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# Chemical and environmental stability of monazite-cheralite solid solutions $\text{Ln}_{1-2}\text{Ca Th PO}_4$ ( $\text{Ln} = \text{Pr, Nd}$ ; $x = 0-0.15$ ): A thermodynamic study

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1           **Chemical and environmental stability of monazite-cheralite solid**  
2           **solutions  $\text{Ln}_{1-2x}\text{Ca}_x\text{Th}_x\text{PO}_4$  ( $\text{Ln} = \text{Pr}, \text{Nd}; x = 0 - 0.15$ ): a**  
3           **thermodynamics study**

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15  
16          **ABSTRACT**

17          Monazite-cheralite ceramics are a promising waste form for actinides. To elucidate the long-  
18          term behavior of this matrix in aqueous solutions, this study measured thermodynamic data for Th-  
19          rhabdophanes  $\text{Ln}_{1-2x}\text{Ca}_x\text{Th}_x\text{PO}_4 \cdot n\text{H}_2\text{O}$  (with  $\text{Ln} = \text{Pr}, \text{Nd}; x = 0 - 0.15$ ) and the associated anhydrous  
20          monazite-cheralites  $\text{Ln}_{1-2x}\text{Ca}_x\text{Th}_x\text{PO}_4$ . Solubility experiments at 298 K and high temperature oxide  
21          melt solution calorimetry were combined for calculation of  $\Delta G_f^\circ$ ,  $\Delta H_f^\circ$  and  $S_m^\circ$  of Th-rhabdophanes  
22          and associated monazite-cheralites. Standard solubility constants were employed in a geochemical  
23          simulation using the PHREEQC software, the results of which confirmed the high chemical stability  
24          of the monazite-cheralite phases and supported their use as a specific conditioning matrix for the  
25          long-term immobilization of actinides.

26  
27          **Keywords:** thorium, rhabdophane, monazite, cheralite, solubility, calorimetry, stability.  
28

## 29 1 Introduction

30 Monazite-cheralite  $\text{Ln}_{1-2x}\text{Ca}_x\text{An}^{\text{IV}}_x\text{PO}_4$  (Ln = La-Gd, An = Th, U, Np, Pu) solid solutions are  
31 promising radioactive waste matrices for the specific conditioning of actinides, as they adopt the  
32 monazite crystal structure (monoclinic,  $\text{P2}_1/\text{n}$ ), which provides high chemical stability, considerable  
33 tetravalent actinide capacity, and good resistance to auto-irradiation (Dacheux et al., 2013). Indeed,  
34 monazites are repeatedly reported as being able to accumulate and immobilize actinides (U/Th) and  
35 their daughter products within their structure even after multiple sedimentations and metamorphic  
36 cycles ( $> 10^9$  y) in the geologic environment (Boatner, 2002). Moreover, no chemical alteration of  
37 monazite has been observed during weathering, erosion and transport processes, which only lead to  
38 mechanical abrasion (Montel et al., 2000; Montel et al., 2011). Such excellent chemical durability  
39 could be explained from both kinetic and thermodynamics points of view. The studies on the  
40 dissolution kinetics of monazites report their low dissolution rates (Gausse, 2016; Gausse et al.,  
41 2018). Even under extreme conditions, the normalized dissolution rate of  $\text{LnPO}_4$  (Ln = La, Ce, Nd,  
42 and Gd) is lower than that of borosilicate glass R7T7, the reference material for high-level waste  
43 conditioning (*i.e.*  $4.0 \times 10^{-3} \text{ g m}^{-2} \text{ d}^{-1}$  at 363 K in  $0.1 \text{ mol L}^{-1} \text{ HNO}_3$  (Gausse, 2016; Gausse et al.,  
44 2018) compared to  $1 \text{ g m}^{-2} \text{ d}^{-1}$  at 363 K in deionized water (Delage and Dussossoy, 1990),  
45 respectively).

46 In addition to the high resistance to dissolution, it is essential to guarantee the thermodynamic  
47 stability of monazite-cheralite in groundwater. Upon leaching in groundwater, the forming phases  
48 might precipitate on the surface of the material limiting further release of radionuclides. For  
49 monazite end-members, the nature of the neoformed phase is temperature-dependent (Du Fou de  
50 Kerdaniel et al., 2007a; Du Fou de Kerdaniel et al., 2007b). As reported by Du Fou de Kerdaniel et  
51 al. (2007b), below a particular temperature (363 K for La, 383 K for Ce, 393 K for Pr) this phase is  
52 a hydrated phosphate compound, rhabdophane  $\text{LnPO}_4 \cdot 0.667\text{H}_2\text{O}$  (monoclinic C2) (Mesbah et al.,  
53 2014), while at higher temperature, the solubility-controlling phase might be monazite itself. Indeed,  
54 the reprecipitation of rhabdophane at low temperature was observed during monazite dissolution  
55 tests, resulting in a decrease of the leaching rate of lanthanides after the initial stage of dissolution  
56 (Du Fou de Kerdaniel, 2007; Du Fou de Kerdaniel et al., 2007b; Gausse et al., 2018).

57 For tetravalent actinide bearing phosphates (*e.g.* monazite-cheralite), the solubility-controlling  
58 phases for tetravalent actinide may be more complex. Du Fou de Kerdaniel (2007) observed a  
59 decrease of the leaching rate during dissolution of several phosphate ceramics (*i.e.* (Nd,Th)-  
60 britholite  $\text{NdCa}_9\text{Nd}_{1-x}\text{Th}_x(\text{PO}_4)_{5-x}(\text{SiO}_4)_{1+x}$ , monazite-cheralite  $\text{Ln}_{1-2x}\text{Ca}_x\text{An}^{\text{IV}}_x\text{PO}_4$  (An = Th, U),  
61 thorium phosphate diphosphate  $\beta\text{-Th}_4(\text{PO}_4)_4\text{P}_2\text{O}_7$ , noted as  $\beta\text{-TPD}$ , and associated  $\beta\text{-TPD/monazite}$   
62 composites. In this study, SEM images confirmed the formation of a mixture of rhabdophane  
63  $\text{Nd}_{1-2x}\text{Ca}_x\text{Th}_x\text{PO}_4 \cdot 0.5\text{H}_2\text{O}/\text{GdPO}_4 \cdot n\text{H}_2\text{O}$ ,  $\text{SiO}_2 \cdot n\text{H}_2\text{O}$ , and  $(\text{U, Th})_2(\text{PO}_4)_2(\text{HPO}_4) \cdot \text{H}_2\text{O}$  (TPHPH-type  
64 solids) on the surface of the sintered pellet. Therefore, Th-rhabdophane, and TPHPH are potential  
65 solubility-controlling phases during the leaching process of Th-monazite-cheralite. Consequently,  
66 there is great interest to determine the thermodynamic properties of these phases, leading to  
67 clarification of the mechanism and driving force governing the solubility of tetravalent actinides  
68 and lanthanides.

69 Several studies have investigated the solubility of hydrated lanthanide or actinide phosphates,  
70 such as rhabdophane and TPHPH) (Clavier, 2004; Clavier et al., 2006; Gausse et al., 2016;  
71 Jonasson et al., 1985; Qin et al., 2017a; Robisson et al., 2002). Their results suggest these  
72 compounds exhibit low Th solubility. Clavier (2004) first reported that the solubility constant,

73  $\lg K_{s,0}^{\circ}$  associated with TPHPH reached  $-66.4 \pm 1.1$  (Clavier, 2004; Clavier et al., 2006). More  
74 recently, this value was refined to  $-71.2 \pm 1.3$  (Qin et al., 2017a). When saturation experiments were  
75 performed in  $1 \text{ mol L}^{-1} \text{ HNO}_3$ , the thorium concentration was found to be  $(1.9 \pm 0.1) \times 10^{-3} \text{ mol L}^{-1}$ .  
76 Gausse et al. (2016) determined the solubility of the  $\text{LnPO}_4 \cdot n\text{H}_2\text{O}$  series ( $\text{Ln} = \text{La-Gd}$ ) from under-  
77 and super-saturation experiments to range from  $-24.1 \pm 0.3$  to  $-25.8 \pm 0.3$ . The obtained lanthanide  
78 concentrations when saturation conditions were reached (in  $0.1 \text{ mol L}^{-1} \text{ HNO}_3$ ) were about  
79  $1 \times 10^{-3} \text{ mol L}^{-1}$ . Due to the interplay between rhabdophane and monazite mentioned above, the  
80 determination of the solubilities of monazite end-members  $\text{LnPO}_4$  ( $\text{Ln} = \text{La-Gd}$ ) should take place  
81 under hydrothermal conditions ( $T = 373 - 523 \text{ K}$ ). Recently, Gysi et al., (2018) and Van Hoozen et  
82 al. (2020) have determined the solubility products of monazite end-members  $\text{LnPO}_4$  ( $\text{Ln} = \text{La-Gd}$ )  
83 ranging from  $-27.7 \pm 0.1$  to  $-32.3 \pm 0.1$ . The concentration of Ln at equilibrium was lower than  
84  $1.1 \times 10^{-4} \text{ mol L}^{-1}$  in  $0.01 \text{ mol L}^{-1} \text{ HClO}_4$ .

85 To investigate the behavior of monazite-cheralite at various temperatures, besides solubility  
86 experiments, it is essential to determine thermodynamics of formation of all structures in the system.  
87 Recently, the enthalpy of formation of rhabdophanes and the related monazites were determined  
88 with the application of high temperature oxide melt solution calorimetry (Shelyug et al., 2018). This  
89 study further suggested that Ln-rhabdophane ( $\text{LnPO}_4 \cdot n\text{H}_2\text{O}$ ;  $\text{Ln} = \text{La-Gd}$ ) was thermodynamically  
90 metastable with respect to the corresponding monazite plus water at all temperatures under 0.1 MPa  
91 water pressure. Another thermodynamic study of hydrated phosphates adopting the churchite  
92 structure ( $\text{LnPO}_4 \cdot 2\text{H}_2\text{O}$ ;  $\text{Ln} = \text{Gd-Lu}$ ) also confirmed its stability in the case of aqueous alteration  
93 of xenotimes, delaying the release of contained actinides into the environment (Subramani et al.,  
94 2019).

