

A revised structure for the rare earth fluoride gagarinite-(Ce) from experimental synthesis by fluid induced alteration of chevkinite-(Ce)



Marcin Stachowicz¹, Petras Jokubauskas¹, Bogusław Bagiński¹, Ray Macdonald¹, Daniel E. Harlov², Krzysztof Woźniak³

¹Department of Geochemistry, Mineralogy and Petrology, Faculty of Geology, University of Warsaw, 089 Warszawa, Poland

Żwirki i Wigury 93, 02-

²Section 3-3, GeoForschungsZentrum, Telegrafenberg, 14473 Potsdam, Germany

³Biological and Chemical Research Centre, Department of Chemistry, University of Warsaw, Żwirki i Wigury 101, Warszawa 02-093, Warszawa Poland

marcin.stachowicz@uw.edu.pl



During a series of experiments on the fluid-induced alteration of the REE-Ti silicate chevkinite-(Ce), a completely unexpected result in one experiment was the formation of gagarinite-(Ce), ideally Na(Ca, Ce)₂F₆.

The chevkinite-group of minerals (CGM), with simplified composition ((Ca,REE)₄Fe²⁺(Fe²⁺,Fe³⁺,Ti,Al)₂Ti₂(Si₂O₇)₂O₈) contain up to 50 wt% REE (expressed as oxides) but also carry significant amounts of high-field-strength elements (HFSE), such as Zr and Nb, and the actinides. It is a very widespread group; we know of hundreds of localities world-wide where they have been recorded.

Understanding the processes by which the rare earth elements (REE) are concentrated to economic levels in the Earth's crust has been a prime goal of ore deposit studies. In some cases, the enrichment has been due to extreme crystal fractionation of REE-rich magmas. However, there is an increasing body of field and experimental studies that have shown that the REE can be concentrated by hydrothermal processes [1]



Exp no.	P(M Pa)	T(°C)	Time (days)	Chevkinite	Quartz	Albite	NaF	H ₂ O
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

• Natural chevkinite in a granitic system + reactive fluids (Ca(OH)₂, NaF, H₂O)

• 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.

Fig. 1 The high P-T experiments were carried out at the *GeoForschungsZentrum Potsdam Hydrothermal laboratory* using standard cold seal autoclaves in conjunction with a hydrothermal high-pressure line. An internal thermocouple was placed such that its tip was located half-way up along a sealed Pt capsule (3 mm wide by 10 mm long) placed at the end of the autoclave. The Pt capsule contained chevkinite-(Ce) grains plus the accompanying minerals and fluids.

Scanning Electron Microscopy, BSE, EDS, EBSD

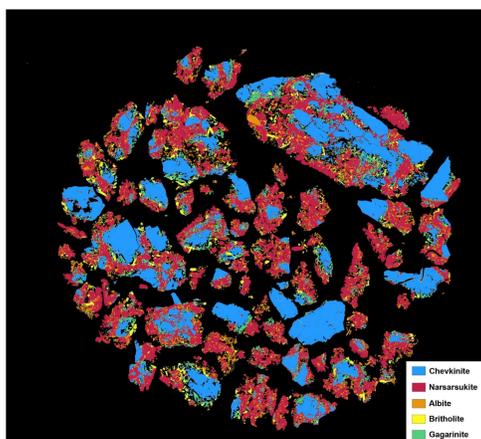


FIG. 2. False-colour scan of metasomatized fragments in CF13. Some 65% of the chevkinite-(Ce) has been replaced, both along the grain edges and internally.

