Supplementary file: Detailed methodology

Experiments

Fluorite synthesis experiments were performed in a 40ml PFA reaction vessel at 60°C, with temperature controlled by an externally heated waterbath and monitored by a teflon-sleeved type-K thermocouple extended into the solution (Fig DR1). The vessel contained 30ml of a starting solution consisting of 2.5 wt% $CaCl_2$, $Ca(NO_3)_2$ or $CaSO_4$ depending on the desired dominating ligand, and 42 trace elements added at levels between 0.25 and 20 ppm (Table DR1). The solution was prepared from >99.9% pure, single element chlorides, sulfates and nitrates dissolved in nano-pure water. When hydrated chemicals were used, the mass fraction water was determined by Thermo-Gravitational Analysis (100mg of sample heated at 20Kmin^{-1} up to 350°C followed by 1min isothermal in a quartz-glass holder using a DuPont TGA951, resulting in a better than 5% reproducibility) and concentrations were adjusted accordingly. Dissociation reactions, mainly involving $TiCl_4$, $ZrOCl_2$, $HfOCl_2$, $SbCl_3$ and $BiCl_3$, resulted in the formation of a minor precipitate in the starting solution that was subsequently removed by filtration, as well as a pH between 2.0 and 2.9. These compounds were not included in NO_3 experiments to minimize Cl-content, and trace element grade HNO_3 was added to generate the same pH. The solution was stirred vigorously by a teflon-coated magnetic stirrer. At the run temperature, 4ml of 1M CsF-solution was injected into the starting solution, causing fluorite precipitation. The amount of F added represented a deficit relative to Ca to avoid precipitation of other phases and a solid to fluid ratio of approximately 500. Experiments were subsequently left for two hours at the run temperature, followed by recovery of fluorite and the reacted solution by filtration through a 0.45µm filter. Cl and SO_4-solutions were clear after one filtration, whereas NO_3-solutions required multiple filtration steps. Solid material was rinsed

repeatedly after filtration with nano-pure water.

Characterization of run products

An aliquot of solid run product was characterized by XRD at the Ceramics Research Centre, Corus RD&T (the Netherlands) using a Bruker D4 instrument. This showed that it consists of well-developed crystalline mono-mineralic fluorite and can therefore be compositionally characterized by a bulk technique. REE concentrations are high in the synthesized fluorite, but do not reflect co-precipitation of REE-fluorides, because the characteristic peaks of these fluorides are absent in the XRD spectra (Fig 2). Furthermore, REE concentrations in the final solution do not increase with atomic mass and are therefore inconsistent with the solubilities of the REE-fluorides (cf. Migdisov et al. 2009). The remaining material was digested using a closed-vessel hot HNO_3-H_3BO_3 method (step 1: 50 mg fluorite + 0.25 ml concentrated HNO_3 + 1.5 ml of 2850 ppm H_3BO_3-solution in a teflon container at 90 °C for 10 minutes; step 2: cooled and left to stand for 24 hours; step 3: 1.5ml of B-solution + 1.5ml 2% HNO_3 added and heated to 90 °C for 4 hours; step 4: taken up in 2% HNO_3 to 10ml). The digested fluorite, starting solutions and reacted solutions were analyzed by ICP-AES at Activation Laboratories (Ancaster, Canada) for major elements and by ICP-MS at the Trace Element Analysis Laboratory of McGill University for trace elements (detection limits of the analyses are given in Table DR2). Partition coefficients were calculated from measured concentrations in fluorite-solution pairs, supplemented with concentrations determined by mass-balance from the starting solution composition where the concentration of an element in one of the end-products could not be determined. The mass-balance method was also used as a check on the measured concentrations. Partition coefficients show large variations in magnitude (Table DR1), as a result of the low temperature of our experiments. This led to analytical challenges as the range of

concentrations exceeds the dynamic range of the ICP-MS. We therefore analyzed all samples at a range of dilutions, providing us with multiple measurements for each element. This approach also provides a means to check for enhancement and suppression matrix effects (none were observed). Experiments involving Cl were conducted in double duplicate and reported partition values are the average of these duplicates with associated 1 sigma experimental + analytical uncertainty. For NO_3 and SO_4 experiments the propagated 2 sigma analytical uncertainty is reported.