95 The present study evaluates the stability of Th-rhabdophanes  $\text{Ln}_{1-2x}\text{Ca}_x\text{Th}_x\text{PO}_4 \cdot n\text{H}_2\text{O}$  ( $\text{Ln} = \text{Pr}$ ,  
96  $\text{Nd}$ ;  $x = 0 - 0.15$ ) and corresponding monazite-cheralite solid solutions. These compositions were  
97 chosen to fulfill critical requirements of ceramic wastefrom for the specific conditioning of  
98 actinides such as the capability to incorporate up to 10 wt.% of highly radioactive actinides within  
99 their structure. The saturation phenomenon were demonstrated, providing means for determination  
100 of the solubility constants of the formed phases. Enthalpies of formation were obtained by high  
101 temperature oxide melt solution calorimetry. Combining these results, the  $\Delta G_f^{\circ}$ ,  $\Delta H_f^{\circ}$  and  $S_m^{\circ}$  values  
102 for Th-rhabdophane/monazite-cheralite solid solution were determined and used in simulations  
103 using PHREEQC software, leading to a better understanding of the chemical stability of these  
104 materials from a thermodynamic point of view.

105  
106

## 2 Materials and methods

### 107 2.1 Preparation and initial characterization of Th-rhabdophane precursors, $\text{Ln}_{1-}$ 108 $2x\text{Ca}_x\text{Th}_x\text{PO}_4 \cdot n\text{H}_2\text{O}$ ( $\text{Ln} = \text{Pr}, \text{Nd}$ ) and associated monazite-cheralite, $\text{Ln}_{1-2x}\text{Ca}_x\text{Th}_x\text{PO}_4$ .

109 The Th-rhabdophanes  $\text{Pr}_{1-2x}\text{Ca}_x\text{Th}_x\text{PO}_4 \cdot n\text{H}_2\text{O}$  ( $x = 0 - 0.15$ ) and  $\text{Nd}_{0.8}\text{Ca}_{0.1}\text{Th}_{0.1}\text{PO}_4 \cdot n\text{H}_2\text{O}$   
110 were synthesized according to the hydrothermal protocol reported in a previous study (Qin et al.,  
111 2017b). The metal salts used as starting materials were analytical grade and provided by Sigma-  
112 Aldrich:  $\text{PrCl}_3 \cdot 6\text{H}_2\text{O}$  (99.9%),  $\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$  (99.9%),  $\text{CaCl}_2 \cdot n\text{H}_2\text{O}$ ,  $\text{Th}(\text{NO}_3)_4 \cdot 4-5\text{H}_2\text{O}$ .  $\text{PrCl}_3$ ,  $\text{NdCl}_3$   
113 and  $\text{CaCl}_2$  were dissolved in 0.1M HCl and  $\text{Th}(\text{NO}_3)_4 \cdot 4-5\text{H}_2\text{O}$  in 4M  $\text{HNO}_3$ . The acids above were  
114 prepared from concentrated HCl (37%, Carlo Erba) and  $\text{HNO}_3$  (69.5%, Carlo Erba). The final  
115 concentration of each cation was determined in solution by inductively coupled plasma – optical

116 emission spectrometry (ICP-OES) and was about 0.5 M for PrCl<sub>3</sub>, NdCl<sub>3</sub>, and Th(NO<sub>3</sub>)<sub>4</sub>·while  
117 about 1.5 M for CaCl<sub>2</sub>.

118 Then, lanthanide, thorium and calcium solutions were weighed and mixed into a Teflon  
119 container. The Ln and Th cations were introduced in the proportion expected in the solid phase,  
120 whereas the stoichiometric ratio Ca/Th in the mixture was equal to 10. Then, 5 mol L<sup>-1</sup> H<sub>3</sub>PO<sub>4</sub>  
121 solution was added to the mixture of cations in order to obtain an excess of 3 mol. % of P with  
122 respect to (Ln + Th). The solution was stirred for 15 min and the Teflon container was placed in a  
123 Parr autoclave. The hydrothermal treatment was performed at 383 K in oven during 4 days. Then,  
124 the obtained precipitate was washed twice in water then once in ethanol and dried at 363 K  
125 overnight. Once the Th-rhabdophane powders were obtained, a part of the samples was calcined at  
126 1373 K for 6 h to obtain the associated monazite-cherelite solid solutions, Ln<sub>1-2x</sub>Ca<sub>x</sub>Th<sub>x</sub>PO<sub>4</sub> (Ln = Pr,  
127 Nd; x = 0 – 0.15) or Nd<sub>0.8</sub>Ca<sub>0.1</sub>Th<sub>0.1</sub>PO<sub>4</sub>.

128 The obtained powders were all characterized with powder X-ray diffraction (PXRD) on a  
129 Bruker D8 Advance diffractometer equipped with copper radiation (Cu Kα<sub>1,2</sub>, λ=1.54184 Å) using  
130 reflection geometry. The powders were placed in a special sample holder to avoid any radioactive  
131 contamination. Each PXRD pattern was collected from 5 to 100 ° (2θ) with a Δθ step of 0.019 °.  
132 For each step, the collection time was 3.68 s, resulting in a total counting time of about 3 hours. The  
133 PXRD patterns confirmed the single-phase nature of the rhabdophane and monazite-cherelite  
134 samples (see *Figure S1* of *Supporting Information*).

135 In order to determine the actual stoichiometry of the prepared Th-rhabdophanes, about 20 mg  
136 of the powders were fully dissolved in 2.5 mL fresh aqua regia. Once the dissolution was completed,  
137 these solutions were diluted with 0.16 mol L<sup>-1</sup> HNO<sub>3</sub> solution so that the elemental concentration of  
138 lanthanide was about 15 mg L<sup>-1</sup>. The elemental concentrations of Th, P, Ca, and Ln were then  
139 determined by ICP-OES on a Spectro Arcos EOP. Prior to analysis, the ICP-OES instrument was  
140 calibrated. The calibration solutions were obtained by dilution of commercially available SPEX  
141 standard solutions (C<sub>initial</sub> = 1000 mg L<sup>-1</sup>) using 0.16 mol L<sup>-1</sup> HNO<sub>3</sub>. The concentrations series of the  
142 calibration solutions for all elements of interest were fixed at 0, 0.25, 0.5, 0.75, 1, 2.5, 5, 10, and  
143 20 mg L<sup>-1</sup> (C<sub>Ca</sub> = C<sub>Th</sub> = C<sub>Nd</sub> = C<sub>P</sub>). For each element, four recommended wavelengths were  
144 considered. The calibration for a wavelength was considered valid if the coefficient of  
145 determination for the calibration curve, R<sup>2</sup>, was over 0.999. The measurement was considered  
146 reliable if the relative error between the values reported from different wavelengths was lower than  
147 5 %. Following this protocol, the detection limits were 2.5 mg L<sup>-1</sup> for Ca, 0.25 mg L<sup>-1</sup> for Th and  
148 Nd, and 1 mg L<sup>-1</sup> for P. The elemental concentration in solution was then calculated as the average  
149 of the values obtained for each emission wavelength. The standard error was estimated as twice the  
150 standard deviation. The chemical composition of the samples are listed in **Table 1**. Since as-  
151 prepared monazite-cherelite powders only partially dissolved in fresh aqua regia, the proportions of  
152 elements of interest were considered the same as in their Th-rhabdophane precursors.

153 The water content in Th-rhabdophane samples was determined by thermogravimetric analysis  
154 coupled with differential scanning calorimetry (TGA-DSC) in a Netzsch STA 449C. About 15 –  
155 20 mg of the powdered Th-rhabdophane sample were placed in a platinum crucible and were  
156 heated under 40 mL min<sup>-1</sup> flow of air to 1273 K at a rate of 10 K min<sup>-1</sup>. Empty crucible was used as  
157 a reference during baseline run prior to the experiment to correct for the drift in weight as a function  
158 of temperature. The calibration of the instrument's heat flow was performed against the heat  
159 capacity of a sapphire disk.

160 **Table 1.** Chemical composition (cationic mole ratios) of the rhabdophane samples  $\text{Ln}_{1-x}\text{Ca}_x\text{Th}_x\text{PO}_4 \cdot n\text{H}_2\text{O}$ , determined by ICP-OES after complete dissolution.  
 161

Sample name	Ln	Ca	Th
$\text{Pr}_{0.9}\text{Ca}_{0.05}\text{Th}_{0.05}\text{PO}_4 \cdot n\text{H}_2\text{O}$	0.892	0.049	0.059
$\text{Pr}_{0.8}\text{Ca}_{0.10}\text{Th}_{0.10}\text{PO}_4 \cdot n\text{H}_2\text{O}$	0.785	0.111	0.105
$\text{Pr}_{0.7}\text{Ca}_{0.15}\text{Th}_{0.15}\text{PO}_4 \cdot n\text{H}_2\text{O}$	0.697	0.150	0.143
$\text{Nd}_{0.8}\text{Ca}_{0.10}\text{Th}_{0.10}\text{PO}_4 \cdot n\text{H}_2\text{O}$	0.804	0.109	0.086

162

## 163 2.2 $\text{Nd}_{0.8}\text{Ca}_{0.10}\text{Th}_{0.10}\text{PO}_4$ solubility experiments

164 Solubility experiments were conducted starting from under-saturated conditions. For each  
 165 experiment, about 100 mg of  $\text{Nd}_{0.8}\text{Ca}_{0.10}\text{Th}_{0.10}\text{PO}_4$  was placed in a 120 mL Savillex jar containing  
 166 100 mL of 1, 0.32, or 0.1 mol L<sup>-1</sup> HNO<sub>3</sub> solution. These solutions were prepared by dilution of 15  
 167 mol L<sup>-1</sup> HNO<sub>3</sub> (69.5 %, Carlo-Erba). These jars were placed in a VWR incubating mini shaker at  
 168 298 K during the entire leaching process. 5 mL of solvent were regularly extracted from the jar and  
 169 were centrifuged for the measurement of Ca, Th, Nd, and P elemental concentrations by ICP-OES.  
 170 As the dissolution vessels were considered as closed systems, the elemental concentrations  
 171 stabilized if a saturation equilibrium was reached once three consecutive analyses of the Th, Nd,  
 172 and P concentrations were not significantly different (relative error ≤ 5 %). The Nd, Th and P  
 173 concentrations at equilibrium were calculated as the average of the last concentrations  
 174 measurements that were not significantly different by considering the experimental uncertainty.  
 175 Then, the uncertainty on the elemental concentrations at equilibrium was determined as twice the  
 176 standard deviation of the selected consecutive measurements. As the monazite matrix exhibited a  
 177 low solubility and as Ca was a minor component in the powder (about only 2 wt.%), its elemental  
 178 concentration was close to the detection limit of ICP-OES ( $C_{\text{Ca}} \leq 2.5 \text{ mg L}^{-1}$ ) leading to a large  
 179 uncertainty on the determined concentration. For experiments performed in the less acidic media,  
 180 the elemental concentration in Ca was thus calculated assuming that the dissolution was  
 181 stoichiometric. Then, these elemental concentration values as well as the proton activity were used  
 182 to calculate the standard solubility constant of monazite-cheralite  $\text{Nd}_{0.8}\text{Ca}_{0.10}\text{Th}_{0.10}\text{PO}_4$ .