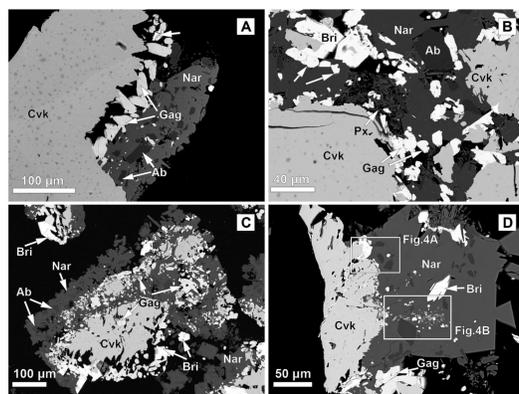


FIG. 3. BSE images of representative textural relationships in CF13. (a) Chevkinite-(Ce) with abundant pore spaces rimmed by subhedral gagarinite-(Ce) and then by massive narsarsukite (Nar) with albite inclusions. (b) More complex textures involving same phases. Px is sodian pyroxene (c) Chevkinite-(Ce) rimmed by variable combinations of gagarinite-(Ce) fluorbritholite-(Ce) (Brt), narsarsukite, albite and voids. (d) Fractured chevkinite-(Ce) rimmed by fluorbritholite-(Ce) containing frankdicksonite (Fds; white spots) and discrete frankdicksonite grains.

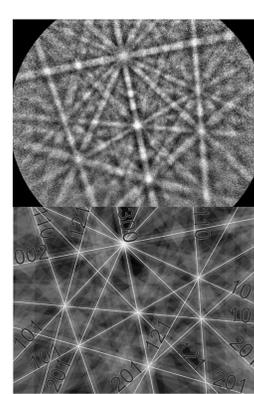


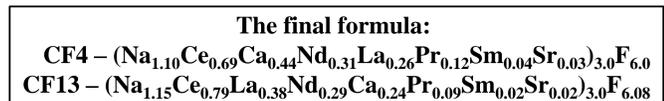
FIG. 4. Representative EBSD experimental pattern (top) and calculated pattern (bottom) with indexed Kikuchi lines for gagarinite-(Ce) from CF13



Fig 5. BSE image of gagarinite-(Ce) from CF22 experiment, single crystals placed on a carbon tape

Table 1. Composition from 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	2.90



X-ray diffraction studies

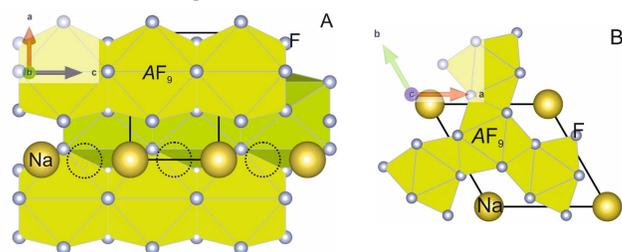
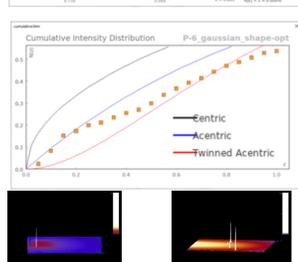
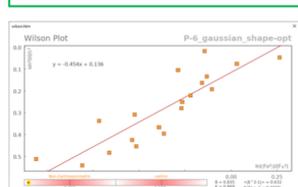


Figure 6. Polyhedral representation of gagarinite-(Ce). View along [010], dotted circles with vac standing for a vacancy (A) and view along [001] (B).

Both space groups were tested

Temperature/K	295.7(8)
Crystal system	hexagonal
Space group	P6 ₃ /m (incorrect)
a/Å	6.1465(2)
b/Å	6.1465(2)
c/Å	3.75950(10)
α/°	90
β/°	90
γ/°	90
V/cm ³	120
ρ _{calc} /cm ³	123.003(9)
Z	1
μ _{max} /cm ³	4.687
μ/mm ²	7.385
F(000)	152.0
Crystal size/mm ³	0.055 × 0.028 × 0.019
Radiation	Ag Kα (λ = 0.56087)
2θ range /°	6.04 to 51.108
Index ranges	-9 ≤ h ≤ 9, -9 ≤ k ≤ 9, -5 ≤ l ≤ 5
Reflections collected	3218
Independent reflections	340 [R _{int} = 0.0373, R _{sigma} = 0.0197]
Data/restraints/parameters	340/0/25
Goodness-of-fit on F ²	1.127
Final R indexes [I>2σ(I)]	R ₁ = 0.0138, wR ₂ = 0.0260
Final R indexes [all data]	R ₁ = 0.0139, wR ₂ = 0.0260
Largest diff. peak/hole / e Å ⁻³	0.45/-0.54
Flack parameter	0.23(7)