Attainment of equilibrium

A key concern for low temperature precipitation experiments is whether the results represent equilibrium. We have several reasons to conclude that the partitioning we observe does reflect equilibrium. Firstly, partition coefficients are highly reproducible as indicated by the four Cl-bearing experiments. Furthermore, despite variations in the actual partition coefficients among these experiments, the systematic differences among coefficients are identical and consistent with lattice-strain control. Secondly, the observation of lattice-strain systematics in our partitioning data is in itself strong evidence of equilibrium, as no such correspondence would be observed if disequilibrium or other processes including absorption control trace element concentrations. This is especially true for the diverse set of elements (in terms of radius and charge) considered in our experiments and for the very large range of D-values obtained. Thirdly, Ca concentrations in the fluid (10 to 18 ppm) are consistent with those expected from fluorite solubility data (19.5 ppm- Richardson and Holland 1979; 13 ppm- Garand and Mucci 2004), indicating that the fluorite is in major-element equilibrium with its solution.

Data fitting and speciation calculations

Radii for the elements were taken from Shannon (1976) for a coordination number of 8, which is the coordination of the single cation site in the fluorite structure. For elements for which 8-coordinated radii were not listed, their radii were estimated using the systematic variations among radius, coordination number and charge that were also employed by Shannon (1976). All radii are given in Table DR1. Partition coefficients were fitted using the lattice-strain equations of Blundy and Wood (1994) and fit parameters for the different experiments are listed in Table DR3. The speciation at 60 °C, 1 bar and the composition of the experimental solution was determined from thermodynamic calculations. Fluorite was the only solid phase considered in the calculations. Thermodynamic properties for the aqueous species were taken from the SupCrt database (http://geopig.asu.edu/supcrt92_data/slop98.dat) supplemented with data for the REE (Migdisov et al. 2009) and Al (Tagirov and Schott 2001). Properties for neutral F-species were estimated using the approach of Shock and Helgeson (1988) and Sverjensky et al. (1997). Speciation-corrected partition coefficients were calculated by dividing bulk coefficients by the fraction of each element residing in the species of interest. Because thermodynamic data on aqueous species are limited, we had to combine all species with a given ligand (see Table DR4).

References

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Figure and table captions

Figure DR1

Schematic drawing of the experimental setup. Experiments were conducted by synthesizing fluorite in an aqueous solution doped with 42 trace elements covering a wide range of radius and charge. Effects of speciation were investigated by varying the dominant ligand of the starting solution among Cl, NO_3 and SO_4. Experiments were conducted in a stirred teflon reaction vessel within a thermostated waterbath at 60 °C. Fluorite precipitation was brought about by injecting a 1M CsF-solution at run temperature.

Table DR1

Compositions of starting solutions of the various experiments (SSL) and the logarithm of resulting partition coefficients between fluorite and aqueous solution. The charge of the elements and their radius in 8-coordination are also given.

Table DR2

Analytical detection limits.

Table DR3

Lattice-strain fit parameters of the experimental partition coefficients.

Table DR4

Fraction of the elements residing as free ion (M), O or OH speciated (MOH), F-speciated (MF) and Cl-speciated (MCl) as determined from thermodynamic modeling for the average composition of final solutions of the FLU-4 series of experiments. Lack of data prevented us from determining fractions for all elements.