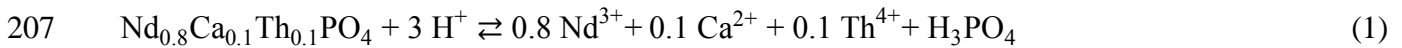
## 183 2.3 Calculation of standard solubility constant of $\text{Nd}_{0.8}\text{Ca}_{0.10}\text{Th}_{0.10}\text{PO}_4$

184 PHREEQC simulations (version 3.3.8.11728) (Parkhurst and Appelo, 2013) were performed  
 185 in order to calculate the activities of  $\text{Ca}^{2+}$ ,  $\text{Nd}^{3+}$ ,  $\text{Th}^{4+}$  and  $\text{H}_3\text{PO}_4$  in the 1, 0.32, and 0.1 mol L<sup>-1</sup>  
 186 HNO<sub>3</sub> solutions from the elemental concentrations at equilibrium. ThermoChimie database (version  
 187 10a) (Giffaut et al., 2014) was employed. The complexation constants of the inorganic species in  
 188 this database were mostly selected from internationally recognized thermodynamic databases.  
 189 Especially, it included the data of thorium species published by NEA-OECD's Thermochemical  
 190 Database (TDB) project (Rand et al., 2009). However, the data associated to neodymium species  
 191 were not included in the ThermoChimie database. In order to solve this problem, the  
 192 thermodynamic data of neodymium inorganic complexes were selected from one of the other well-  
 193 recognized database (LLNL-TDB) (Lawrence Livermore National Laboratory TDB) (Johnson et al.,  
 194 2000). Moreover, since rhabdophane  $\text{NdPO}_4 \cdot 0.667\text{H}_2\text{O}$  and  $\text{Th}_2(\text{PO}_4)_2(\text{HPO}_4) \cdot \text{H}_2\text{O}$  (TPHPH) are  
 195 considered potentially forming phases during the solubility experiments, their solubility constant

196 values, evaluated in the previous works (Gausse et al., 2016; Qin et al., 2017a), were introduced in  
 197 the used database as well.

198 The solubility tests were conducted in acidic conditions (*i.e.*, pH = 0 – 1) because of the very  
 199 high chemical durability of the materials. However, only a small amount of monazite solid was  
 200 dissolved during the whole test, *e.g.*, less than 7 mg of sample when making the test in 100 mL of  
 201 1 mol L<sup>-1</sup> HNO<sub>3</sub>. This result suggests that the concentration of HNO<sub>3</sub> can be considered as  
 202 unchanged and that the pH value can be deduced from the initial concentration of HNO<sub>3</sub>. The  
 203 method used to calculate the pH is described in the **Supporting Information**. The obtained values of  
 204 pH were equal to 0.13 ± 0.02, 0.63 ± 0.02 and 1.10 ± 0.02 for 0.1, 0.32 and 1 mol L<sup>-1</sup> HNO<sub>3</sub>,  
 205 respectively.

206 A protonation equilibrium is involved in the dissolution reaction.



208 Therefore, the solubility product of the monazite-cheralite solid solution <sup>\*</sup>K<sub>s</sub> can be defined  
 209 as follows:

$$210 \text{ }^*\text{K}_s(\text{monazite} - \text{cheralite}) = \frac{[\text{Nd}^{3+}]^{0.8}[\text{Ca}^{2+}]^{0.1}[\text{Th}^{4+}]^{0.1}[\text{H}_3\text{PO}_4]}{[\text{H}^+]^3} \quad (2)$$

211 where [i] denotes the molarity of species (expressed in mol L<sup>-1</sup>).

212 The conversion between molarity and molality, m<sub>i</sub> (mol kg<sup>-1</sup>), was done using the following  
 213 expression:

$$214 m_i = \frac{1000 [i]}{1000 \rho - [i] M_i} \quad (3)$$

215 where ρ (kg L<sup>-1</sup>) is the density of the solution, and M<sub>i</sub> (g mol<sup>-1</sup>) is the molar mass of species, *i*. The  
 216 density of HNO<sub>3</sub> solutions was calculated using the model proposed by Novotny and Söhnel  
 217 (Novotny and Söhnel, 1988) (see **Table S1** of **Supporting Information**).

218 The solubility product, expressed as a function of the molalities, <sup>\*</sup>K<sub>s</sub><sup>m</sup>, is given below:

$$219 \text{ }^*\text{K}_s^m(\text{monazite-cheralite}) = \frac{m_{\text{Nd}^{3+}}^{0.8} \times m_{\text{Ca}^{2+}}^{0.1} \times m_{\text{Th}^{4+}}^{0.1} \times m_{\text{H}_3\text{PO}_4}}{m_{\text{H}^+}^3} \quad (4)$$

220 The standard solubility constant of the monazite-cheralite Nd<sub>0.8</sub>Ca<sub>0.10</sub>Th<sub>0.10</sub>PO<sub>4</sub> is defined as:

$$221 \text{ }^*\text{K}_s^\circ(\text{monazite-cheralite}) = \frac{(\text{Nd}^{3+})^{0.8} \times (\text{Ca}^{2+})^{0.1} \times (\text{Th}^{4+})^{0.1} \times (\text{H}_3\text{PO}_4)}{(\text{H}^+)^3} \quad (5)$$

222 where (i) denotes the activity of species, *i*.

223 The Specific Ion interaction Theory (SIT) was used to estimate the activity coefficient, γ<sub>i</sub>, that  
 224 relates the activity of the species, (i) to its molality, m<sub>i</sub> (Ciavatta, 1980). The lg γ<sub>i</sub> was evaluated as:

$$225 \lg \gamma_i = -z_i^2 D + \sum_j \varepsilon(i,j) m_j \quad (6)$$

226 where, z<sub>i</sub> is the charge of species *i*, ε(*i*, *j*) is the interaction coefficient between ion *i* and counter-ion  
 227 *j* (see **Table S2** of **Supporting Information**) and D is the term of Debye-Hückel expressed as:

228 
$$D = \frac{A\sqrt{I_m}}{1+B a_j\sqrt{I_m}} \quad (7)$$

229 where, A and B are temperature and pressure dependent constants, and  $a_j$  is an ion size parameter  
 230 for the hydrated ion,  $j$ . The value of the Debye-Hückel limiting slope, A, is  $(0.509 \pm$   
 231  $0.001) \text{ kg}^{1/2} \text{ mol}^{-1/2}$  at 298 K and 1 bar. The recommended  $B a_j$  value is equal to  $1.5 \text{ kg}^{1/2} \text{ mol}^{-1/2} \text{ m}^{-1}$  at  
 232 298 K and 1 bar (Rand et al., 2009).

233 Combining equations (4-6) leads to following expression:

234 
$$\lg {}^*K_s^\circ = \Delta z^2 D + \Delta \varepsilon I_m + \lg {}^*K_s^m \quad (8)$$

235 where  $\Delta X$  stands for  $\sum_i \nu_i X_i$ .

236 The  $\Delta \varepsilon$  term in equation (8) was simplified by considering only the interactions between the  
 237 ions participating in the reaction and the ions of the electrolyte solution. This approximation could  
 238 be done because the ions of the electrolyte solution have concentrations much higher than those  
 239 participating in the reaction. Moreover, the  $\varepsilon(i,j)$  value for ions with the same charge sign is equal  
 240 zero. It is also null for uncharged species.

241 The standard solubility constants  $K_{s,0}^\circ$  were also calculated by using  $\text{PO}_4^{3-}$  species:

242 
$$K_{s,0}^\circ (\text{monazite-cherallite}) = (\text{Nd}^{3+})^{0.8} \times (\text{Ca}^{2+})^{0.1} \times (\text{Th}^{4+})^{0.1} \times (\text{PO}_4^{3-}) \quad (9)$$

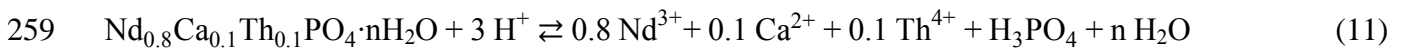
243 It is worth noting that  $K_{s,0}^\circ$  can be deduced from  ${}^*K_s^\circ$  according to:

244 
$$K_{s,0}^\circ = {}^*K_s^\circ \times K_{a1} \times K_{a2} \times K_{a3} \quad (10)$$

245 where,  $K_{a1}$ ,  $K_{a2}$ ,  $K_{a3}$  are the phosphoric acid constants at 298 K related to  $\text{H}_3\text{PO}_4/\text{H}_2\text{PO}_4^-$  ( $\text{p}K_{a1} =$   
 246  $2.14$ ),  $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$  ( $\text{p}K_{a2} = 7.212$ ), and  $\text{HPO}_4^{2-}/\text{PO}_4^{3-}$  ( $\text{p}K_{a3} = 12.35$ ), respectively (see **Table S3**  
 247 of **Supporting Information**).

