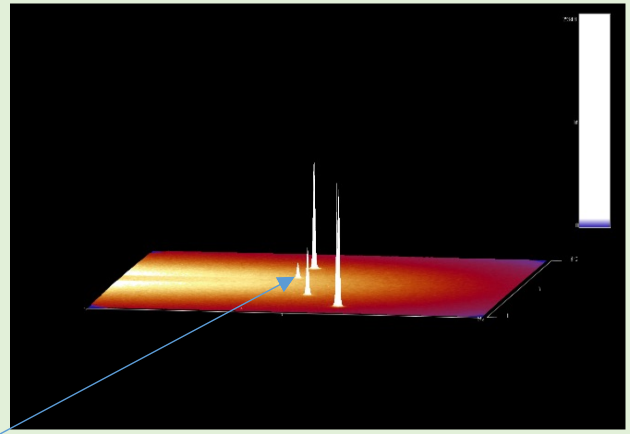
Gagarinite-(Ce)

New space group – additional unique site for REE and Ca – preferential allocation of Ca

$Na_{0.90}Ca_{0.92}(Ce_{0.51}La_{0.26}Y_{0.08}Nd_{0.18}Gd_{0.06}Sm_{0.02}Dy_{0.01})_{\Sigma 1.12}F_6$ Sciberras et. al (2011)

a	c	Space group	
6.0861(12)	3.6810(8)	$P6_3/m$	Sciberras et. al (2011)
6.1465(2)	3.75950(10)	$P\bar{6}$	This study





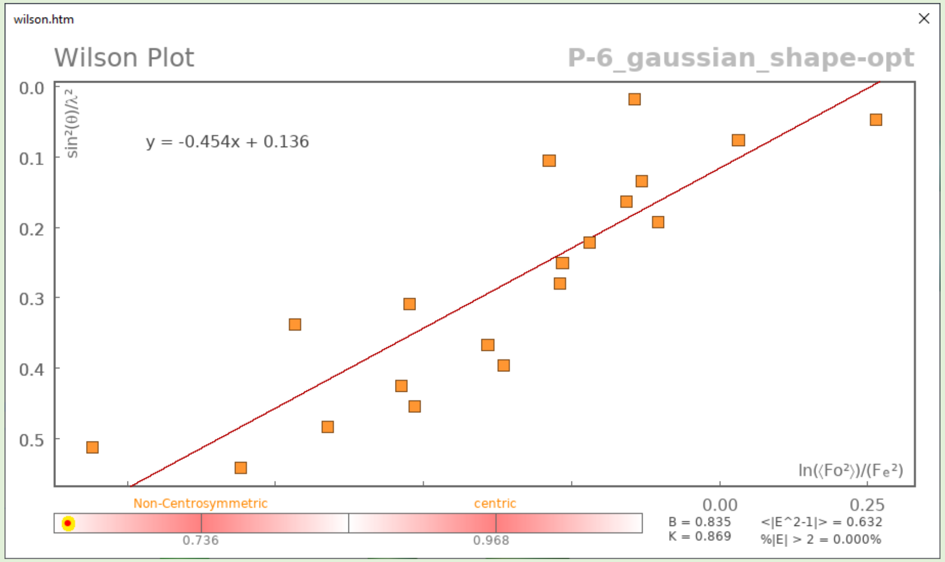
6_3 screw axis:
allowed only l=2n for 00l reflections

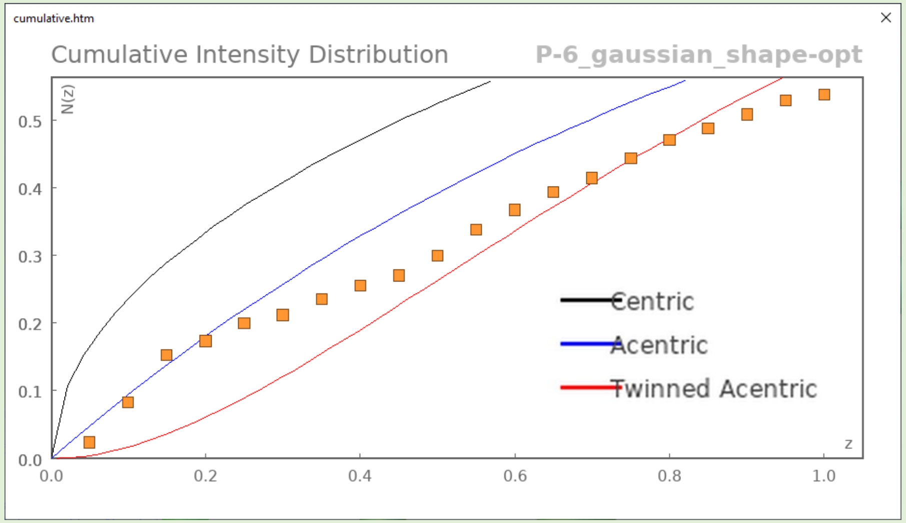
The 001 and 003 reflections should be systematically absent with 6_3 symmetry