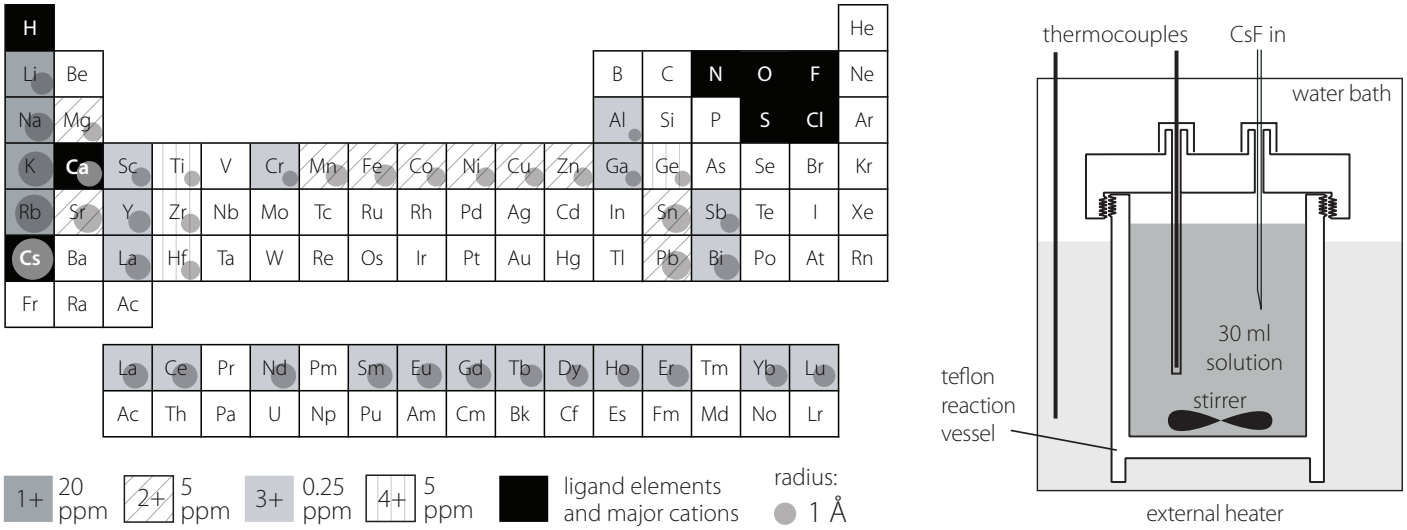
H He
Li Be B C N O F Ne
Na Mg Al Si P S Cl Ar
K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr
Rb Sr Y Zr Nb Mo Tc Ru Rh Pd Ag Cd In Sn Sb Te I Xe
Cs Ba La Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po At Rn
Fr Ra Ac
La Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu
Ac Th Pa U Np Pu Am Cm Bk Cf Es Fm Md No Lr
1+ 20 ppm
2+ 5 ppm
3+ 0.25 ppm
4+ 5 ppm
ligand elements and major cations
radius:
1 Å
thermocouples
CsF in
water bath
30 ml solution
stirrer
teflon reaction vessel
external heater

Figure DR1

Table DR1. Compositions of starting solutions of the various experiments (SSL) and the logarithm of resulting partition coefficients between fluorite and aqueous solution. The charge of the elements and their radius in 8-coordination are also given.