248 Several neoformed phases such as rhabdophane, TPHPH, Th-rhabdophane,  
 249  $\text{Nd}_{0.8}\text{Ca}_{0.10}\text{Th}_{0.10}\text{PO}_4 \cdot n\text{H}_2\text{O}$  or the monazite-cherallite  $\text{Nd}_{0.8}\text{Ca}_{0.10}\text{Th}_{0.10}\text{PO}_4$  itself could act as  
 250 solubility-controlling phase in our experiments. Indeed, Shelyug *et al.* (Shelyug et al., 2018) already  
 251 reported the Gibbs free energy of reaction from rhabdophane  $\text{NdPO}_4 \cdot 0.746\text{H}_2\text{O}$  to monazite  $\text{NdPO}_4$   
 252 plus water at 298 K as  $-9.1 \pm 9.5 \text{ kJ mol}^{-1}$ . As the Gibbs free energy at 298 K is close to 0 taking  
 253 into account the uncertainty associated to this value, monazite  $\text{NdPO}_4$  appears as stable as  
 254 rhabdophane  $\text{NdPO}_4 \cdot n\text{H}_2\text{O}$ . The Gibbs free energy of the reaction from  $\text{Nd}_{0.8}\text{Ca}_{0.10}\text{Th}_{0.10}\text{PO}_4 \cdot n\text{H}_2\text{O}$   
 255 to monazite-cherallite  $\text{Nd}_{0.8}\text{Ca}_{0.10}\text{Th}_{0.10}\text{PO}_4$  plus water could be also close to zero, which would  
 256 mean that both Th-rhabdophane and monazite-cherallite could act as the solubility controlling-phase.

257 Assuming that the Th-rhabdophane is the phase that controls the equilibrium, the dissolution-  
 258 precipitation of  $\text{Nd}_{0.8}\text{Ca}_{0.10}\text{Th}_{0.10}\text{PO}_4 \cdot n\text{H}_2\text{O}$  at  $\text{pH} = 0 - 1$  can be written as follows:



260 Thus, the standard solubility constant  ${}^*K_s^\circ$  of  $\text{Nd}_{0.8}\text{Ca}_{0.10}\text{Th}_{0.10}\text{PO}_4 \cdot n\text{H}_2\text{O}$  rhabdophane can be  
 261 calculated as:



262 
$$K_{s,0}^{\circ}(\text{rhabdophane}) = \frac{(\text{Nd}^{3+})^{0.8} \times (\text{Ca}^{2+})^{0.1} \times (\text{Th}^{4+})^{0.1} \times (\text{H}_3\text{PO}_4) \times (\text{H}_2\text{O})^n}{(\text{H}^+)^3} \quad (12)$$

263 The standard solubility constants  $K_{s,0}^{\circ}$  were also calculated by using  $\text{PO}_4^{3-}$  species:

264 
$$K_{s,0}^{\circ}(\text{rhabdophane}) = (\text{Nd}^{3+})^{0.8} \times (\text{Ca}^{2+})^{0.1} \times (\text{Th}^{4+})^{0.1} \times (\text{PO}_4^{3-}) \times (\text{H}_2\text{O})^n \quad (13)$$

265 Thus, the difference between the values of  $K_{s,0}^{\circ}(\text{rhabdophane})$  and of  $K_{s,0}^{\circ}(\text{monazite-cherallite})$   
 266 can be expressed as:

267 
$$\lg K_{s,0}^{\circ}(\text{rhabdophane}) = \lg K_{s,0}^{\circ}(\text{monazite-cherallite}) + n \times \lg (\text{H}_2\text{O}) \quad (14)$$

268 The activity of water in  $\text{HNO}_3$  can be calculated from:

269 
$$\lg(\text{H}_2\text{O}) = - \frac{2 \times m_{\text{HNO}_3} \times \phi_m}{\ln 10 \times 55.508} \quad (15)$$

270 where  $\phi_m$  is the osmotic coefficient of the mixture and  $55.508 \text{ mol kg}^{-1}$  is the molality of pure water.  
 271 Lewis and Randall (Lewis et al., 1961) have given a general formula to determine the osmotic  
 272 coefficient for an ionic medium with concentration much larger than those of the reacting ions.  
 273 Therefore, the osmotic coefficient of the  $\text{HNO}_3$  solutions can be calculated as follows:

274 
$$1 - \phi_m = \frac{A \times \ln 10}{I_m \times (\text{Ba}_j)^3} \left[ 1 + \text{Ba}_j \sqrt{I_m} - 2 \times \ln(1 + \text{Ba}_j \sqrt{I_m}) - \frac{1}{1 + \text{Ba}_j \sqrt{I_m}} \right] - 0.5 \times \ln 10 \times \varepsilon (\text{H}^+, \text{NO}_3^-) \times m_{\text{HNO}_3} \quad (16)$$

## 275 **2.4 High-temperature oxide melt solution calorimetry**

276 Rhabdophane and monazite-cherallite samples were all submitted to high-temperature oxide  
 277 melt solution calorimetry. The experiments were performed in a custom-built Tian-Calvet twin  
 278 calorimeter (Navrotsky, 1977, 2014). The methodology was the same as in the earlier studies of  
 279 rhabdophane end-members  $\text{LnPO}_4 \cdot n\text{H}_2\text{O}$  (Shelyug et al., 2018) and other materials (Hirsch et al.,  
 280 2017; Neumeier et al., 2017). About 5 mg of the sample powder was pressed into pellet and  
 281 dropped into molten lead borate ( $2\text{PbO} \cdot \text{B}_2\text{O}_3$ ) kept in a Pt crucible inside the cell at 1073 K. The  
 282 cell was flushed ( $40 \text{ mL min}^{-1}$ ) and the solvent was bubbled ( $4.5 \text{ mL min}^{-1}$ ) with oxygen to remove  
 283 the water vapor from the cell and to promote dissolution. The measured signal of heat flow over  
 284 time was integrated using CALISTO (Setaram) software to calculate the enthalpy of drop solution.  
 285 Eight measurements were taken for each sample to collect statistics.

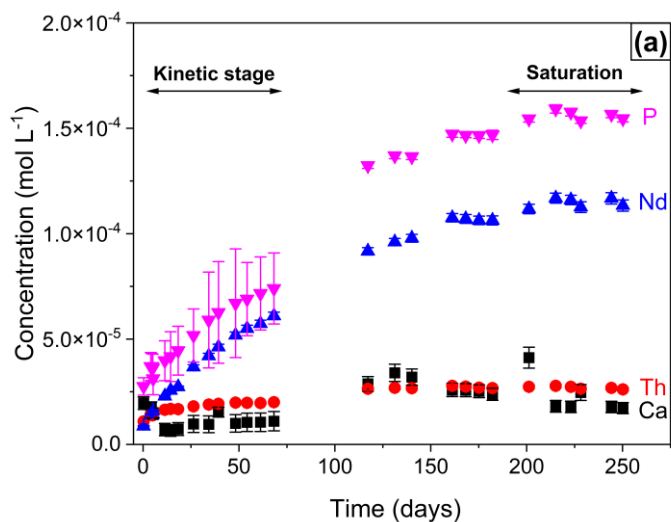
286

## 287 **3 Results and Discussion**

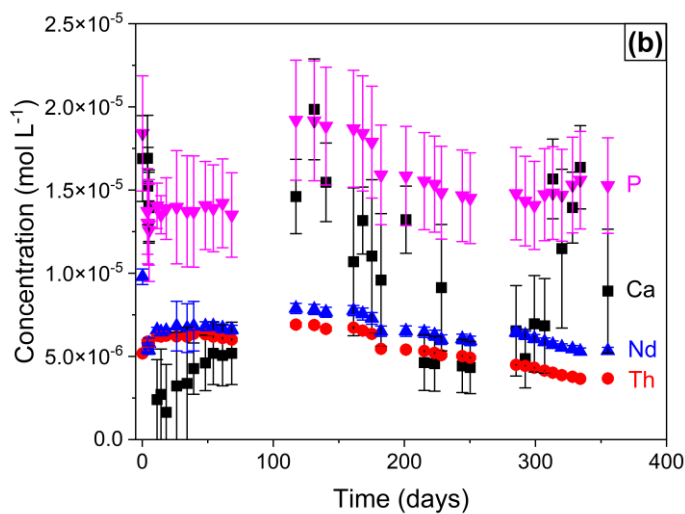
### 288 **3.1 Solubility experiments**

289 The evolution of elemental concentrations during the leaching of monazite-cherallite  
 290  $\text{Nd}_{0.8}\text{Ca}_{0.10}\text{Th}_{0.10}\text{PO}_4$  in  $1 \text{ mol L}^{-1} \text{HNO}_3$  is presented in **Figure 1a**. The elemental concentrations  
 291 increased gradually, and then reached a plateau after about 200 days, which suggested the  
 292 establishment of thermodynamic equilibrium. The elemental concentrations determined at  
 293 thermodynamic equilibrium are listed in **Table 2**. The evolution of Th, Nd and P concentrations  
 294 stated the stoichiometric dissolution of the monazite-cherallite within the experimental error (*i.e.*

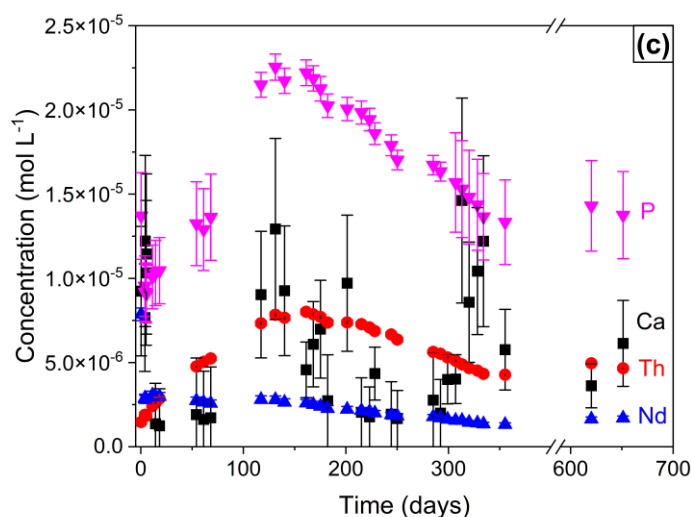
295 [Th]/[P] =  $0.17 \pm 0.02$ , [Nd]/[P] =  $0.74 \pm 0.05$ , [Ca]/[P] =  $0.12 \pm 0.04$  and  $\Sigma[\text{cations}]/[\text{P}] = 1.0 \pm$   
 296  $0.4$ ). This result suggested that stoichiometric saturation occurred and that the composition of the  
 297 monazite-cherlita remained invariant during the experiment. The Ca concentration showed  
 298 significant fluctuations due to the higher detection limit of ICP-OES for this element and/or  
 299 potential contamination. The thorium concentration was equal to  $(2.7 \pm 0.1) \times 10^{-5} \text{ mol L}^{-1}$  and the  
 300 associated relative mass loss reached  $6.3 \pm 0.3 \%$  of the initial Th in monazite-cherlita (**Table 2**).  
 301 These values were obtained in the most acidic solution (*i.e.*  $1 \text{ mol L}^{-1} \text{ HNO}_3$ ) confirming its strong  
 302 chemical durability.