Both space groups tested

Racemic twinning – pseudo-center of symmetry, high R_{int} for incorrect centrosymmetric space group

Temperature/K	**295.7(8)**	**295.7(8)**
Crystal system	**hexagonal**	**hexagonal**
Space group	**P-6**	**$P6_3/m$**
a/Å	**6.1465(2)**	**6.1465(2)**
b/Å	**6.1465(2)**	**6.1465(2)**
c/Å	**3.75950(10)**	**3.75950(10)**
α/°	**90**	**90**
β/°	**90**	**90**
γ/°	**120**	**120**
Volume/Å^3	**123.003(9)**	**123.003(9)**
Z	**1**	**1**
ρ_{calc}g/cm^3	**4.687**	**4.695**
μ/mm^{-1}	**7.385**	**7.318**
F(000)	**152.0**	**153.0**
Crystal size/mm^3	**0.055 × 0.028 × 0.019**	**0.055 × 0.028 × 0.019**
Radiation	**Ag Kα (λ = 0.56087)**	**Ag Kα (λ = 0.56087)**
2Θ range for data collection/°	**6.04 to 51.108**	**6.04 to 51.108**
Index ranges	**-9 ≤ h ≤ 9, -9 ≤ k ≤ 9, -5 ≤ l ≤ 5**	**-9 ≤ h ≤ 9, -9 ≤ k ≤ 9, -5 ≤ l ≤ 5**
Reflections collected	**3218**	**3203**
Independent reflections	**340 [R_{int} = 0.0373, R_{sigma} = 0.0197]**	**173 [R_{int} = 0.0385, R_{sigma} = 0.0146]**
Data/restraints/parameters	**340/0/25**	**173/0/14**
Goodness-of-fit on F^2	**1.127**	**1.629**
Final R indexes [I>=2σ (I)]	**R_1 = 0.0138, wR_2 = 0.0260**	**R_1 = 0.0475, wR_2 = 0.1352**
Final R indexes [all data]	**R_1 = 0.0139, wR_2 = 0.0260**	**R_1 = 0.0482, wR_2 = 0.1354**
Largest diff. peak/hole / e Å^{-3}	**0.45/-0.54**	**2.61/-3.48**
Flack parameter	**0.23(7)**	**P-6_gaussian_shape-opt**