Experiment	FLU - 4							FLU - 6				FLU - 8				element props	
Ligand	Cl							NO_3				SO_4					
Temperature	60 °C							60 °C				60 °C					
Pressure	1 bar							1 bar				1 bar					
Element	**SSL-4**	**FLU-4A**	**1 stdev**		**FLU-4B**	**1 stdev**		**SSL-6**	**FLU-6.1**	**2 stdev**		**SSL-8**	**FLU-8.2**	**2 stdev**		**radius**	**charge**
	ppm	**log D**	**-**	**+**	**log D**	**-**	**+**	**ppm**	**log D**	**-**	**+**	**ppm**	**log D**	**-**	**+**	**Å**	
Li	20.47	1.34	0.10	0.08	1.40	0.19	0.13	21.65	1.42	0.15	0.11	14.82	0.95	0.08	0.07	0.920	1 +
Na	17.77	2.01	0.08	0.07	2.15	0.92	0.27	17.91	1.82	0.05	0.04	21.00	2.19	0.14	0.11	1.180	1 +
K	19.04	1.14	0.22	0.15	0.84	0.39	0.20	19.65	0.59	0.05	0.04	42.80	0.39	0.14	0.11	1.510	1 +
Rb	20.65	-0.27	0.08	0.07	-0.66	0.42	0.21	21.12	-1.30	0.07	0.06	15.30	0.05	0.26	0.16	1.610	1 +
Mg	5.19	2.68	0.20	0.14	2.69	1.12	0.28	5.51	2.22	0.20	0.14	7.05	2.01	0.02	0.02	0.890	2 +
Sr	5.07	3.70	0.22	0.14	4.14	-	0.33	6.49	2.56	0.11	0.09	3.64	2.16	0.01	0.01	1.260	2 +
Pb	4.72	3.44	0.32	0.18	4.58	0.01	0.01	5.21	2.88	-	0.33	3.92	1.96	0.02	0.02	1.290	2 +
Co	4.91	1.08	0.68	0.25	1.37	-	0.36	4.93	1.09	0.22	0.15	3.71	0.80	0.01	0.01	0.900	2 +
Ni	4.70	0.24	0.15	0.11	0.38	0.10	0.08	5.30	0.24	0.26	0.16	3.67	0.62	0.02	0.02	0.855	2 +
Cu	5.46	1.45	0.10	0.08	1.77	0.07	0.06	5.03	1.48	0.23	0.15	3.06	1.17	0.04	0.04	0.889	2 +
Zn	6.24	2.02	0.38	0.20	2.16	-	0.35	5.82	2.00	0.15	0.11	3.65	1.28	0.03	0.03	0.900	2 +
Mn	5.14	2.39	0.23	0.15	2.58	-	0.31	5.13	2.27	0.07	0.06	3.68	1.77	0.02	0.02	0.960	2 +
Fe	4.90	3.05	0.06	0.06	2.99	-	0.36	4.45	1.88	0.05	0.04	10.15	1.87	0.02	0.02	0.920	2 +
Sn	1.16	2.83	0.17	0.12	3.34	1.27	0.29	3.17	1.73	0.11	0.09	0.01	< d.l.f.	-	-	1.263	2 +
Al	4.64	< d.l.f.	-	-	2.57	1.18	0.29	4.36	4.87	0.05	0.04	10.34	2.51	0.03	0.02	0.649	3 +
Ga	14.31	4.06	0.20	0.13	4.53	0.42	0.21	18.78	3.64	-	0.79	11.26	1.94	0.01	0.01	0.736	3 +
Sc	4.88	5.41	0.35	0.19	5.69	0.12	0.09	n.p.	n.p.	-	-	5.08		0.02	0.02	0.870	3 +
Sb	0.06	1.97	0.33	0.18	2.74	-	0.32	n.p.	n.p.	-	-	0.01	0.95	0.06	0.05	0.879	3 +
Bi	0.05	3.88	0.01	0.01	4.42	-	0.35	n.p.	n.p.	-	-	6.29	2.14	0.02	0.02	1.170	3 +
Cr	5.36	1.60	0.52	0.23	1.70	-	0.37	5.15	0.21	-	1.87	4.50	0.40	0.01	0.01	0.731	3 +
Y	0.33	< d.l.f.	-	-	5.52	0.46	0.22	0.29	5.33	0.03	0.03	0.43	5.24	0.55	0.24	1.019	3 +
La	0.25	5.61	1.29	0.29	5.46	0.66	0.25	0.26	5.70	0.92	0.27	0.45	4.10	0.02	0.02	1.160	3 +
Ce	0.28	5.14	0.59	0.24	5.08	0.12	0.10	0.27	5.18	0.20	0.13	0.47	5.24	0.11	0.09	1.143	3 +
Nd	0.27	5.20	0.47	0.22	5.52	0.83	0.27	0.28	< d.l.f.	-	-	0.46	5.00	0.16	0.12	1.109	3 +
Sm	0.26	6.12	2.58	0.30	5.93	-	0.34	0.28	< d.l.f.	-	-	0.43	5.06	0.25	0.16	1.079	3 +
Eu	0.25	5.76	0.07	0.06	5.48	0.90	0.27	0.28	4.81	0.23	0.15	0.47	4.96	0.17	0.12	1.066	3 +
Gd	0.25	5.70	0.49	0.23	5.49	0.67	0.25	0.28	5.91	0.25	0.16	0.36	5.21	0.31	0.18	1.053	3 +
Tb	0.26	6.23	0.47	0.22	5.97	-	0.34	0.28	< d.l.f.	-	-	0.46	5.19	0.34	0.19	1.040	3 +
Dy	0.27	< d.l.f.	-	-	5.30	0.80	0.27	0.28	< d.l.f.	-	-	0.46	5.17	0.28	0.17	1.027	3 +
Ho	0.26	5.73	0.21	0.14	5.52	0.78	0.26	0.28	5.63	0.16	0.12	0.41	5.25	0.32	0.18	1.015	3 +
Er	0.26	< d.l.f.	-	-	5.48	0.66	0.25	0.28	< d.l.f.	-	-	0.47	5.18	0.51	0.23	1.004	3 +
Yb	0.27	5.91	0.53	0.23	5.64	1.37	0.29	0.27	6.11	0.25	0.16	0.44	5.28	0.54	0.23	0.985	3 +
Lu	0.27	< d.l.f.	-	-	5.23	0.83	0.27	0.27	< d.l.f.	-	-	0.47	5.31	0.50	0.23	0.977	3 +
Ti	4.22	3.14	0.07	0.06	3.81	0.18	0.13	n.p.	n.p.	-	-	3.15	< d.l.f.	-	-	0.740	4 +
Zr	2.43	4.46	0.21	0.14	4.37	-	0.37	n.p.	n.p.	-	-	2.24	3.54	0.06	0.06	0.840	4 +
Ge	3.64	2.08	0.53	0.23	2.11	-	0.35	n.p.	n.p.	-	-	0.83	0.97	0.03	0.03	0.669	4 +
Hf	4.77	4.45	0.02	0.02	4.57	0.02	0.02	n.p.	n.p.	-	-	4.12	3.34	0.05	0.04	0.830	4 +