303



304



305

306 **Figure 1.** Evolution of elemental concentrations obtained during the leaching of  
 307  $\text{Nd}_{0.8}\text{Ca}_{0.10}\text{Th}_{0.10}\text{PO}_4$  in  $1 \text{ mol L}^{-1}$  (a),  $0.32 \text{ mol L}^{-1}$  (b) and  $0.1 \text{ mol L}^{-1}$ (c) of  $\text{HNO}_3$  at  
 308 298 K. C(Ca) (■), C(Th) (●), C(Nd) (▲) and C(P) (▼).

309

310 **Table 2.** Elemental concentrations of Ca, Th, Nd and P at equilibrium (average of the last  
 311 concentrations measurements that were not significantly different, uncertainty  
 312 determined as twice the standard deviation of the selected consecutive measurements),  
 313 and relative mass loss of thorium obtained at the end of the solubility tests of  
 314  $\text{Nd}_{0.8}\text{Ca}_{0.10}\text{Th}_{0.10}\text{PO}_4$  at 298 K.

$C_{\text{HNO}_3}$ [ $\text{mol L}^{-1}$ ]	[Ca] [ $\times 10^{-5} \text{ mol L}^{-1}$ ]	[Th] [ $\times 10^{-5} \text{ mol L}^{-1}$ ]	[Nd] [ $\times 10^{-5} \text{ mol L}^{-1}$ ]	[P] [ $\times 10^{-5} \text{ mol L}^{-1}$ ]	$\frac{m_{\text{Th(dissolved)}}}{m_{\text{Th(solid)}}}$ [%]
$1.00 \pm 0.02$	$1.9 \pm 0.6$	$2.7 \pm 0.1$	$11.5 \pm 0.4$	$15.6 \pm 0.5$	$6.3 \pm 0.3$
$0.32 \pm 0.01$	$1.0 \pm 0.9$	$0.5 \pm 0.2$	$0.6 \pm 0.2$	$1.6 \pm 0.4$	$1.0 \pm 0.5$
$0.10 \pm 0.01$	$0.8 \pm 0.8$	$0.47 \pm 0.06$	$0.2 \pm 0.1$	$1.4 \pm 0.3$	$1.1 \pm 0.3$

315

316 For the system with  $0.32 \text{ mol L}^{-1} \text{ HNO}_3$  (**Figure 1b**), the elemental concentrations of Th, Nd,  
 317 and P, first increased gradually and reached a maximum after about 100 days. Then, the  
 318 concentrations decreased slowly to reach a plateau after about 350 days. The rate of release of the  
 319 elements was lower and the concentration at equilibrium was lower by one order of magnitude than  
 320 in  $1 \text{ mol L}^{-1} \text{ HNO}_3$ . Likewise, when  $0.1 \text{ mol L}^{-1} \text{ HNO}_3$  was used, the evolution of elemental  
 321 concentrations was even slower than that reported in  $0.32 \text{ mol L}^{-1} \text{ HNO}_3$ . The maximum of the  
 322 concentrations took place at about 150 days whereas the equilibrium was reached after 600 days. In  
 323 both cases, the evolution of the concentrations indicated that the dissolution of the monazite-  
 324 cheralite was not stoichiometric. The shape of the curves suggested that super-saturated conditions  
 325 were attained before the precipitation of a phase incorporating all the elements released in solution.  
 326 However, even if the proportion of Th in the solution was considered to be over-stoichiometric  
 327 compared to the initial powder, only 1 % of Th was released in the solution (see **Table 2**). Unlike  
 328 what happened in  $1 \text{ mol L}^{-1} \text{ HNO}_3$ , the results obtained in  $0.32$  and  $0.1 \text{ mol L}^{-1} \text{ HNO}_3$  solutions  
 329 clearly did not meet the criteria for stoichiometric saturation as defined in (Bruno et al., 2007).  
 330 Nevertheless, we decided to calculate the monazite-cheralite standard solubility constant in the  
 331 three leaching media and to compare the obtained values with the reference data obtained in  $1 \text{ mol}$   
 332  $\text{L}^{-1} \text{ HNO}_3$ .

333 According to the thorium loss, the amount of dissolved monazite-cheralite reached about  
334  $3 \times 10^{-5}$  mol in  $1 \text{ mol L}^{-1} \text{ HNO}_3$ , and  $0.4 \times 10^{-5}$  mol in  $0.32$  and  $0.1 \text{ mol L}^{-1} \text{ HNO}_3$ . Based on Eq. (1),  
335 the associated consumption of  $\text{H}^+$  was about  $8 \times 10^{-4}$  mol and  $1 \times 10^{-4}$  mol in  $1 \text{ mol L}^{-1} \text{ HNO}_3$  and  
336 in  $0.32$  or  $0.1 \text{ mol L}^{-1} \text{ HNO}_3$ , respectively. Therefore, the proportion of  $\text{H}^+$  consumed by the  
337 dissolution of monazite-cheralite reached  $0.8 \%$ ,  $0.4 \%$  and  $1.3 \%$  of the total amount of available  
338 protons in  $1$ ,  $0.32$ , and  $0.1 \text{ mol L}^{-1}$  of  $\text{HNO}_3$ , respectively. All these results validated the hypothesis  
339 made concerning the invariant proton concentration during the solubility experiments.

340 The speciation in solution was then simulated by PHREEQC considering the elemental  
341 concentrations measured at equilibrium (**Table 2**) and the calculated pH values (**Table 3**)  
342 (Parkhurst and Appelo, 2013). The calculated molalities and activities of the species of interest (*i.e.*,  
343  $\text{Ca}^{2+}$ ,  $\text{Th}^{4+}$ ,  $\text{Nd}^{3+}$ ,  $\text{H}_3\text{PO}_4$ ) are also listed in **Table 3**.

344

345 **Table 3.** pH values and calculated molalities and activities of the species of interest obtained at  
 346 thermodynamic equilibrium during solubility experiments of Nd<sub>0.8</sub>Ca<sub>0.10</sub>Th<sub>0.10</sub>PO<sub>4</sub> at  
 347 298 K

$C_{\text{HNO}_3}$ [mol L <sup>-1</sup> ]	pH	Molalities [ $\times 10^{-5}$ mol kg <sup>-1</sup> ]				Activities [ $\times 10^{-5}$ ]			
		$m_{\text{Ca}^{2+}}$	$m_{\text{Th}^{4+}}$	$m_{\text{Nd}^{3+}}$	$m_{\text{H}_3\text{PO}_4}$	$\text{Ca}^{2+}$	$\text{Th}^{4+}$	$\text{Nd}^{3+}$	$\text{H}_3\text{PO}_4$
1.00	0.13	1.9 ± 0.6	0.049 ± 0.002	7.6 ± 0.3	14.9 ± 0.6	3 ± 1	(1.3 ± 0.1) $\times 10^{-4}$	0.11 ± 0.01	14.9 ± 0.4
0.32	0.63	1.0 ± 0.9	0.3 ± 0.1	0.5 ± 0.1	1.5 ± 0.3	0.2 ± 0.2	(1.7 ± 0.7) $\times 10^{-3}$	0.02 ± 0.01	1.5 ± 0.3
0.10	1.10	0.8 ± 0.8	0.32 ± 0.04	0.13 ± 0.02	1.3 ± 0.2	0.3 ± 0.3	(7 ± 1) $\times 10^{-3}$	0.01 ± 0.01	1.3 ± 0.2

348

349 Assuming the dissolving monazite-cheralite to be the solubility-controlling phase, the values  
 350 of  $\lg^*K_s^m$  (monazite-cheralite) were calculated according to Eq. (4) as  $-7.8 \pm 0.1$ ,  $-8.2 \pm 0.3$ ,  
 351 and  $-7.4 \pm 0.2$  in 1, 0.32, and 0.1 mol L<sup>-1</sup> HNO<sub>3</sub>, respectively. The  $\lg^*K_s^o$  (monazite-cheralite) values  
 352 were calculated from Eq. (5) as  $-9.6 \pm 0.1$ ,  $-9.6 \pm 0.3$  and  $-8.4 \pm 0.2$  for 1, 0.32, and 0.1 mol L<sup>-1</sup>  
 353 HNO<sub>3</sub>, respectively. According to Eq. (9), the associated values of standard solubility constant,  
 354  $\lg K_{s,0}^o$  (monazite-cheralite), were  $-31.1 \pm 0.1$ ,  $-31.3 \pm 0.4$ , and  $-30.1 \pm 0.3$ , respectively. All the  
 355 values obtained in the three leaching media are reported in **Table 4**.

356 On the contrary, if Th-rhabdophane was the solubility-controlling phase, the solubility  
 357 constant could be calculated using Eq. (14). According to TG analysis, the number of water  
 358 molecules in the chemical formula for this sample was 0.820. Based on Eq. (15) and (16), the  
 359 values of  $n \times \lg(\text{H}_2\text{O})$  reached  $-0.015$ ,  $-0.005$  and  $-0.001$  in 1, 0.32, and 0.1 mol L<sup>-1</sup> HNO<sub>3</sub>,  
 360 respectively. Since these values were an order of magnitude smaller than the uncertainty associated  
 361 with  $\lg K_{s,0}^o$  (monazite-cheralite) (*i.e.* 0.1 – 0.4), it was assumed that  $\lg K_{s,0}^o$  (Th-rhabdophane) and  
 362  $\lg K_{s,0}^o$  (monazite-cheralite) were not significantly different.

363 The  $\lg K_{s,0}^o$  values determined at pH = 0.13 and 0.63 are consistent taking into account the  
 364 associated uncertainties. Meanwhile, the  $\lg K_{s,0}^o$  value determined at pH = 1.10 was slightly higher  
 365 than the values determined at lower pH. One explanation for this difference was that  
 366 thermodynamic equilibrium could not have been attained at pH 1.1 due to the very slow decrease of  
 367 the elemental concentrations in solution, or the dissolving monazite-cheralite was not the phase that  
 368 controlled the elemental concentration at saturation. Thus, this value was not used in the estimation  
 369 of the final  $\lg K_{s,0}^o$  (Th-rhabdophane or monazite-cheralite) value at 298 K. The selected value for  
 370  $\lg K_{s,0}^o$  (Th-rhabdophane or monazite-cheralite) at 298 K was  $-31.2 \pm 0.3$ .