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



The 001 and 003 reflections, should be systematically absent with 6₃ symmetry

The mineral, previously named zajacite-(Ce), is known from only one natural occurrence, a hypersolvus granite from the Strange Lake Zr-Y-REE-Nb-Be deposit, Quebec-Labrador. The space group was identified as P3̄, with unit cell parameters a=6.099(1), c=11.064(2)(2) Å and formula Na_{0.9}[(REE)_{1.2}Ca_{0.92}]_{2.04}F₆ [2]. A subsequent single-crystal determination showed that it is isostructural with gagarinite-(Y) and its name was changed, with IMA-CNMNC approval, to gagarinite-(Ce), space group P6₃/m, with a=6.0861(12) and c=3.6810(8) Å [3]. The gagarinite-(Ce) in our experiments crystallized in P6̄, with a = 6.1465(2), c = 3.75950(10), R₁=1.37%. We observed 26% twinning by a twin center. The structure is derived from that of UCl₃ [3] with the addition of extra ^BNa⁺ into the crystal lattice, where REE³⁺ and Ca²⁺ fill both the cation sites (A) of the uranium salt [4,5].

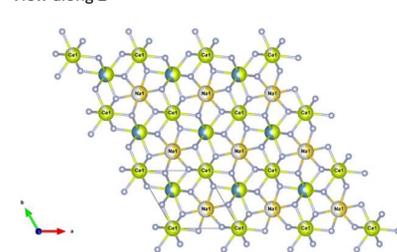
The experiments have provided new information on cation distribution and substitution mechanisms in gagarinite-(Ce). The structure is derived from that of UCl₃ with the addition of extra ^BNa⁺ into the crystal lattice, where REE³⁺ and Ca²⁺ fill both the cation sites (A) of the uranium salt. Previous studies assumed full occupancy of the REE+Ca, compositionally disordered, site. To charge balance the substitution 2^AREE³⁺ → ^ACa²⁺ + ^AREE³⁺ + ^BNa⁺, the amount of extra Na⁺ must equal Ca²⁺ in the final formula, giving Na_x(Ca_xREE_{2-x})F₆. ^BNa⁺ positions in the crystal lattice are separated by ca. 1.8 Å, which is shorter than the sum of ionic radii of neighbouring ions. In the extra ^BNa⁺ site every second position has to remain vacant, so the maximum allowed occupancy is 0.5 (Fig 6a). Gagarinite-(Ce) from CF4 shows surplus Na over Ca with a ratio close to 2:1, respectively. A vacancy in the REE site is necessary, equal to 1/3 of the redundant Na to remain in charge balance. If the Na content exceeds 1 in the formula unit, Na has to substitute for REE in the cation site. **The overall substitution mechanism is:** (2x-y)REE³⁺ → y ^BNa⁺ + (x-y) ^ANa⁺ + y ^ACa²⁺ + (x-y)/3 □, where □ stands for vacancy and x > y.

The crystal structure of gagarinite-(Ce) from hydrothermal alteration experiment

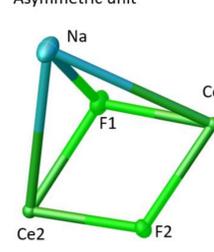
New space group P6̄ additional unique site for REE and Ca – preferential allocation of Ca in the A(2) site

Space group P6̄

View along Z



Asymmetric unit



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	

References

1. A.E. Williams-Jones, A.A. Migdisov, and I.M. Samsom, *Elements*, 8 (2012), 355-360.
2. J.L. Jambor, A.C. Roberts, D.R. Owens, J.D. Grice, *The Canadian Mineralogist*, 34 (1996) 1299-1304.
3. M.J. Sciberras, P. Leverett, P.A. Williams, D.E. Hibbs, A.C. Roberts, J.D. Grice, *The Canadian Mineralogist*, 49 (2011) 1111-1114.
4. W.H. Zachariasen, *Acta Crystallographica*, 1 (1948) 265-268.
5. A.A. Voronkov, N.G. Shumyatskaya, Y.A. Pyatenko, *Journal of Structural Chemistry*, 3 (1962) 665-669.
6. J.M. Hughes, J.W. Drexler, *The Canadian Mineralogist*, 32 (1994) 563-565.