Footnotes: n.p. not present in the starting solution, <d.l.f below the limit of detection in the reacted solution, standard deviations are duplicate uncertainty for FLU-4A and 4B, and count statistical analytical error for FLU-6 and 8

Table DR2. Analytical detection limits

Element	d.l (ppb)
Li	0.19
Na	100
K	100
Rb	0.008
Mg	2.59
Sr	0.048
Pb	0.067
Co	0.015
Ni	0.093
Cu	0.44
Zn	1.38
Mn	0.038
Fe	10
Sn	0.046
Al	100
Ga	0.014
Sc	0.17
Sb	0.004
Bi	0.006
Cr	0.20
Y	0.004
La	0.043
Ce	0.044
Nd	0.017
Sm	0.003
Eu	0.003
Gd	0.004
Tb	0.002
Dy	0.002
Ho	0.005
Er	0.003
Yb	0.002
Lu	0.002
Ti	0.09
Zr	0.012
Ge	0.12
Hf	0.006

Table DR3. Lattice-strain fit parameters of the experimental partition coefficients.

Experiment	**FLU-4A**	**FLU-4B**	**FLU-4**	**FLU-6.1**	**FLU-8.2**
1+ elements					
log D_0	2.02	2.15	2.09	1.84	2.24
E	16.0	18.8	17.4	15.5	23.0
r_0	1.20	1.20	1.20	1.14	1.23
2+ elements					
log D_0	4.63	4.85	4.76	3.92	3.70
E	90	85	95	90	90
r_0	1.14	1.15	1.14	1.13	1.12
3+ elements					
log D_0	6.14	5.78	6.00	5.78	5.26
E	104	80	92	110	110
r_0	1.00	1.02	1.01	1.05	1.02
4+ elements					
log D_0	5.31	5.34	5.32	n.a.	4.54
E	66	60	63	n.a.	66
r_0	1.00	1.00	1.00	n.a.	1.02

Table DR4. Fraction of the elements residing as free ion (M), O or OH speciated (MOH), F-speciated (MF) and Cl-speciated (MCl) as determined from thermodynamic modeling for the average composition of final solutions of the FLU-4 series of experiments. Lack of data prevented us from determining this for all elements.

Element	M	MOH	MF	MCl
Li	0.9991	0.0000	0.0002	0.0008
Na	0.9959	0.0000	0.0000	0.0041
K	0.9997	0.0000	0.0001	0.0001
Rb	0.9953	0.0000	0.0011	0.0036
Mg	0.9850	0.0000	0.0025	0.0125
Sr	0.9869	0.0000	0.0002	0.0129
Ba	0.9919	0.0000	0.0001	0.0080
Pb	0.6565	0.0000	0.0059	0.3376
Co	0.9464	0.0000	0.0011	0.0526
Ni	0.9967	0.0000	0.0014	0.0020
Cu	0.9568	0.0000	0.0031	0.0401
Zn	0.8657	0.0000	0.0013	0.1330
Cd	0.4590	0.0000	0.0006	0.5404
Mn	0.9746	0.0000	0.0008	0.0246
Fe	0.9855	0.0000	0.0026	0.0119
Sn	0.0000	0.0000	0.0002	0.0048
Al	0.0000	0.0000	1.0000	0.0000
La	0.5595	0.0000	0.4102	0.0303
Ce	0.4216	0.0000	0.5586	0.0198
Nd	0.4878	0.0000	0.4984	0.0139
Sm	0.3673	0.0000	0.6195	0.0132
Eu	0.2544	0.0000	0.7307	0.0149
Gd	0.3068	0.0000	0.6772	0.0160
Tb	0.2359	0.0000	0.7522	0.0119
Dy	0.2175	0.0000	0.7717	0.0109
Ho	0.2178	0.0000	0.7714	0.0108
Er	0.2153	0.0000	0.7728	0.0119
Yb	0.1886	0.0000	0.8012	0.0102
Lu	0.1790	0.0000	0.8109	0.0100