371

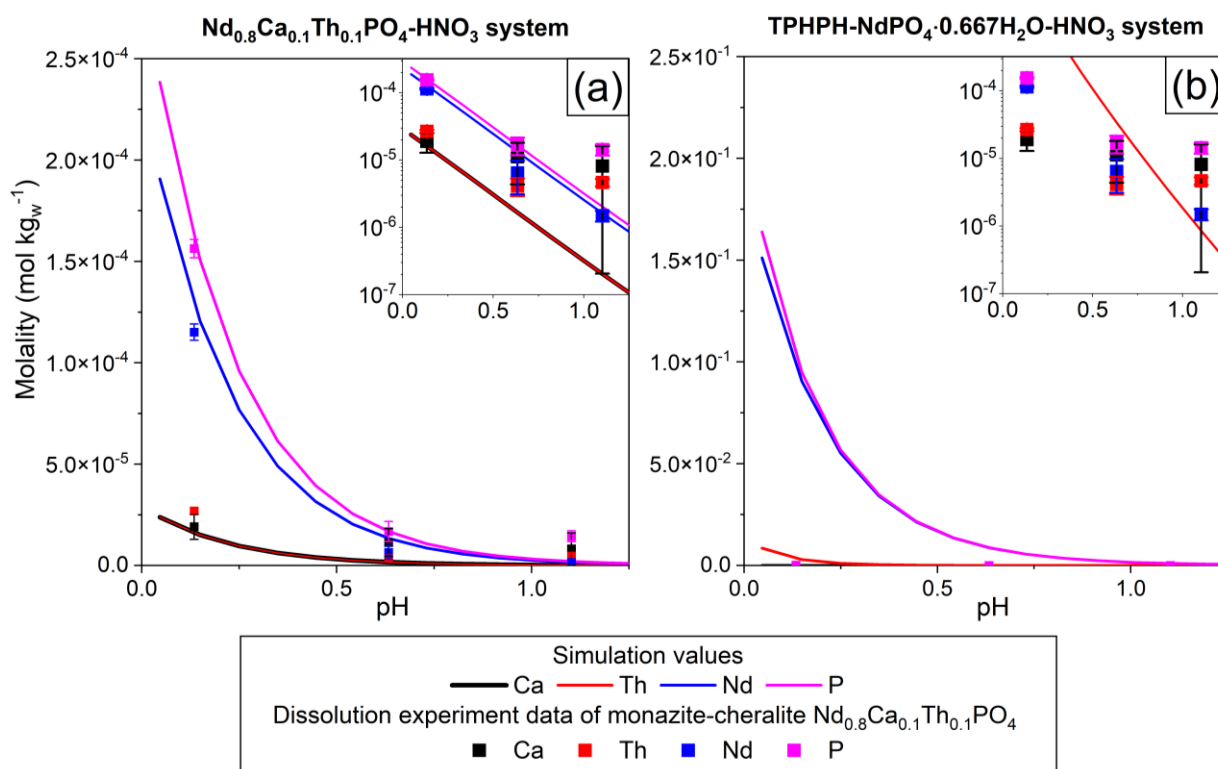
372 **Table 4.** Solubility products and standard solubility constants obtained at thermodynamic  
 373 equilibrium during solubility experiments of  $\text{Nd}_{0.8}\text{Ca}_{0.10}\text{Th}_{0.10}\text{PO}_4$  at 298 K in several  
 374 nitric acid media.

pH	$\lg^* K_s^m$	$\lg^* K_s^\circ$	$\lg K_{s,0}^\circ$
$0.13 \pm 0.01$	$-7.8 \pm 0.1$	$-9.6 \pm 0.1$	$-31.1 \pm 0.1$
$0.63 \pm 0.01$	$-8.2 \pm 0.3$	$-9.6 \pm 0.3$	$-31.3 \pm 0.4$
$1.10 \pm 0.01$	$-7.4 \pm 0.2$	$-8.4 \pm 0.2$	$-30.1 \pm 0.3$

375

376 Once the  $\lg K_{s,0}^\circ$  was determined, it was introduced into the ThermoChimie database and  
 377 PHREEQC simulations were performed for the  $\text{Nd}_{0.8}\text{Th}_{0.1}\text{Ca}_{0.1}\text{PO}_4\text{-HNO}_3$  and  
 378  $\text{TPHPH+NdPO}_4\cdot 0.667\text{H}_2\text{O/HNO}_3$  systems. The evolution of the elemental concentrations at  
 379 thermodynamic equilibrium as the function of pH is presented in **Figure 2**. The results of the  
 380 PHREEQC simulation of the  $\text{Nd}_{0.8}\text{Th}_{0.1}\text{Ca}_{0.1}\text{PO}_4/\text{HNO}_3$  system (**Figure 2a**) were consistent with the  
 381 experimental data reported in **Table 2**. However, the simulations suggested that the Nd and P  
 382 elemental concentrations should be about three orders of magnitude higher than the experimental  
 383 data if controlled by the  $\text{TPHPH+NdPO}_4\cdot 0.667\text{H}_2\text{O/HNO}_3$  system (**Figure 2b**). Meanwhile, if  
 384 controlled by the  $\text{TPHPH+NdPO}_4\cdot 0.667\text{H}_2\text{O/HNO}_3$  system, the simulated Th concentration should  
 385 be two orders of magnitude higher than that obtained at  $\text{pH} = 0.1$ . However, at  $\text{pH} = 1.1$ , the  
 386 simulated Th concentration controlled by the  $\text{TPHPH+NdPO}_4\cdot 0.667\text{H}_2\text{O/HNO}_3$  system was closer  
 387 to the experimental data than in the case of equilibrium with the Th-rhabdophane or monazite-  
 388 cheralite. This result suggested that the solubility-controlling phase was always Th-rhabdophane  
 389  $\text{Nd}_{0.8}\text{Th}_{0.1}\text{Ca}_{0.1}\text{PO}_4\cdot n\text{H}_2\text{O}$  or monazite-cheralite  $\text{Nd}_{0.8}\text{Th}_{0.1}\text{Ca}_{0.1}\text{PO}_4$  when the concentration of  $\text{HNO}_3$   
 390 was in the range between 0.32 and 1 mol  $\text{L}^{-1}$ . However, for acid concentration equal to or lower than  
 391 0.1 mol  $\text{L}^{-1}$ , TPHPH could have formed and control the concentration of thorium. This might be  
 392 another reason for incongruity between the elemental concentrations observed during the  
 393 solubility experiment performed in 0.1 mol  $\text{L}^{-1}$   $\text{HNO}_3$ . It could also explain why the  $\lg K_{s,0}^\circ$   
 394 determined at  $\text{pH} = 1.1$  was not consistent with the values obtained at  $\text{pH} = 0.13$  and 0.63 (**Table 4**).

395



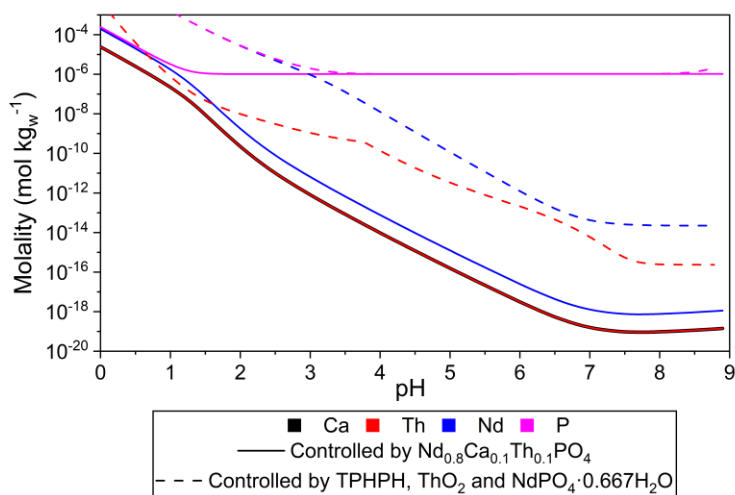
396

397 **Figure 2.** Evolution of elemental concentrations at thermodynamic equilibrium vs. pH and  
 398 comparison of the experimental data obtained with the results of the simulations  
 399 considering that the monazite-cheralite,  $\text{Nd}_{0.8}\text{Th}_{0.1}\text{Ca}_{0.1}\text{PO}_4$  (a) or the  
 400 TPHPH+ $\text{NdPO}_4 \cdot 0.667\text{H}_2\text{O}$  (b) are the solubility controlling phases.

401

402 Finally, as the aqueous conditions in the repository site are neutral or slightly alkaline  
 403 (OCDE/AEN, 1999), a complementary simulation by PHREEQC was performed from pH 0 to 8.5  
 404 in order to determine the elemental concentrations obtained when reaching saturation conditions for  
 405 both TPHPH+ $\text{ThO}_2$ + $\text{NdPO}_4 \cdot 0.667\text{H}_2\text{O}/\text{HNO}_3/\text{NaOH}$  and  $\text{Nd}_{0.8}\text{Th}_{0.1}\text{Ca}_{0.1}\text{PO}_4/\text{HNO}_3/\text{NaOH}$  systems  
 406 (**Figure 3**). It is worth noting that in order to better simulate the contribution of other phosphate  
 407 minerals to the elemental concentration in phosphorus, it was set to  $10^{-6} \text{ mol L}^{-1}$  during the whole  
 408 simulation. For the first system, the thorium molality dropped below  $10^{-12} \text{ mol kg}_w^{-1}$  when the pH  
 409 was above 6 and its solubility-controlling phase was  $\text{ThO}_2$ . For the second system,  $m_{\text{Th}}$  was even  
 410 less than  $10^{-17} \text{ mol kg}_w^{-1}$  for  $\text{pH} \geq 6$ , which was even lower than in the case where  $\text{ThO}_2$  was the  
 411 solubility-controlling phase. Consequently, by applying the  $\lg K_{s,0}^\circ$  value determined in this study,  
 412 these simulation results suggest that  $\text{Nd}_{0.8}\text{Th}_{0.1}\text{Ca}_{0.1}\text{PO}_4$  has exceptional chemical stability in near  
 413 neutral conditions and that using this phase as a conditioning matrix guarantees virtually no Th  
 414 release in the groundwater in the long term.