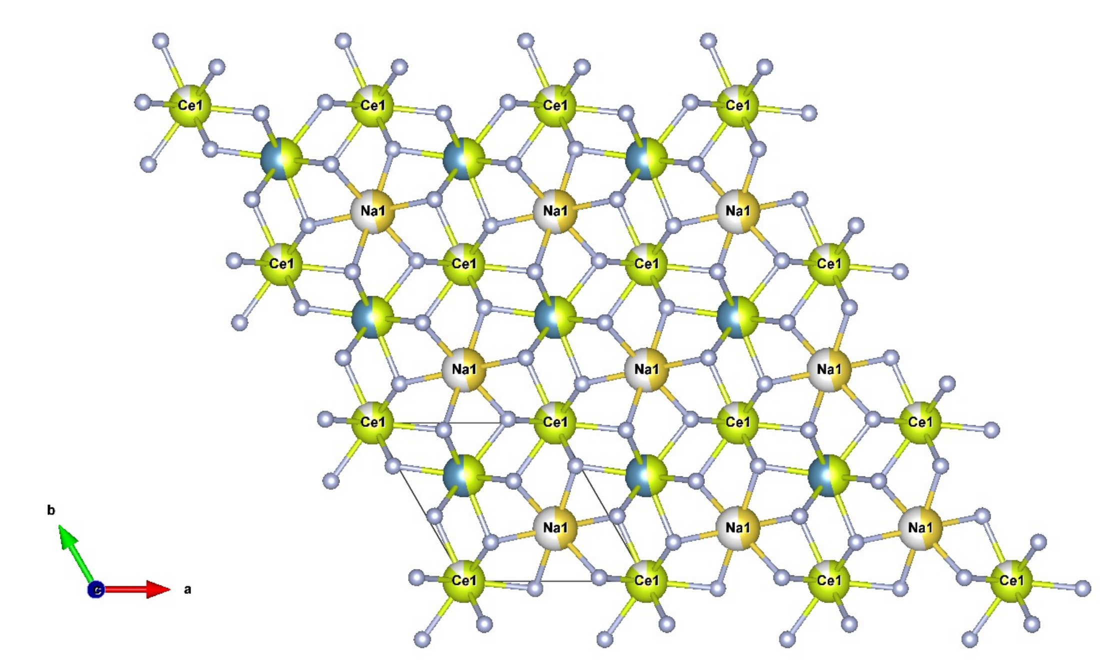




The crystal structure of ggarinite-(Ce) from experiment

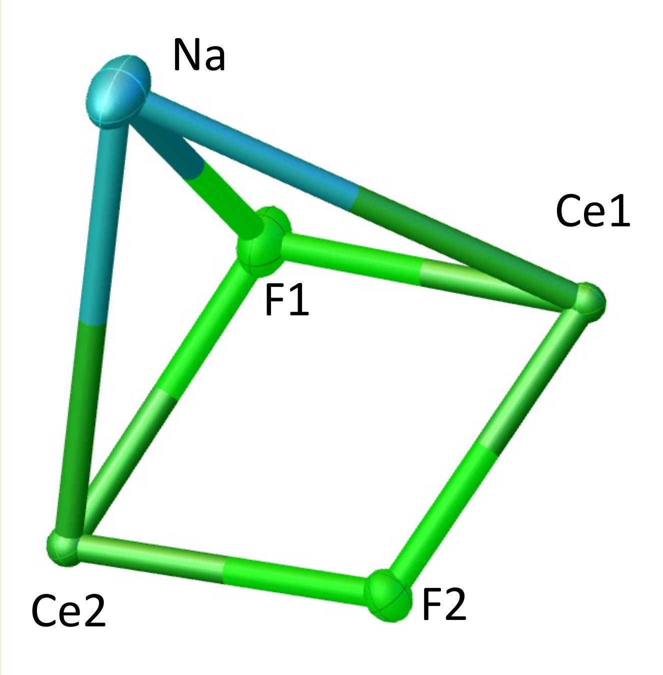
Atom site	Refined occupancy	Site occupation factor	Bond Valence Sum
Ce1	0.894(8)	51.9	2.98
Ce2	0.620(6)	36	2.72
Na	0.457(12)	5.0	0.78
F1	Fixed to 1	9	
F2	Fixed to 1	9	

View along Z



Selected bond valence sums:

Atom no.	Valence state assumed	Most consistent valence state	Bond Valence Sum	% Deviation from assumed valence state
Ce2	Ce2(3)	*	2.715	10
Ce2	Ce2(4)		2.427	39
Ca2	Ca2(2)	*	1.608	20
Ce1	Ce1(3)	*	2.982	1
Ce1	Ce1(4)		2.667	33
F1	---		---	---
F2	---		---	---
Na1	Na1(1)	*	.783	22



Asymmetric unit

Summary

- Experimentally induced hydrothermal alteration in chevkinite group minerals led to a formation of synthetic analogue of Gagarinite-(Ce), a rare mineral known from only one locality, found in a hypersolvus granite from the Strange Lake Zr-Y-REE-Nb-Be deposit, Quebec-Labrador (Jambor et al., 1996)
- Multiple EDS analyses allowed for a better determination of the chemical composition
- The crystal structure with $P\bar{6}$ space group is different than $P6_3/m$ introduced by Sciberras et. al (2011)
  - REE site splits into two distinct unique positions
  - Ca shows preferential site allocation to Ce2 site
- There is a possibility of a new, yet undiscovered mineral similar to gagarinite-(Ce)

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