415



416

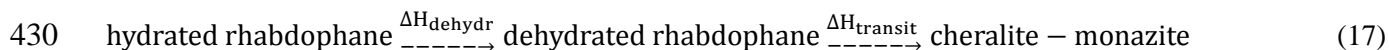
417 **Figure 3.** Molalities obtained at thermodynamic equilibrium in near neutral conditions when  
 418 considering the TPHPH+ThO<sub>2</sub>+NdPO<sub>4</sub>·0.667H<sub>2</sub>O/HNO<sub>3</sub>/NaOH system and the  
 419 Nd<sub>0.8</sub>Th<sub>0.1</sub>Ca<sub>0.1</sub>PO<sub>4</sub>/HNO<sub>3</sub>/NaOH system with [P]<sub>min</sub> = 10<sup>-6</sup> mol L<sup>-1</sup>.

420

## 421 3.2 High temperature calorimetry

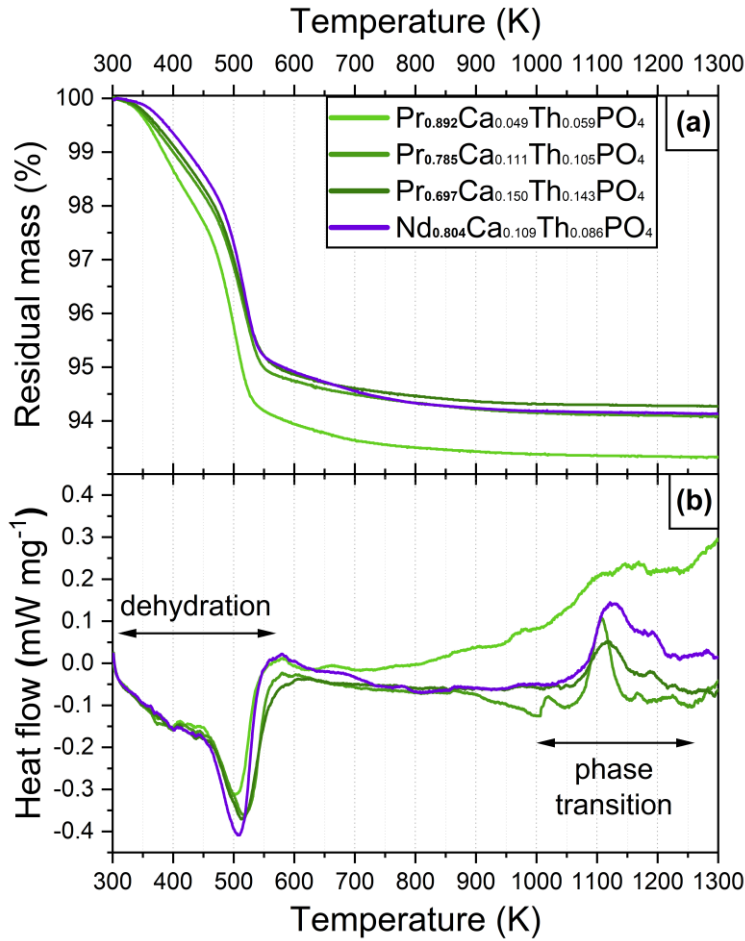
### 422 3.2.1 Thermal behavior and data from TG-DSC analyses

423 Prior to further thermodynamic investigations, all samples were studied by TGA-DSC. The  
 424 recorded scans are given in **Figure 4**. The first endothermic heat effect and the associated mass loss  
 425 are most likely the loss of bonded water, while the exothermic peak at constant mass is the phase  
 426 transition between the Th-rhabdophane and the cheralite-monazite phase. Dehydration occurred  
 427 between 300 and 580 K, whereas the transition from dehydrated rhabdophane to monazite-cheralite  
 428 occurred between 1000 and 1250 K. Similar processes were observed before for the Ln-  
 429 rhabdophane series in Shelyug et al., (2018) and occur in the following steps:



431



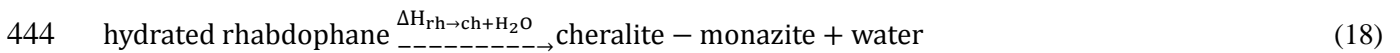


432

433 **Figure 4** TGA (a) and DSC (b) scans of the Th-rhabdophane samples in this study. For simplicity,  
 434 structural water ( $n\text{H}_2\text{O}$ ) is omitted from samples names.

435

436 The enthalpies of dehydration,  $\Delta H_{\text{dehydr}}$ , and phase transition,  $\Delta H_{\text{transit}}$ , can be found from  
 437 direct integration of the heat flow signal and recalculated per mole of sample and are listed in **Table**  
 438 **5**. The water contents of the samples are calculated from water loss and are larger for the samples  
 439 with higher lanthanide content considering the large ionic radius of Ln ions, which defines the size  
 440 of the rhabdophane structure channels. The average enthalpy of dehydration for the samples in this  
 441 study is less endothermic than that of Ln-rhabdophanes studied before ( $40.8 \pm 0.8$  vs  $50.3 \pm 1.4$ )  
 442 (Shelyug et al., 2018). In order to evaluate overall stability of the monazite-cheralite solid solution  
 443 in contact with water, the following reaction is considered:



445 Its enthalpy is calculated at room temperature as:

446  $\Delta H_{\text{rh} \rightarrow \text{ch} + \text{H}_2\text{O}}^{\text{DSC}} = \Delta H_{\text{dehydr}} + \Delta H_{\text{transit}} - z \times \Delta H_{\text{vapor}}$  (19)

447 where  $\Delta H_{\text{vapor}} = 44 \text{ kJ mol}^{-1}$  is the heat of water vaporization at 298 K. According to this  
 448 equation, the enthalpy of reaction of Th-rhabdophane to cheralite-monazite plus water at 298 K is  
 449 between  $-15$  and  $-30 \text{ kJ mol}^{-1}$ , which is slightly more exothermic compared to the values of the  
 450 corresponding reaction in the Ln-rhabdophane series (Shelyug et al., 2018) meaning even less

451 favorable interaction of monazite-cheralite with water to form rhabdophane. This means that the  
 452 incorporation of Th might strengthen the thermal stability of the monazite-cheralite solid solution.

453 The enthalpy of this reaction was also evaluated from the drop-solution experiments  
 454 according to the equation:

$$455 \quad \Delta H_{\text{rh} \rightarrow \text{ch} + \text{H}_2\text{O}} = \Delta H_{\text{ds},1073}^{\text{rh}} - \Delta H_{\text{ds},1073}^{\text{ch}} - z \times \Delta H_5 \quad (20)$$

456 and was found to be the same within experimental error as the values obtained via TGA-DSC (see  
 457 **Table 5**).

458

459 **Table 5.** Water content and enthalpies of dehydration ( $\Delta H_{\text{dehydr}}$ ), phase transition ( $\Delta H_{\text{transit}}$ ), and  
 460 reaction of Th-rhabdophane to monazite-cheralite plus water ( $\Delta H_{\text{rh} \rightarrow \text{ch} + \text{H}_2\text{O}}$ ) of the  
 461 samples as obtained from TGA-DSC and drop solution calorimetry.

Composition	Water content	$\Delta H_{\text{dehydr}} \pm 2$ [kJ mol <sup>-1</sup> ]	$\Delta H_{\text{transit}} \pm 2$ [kJ mol <sup>-1</sup> ]	$\Delta H_{\text{rh} \rightarrow \text{ch} + \text{H}_2\text{O}}$ [kJ mol <sup>-1</sup> ]	
				DSC $\pm 2$	Drop solution $\pm 1$
Pr <sub>0.892</sub> Ca <sub>0.049</sub> Th <sub>0.059</sub> PO <sub>4</sub>	0.927	40.9	-25.3	-30	-29
Pr <sub>0.785</sub> Ca <sub>0.111</sub> Th <sub>0.105</sub> PO <sub>4</sub>	0.803	39.8	-21.3	-23	-21
Pr <sub>0.697</sub> Ca <sub>0.15</sub> Th <sub>0.143</sub> PO <sub>4</sub>	0.774	41.9	-25.8	-15	-18
Nd <sub>0.804</sub> Ca <sub>0.109</sub> Th <sub>0.086</sub> PO <sub>4</sub>	0.820	40.5	-32.7	-25	-23
	Average	40.8 $\pm$ 0.8			

462

### 463 3.2.2 Enthalpies of drop solution, formation from oxides and elements

464 The measured enthalpies of drop solution are listed in **Table 6** along with the values of  
 465 enthalpy of formation from oxides and elements calculated using thermodynamic cycle provided in  
 466 **Table 7**.

467

468 **Table 6.** Enthalpies of drop solution ( $\Delta H_{\text{ds},1073}$ ), formation from oxides ( $\Delta H_{\text{f ox},298}$ ) and from  
 469 elements ( $\Delta H_{\text{f el},298}$ ) of monazite-cheralite and Th-rhabdophane samples (expressed in  
 470 kJ mol<sup>-1</sup>).

Composition	rhabdophanes			monazite-cheralites		
	$\Delta H_{\text{ds},1073}^{\text{rh}}$	$\Delta H_{\text{f ox},298}^{\text{rh}}$	$\Delta H_{\text{f el},298}^{\text{rh}}$	$\Delta H_{\text{ds},1073}^{\text{ch}}$	$\Delta H_{\text{f ox},298}^{\text{ch}}$	$\Delta H_{\text{f el},298}^{\text{ch}}$
Pr <sub>0.892</sub> Ca <sub>0.049</sub> Th <sub>0.059</sub> PO <sub>4</sub> · 0.927H <sub>2</sub> O	206.64(7) $\pm$ 1.76	-297 $\pm$ 9	-2225 $\pm$ 9	167.28(6) $\pm$ 0.51	-326 $\pm$ 8	-1989 $\pm$ 9
Pr <sub>0.785</sub> Ca <sub>0.111</sub> Th <sub>0.105</sub> PO <sub>4</sub> · 0.803H <sub>2</sub> O	200.46(7) $\pm$ 1.18	-297 $\pm$ 8	-2188 $\pm$ 9	162.64(6) $\pm$ 0.44	-318 $\pm$ 8	-1980 $\pm$ 8
Pr <sub>0.697</sub> Ca <sub>0.15</sub> Th <sub>0.143</sub> PO <sub>4</sub> · 0.774H <sub>2</sub> O	197.26(9) $\pm$ 0.63	-293 $\pm$ 8	-2168 $\pm$ 8	158.62(7) $\pm$ 0.49	-311 $\pm$ 8	-1965 $\pm$ 8
Nd <sub>0.804</sub> Ca <sub>0.109</sub> Th <sub>0.086</sub> PO <sub>4</sub> · 0.820H <sub>2</sub> O	195.86(8) $\pm$ 0.95	-295 $\pm$ 8	-2182 $\pm$ 9	158.79(6) $\pm$ 0.25	-317 $\pm$ 8	-1971 $\pm$ 8

471

472

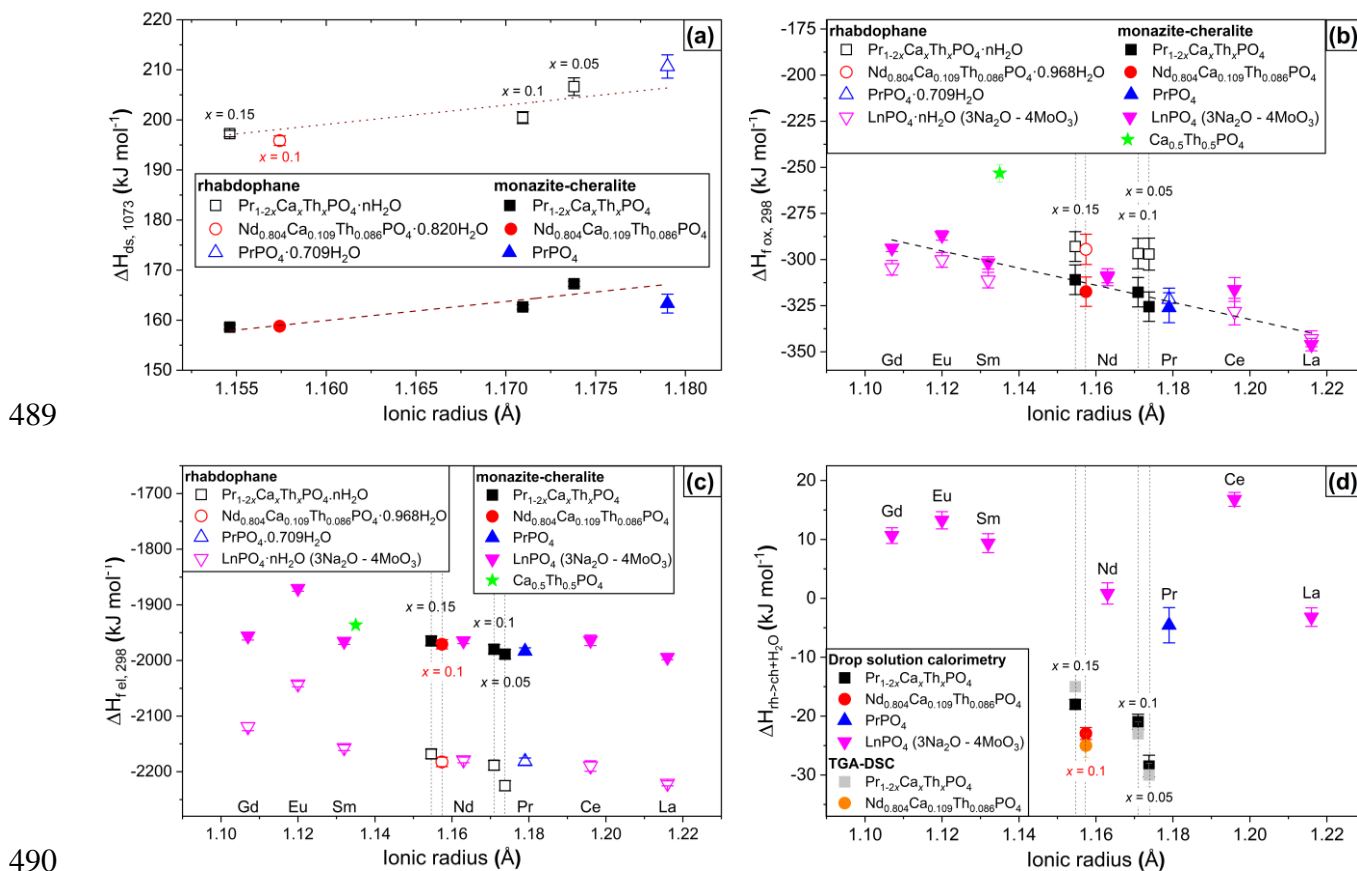
**Table 7.** Thermodynamic cycle for calculation of enthalpy of formation from oxides, from elements and enthalpy of reaction of rhabdophane to cheralite-monazite plus water

Reaction	Enthalpy, [kJ mol <sup>-1</sup> ]
$\text{Ln}_{(1-x-y)}\text{Ca}_x\text{Th}_y\text{PO}_4 \cdot z\text{H}_2\text{O}_{(\text{rh},298)} \rightarrow$ $\rightarrow 0.5(1-x-y)\text{Ln}_2\text{O}_3_{(\text{sln},1073)} + x\text{CaO}_{(\text{sln},1073)} + y\text{ThO}_2_{(\text{sln},1073)} + 0.5\text{P}_2\text{O}_5_{(\text{sln},1073)} + z\text{H}_2\text{O}_{(\text{g},1073)}$	$\Delta\text{H}_{\text{ds},1073}^{\text{rh}}$ (see <i>Table 6</i> )
$\text{Ln}_{(1-x-y)}\text{Ca}_x\text{Th}_y\text{PO}_4_{(\text{ch},298)} \rightarrow$ $\rightarrow 0.5(1-x-y)\text{Ln}_2\text{O}_3_{(\text{sln},1073)} + x\text{CaO}_{(\text{sln},1073)} + y\text{ThO}_2_{(\text{sln},1073)} + 0.5\text{P}_2\text{O}_5_{(\text{sln},1073)}$	$\Delta\text{H}_{\text{ds},1073}^{\text{ch}}$ (see <i>Table 6</i> )
$\text{Ln}_2\text{O}_3_{(\text{s},298)} \rightarrow \text{Ln}_2\text{O}_3_{(\text{sln},1073)}$	$\Delta\text{H}_1(\text{Nd}) = 11.82 \pm 0.99$ (Hosseini and Navrotsky, 2013) $\Delta\text{H}_1(\text{Pr}) = 16.50 \pm 0.20$ (Zhang and Navrotsky, 2004)
$\text{CaO}_{(\text{s},298)} \rightarrow \text{CaO}_{(\text{sln},1073)}$	$\Delta\text{H}_2 = -7.08 \pm 2.31$ (Cheng and Navrotsky, 2005)
$\text{ThO}_2_{(\text{s},298)} \rightarrow \text{ThO}_2_{(\text{sln},1073)}$	$\Delta\text{H}_3 = 98.10 \pm 1.70$ (Mazeina et al., 2005)
$\text{P}_2\text{O}_5_{(\text{s},298)} \rightarrow \text{P}_2\text{O}_5_{(\text{sln},1073)}$	$\Delta\text{H}_4 = -342.1 \pm 7.9$ (Popa et al., 2008)
$\text{H}_2\text{O}_{(\text{l},298)} \rightarrow \text{H}_2\text{O}_{(\text{g},1073)}$	$\Delta\text{H}_5 = 73.2$ (Guo et al., 2015)
$2\text{Ln}_{(\text{s},298)} + 1.5 \text{O}_2_{(\text{g},298)} \rightarrow \text{Ln}_2\text{O}_3_{(\text{s},298)}$	$\Delta\text{H}_6(\text{Nd}) = -1806.9 \pm 3.0$ (Navrotsky et al., 2015) $\Delta\text{H}_6(\text{Pr}) = -1809.9 \pm 3.3$ (Navrotsky et al., 2015)
$2\text{P}_{(\text{s},298)} + 2.5 \text{O}_2_{(\text{g},298)} \rightarrow \text{P}_2\text{O}_5_{(\text{s},298)}$	$\Delta\text{H}_7 = -1504.9 \pm 0.5$ (Robie and Hemingway, 1995)
$\text{Ca}_{(\text{s},298)} + 0.5 \text{O}_2_{(\text{g},298)} \rightarrow \text{CaO}_{(\text{s},298)}$	$\Delta\text{H}_8 = -635.1 \pm 0.9$ (Robie and Hemingway, 1995)
$\text{Th}_{(\text{s},298)} + \text{O}_2_{(\text{g},298)} \rightarrow \text{ThO}_2_{(\text{s},298)}$	$\Delta\text{H}_9 = -1226.4 \pm 3.5$ (Robie and Hemingway, 1995)
$\text{H}_2_{(\text{g},298)} + 0.5 \text{O}_2_{(\text{g},298)} \rightarrow \text{H}_2\text{O}_{(\text{s},298)}$	$\Delta\text{H}_{10} = -285.8 \pm 0.1$ (Robie and Hemingway, 1995)
$0.5(1-x-y)\text{Ln}_2\text{O}_3_{(\text{s},298)} + x\text{CaO}_{(\text{s},298)} + y\text{ThO}_2_{(\text{s},298)} + 0.5\text{P}_2\text{O}_5_{(\text{s},298)} + z\text{H}_2\text{O}_{(\text{l},298)} \rightarrow$ $\rightarrow \text{Ln}_{(1-x-y)}\text{Ca}_x\text{Th}_y\text{PO}_4 \cdot z\text{H}_2\text{O}_{(\text{rh},298)}$	$\Delta\text{H}_{\text{f ox},298}^{\text{rh}}$ (see <i>Table 6</i> )
$0.5(1-x-y)\text{Ln}_2\text{O}_3_{(\text{s},298)} + x\text{CaO}_{(\text{s},298)} + y\text{ThO}_2_{(\text{s},298)} + 0.5\text{P}_2\text{O}_5_{(\text{s},298)} \rightarrow$ $\rightarrow \text{Ln}_{(1-x-y)}\text{Ca}_x\text{Th}_y\text{PO}_4_{(\text{ch},298)}$	$\Delta\text{H}_{\text{f ox},298}^{\text{ch}}$ (see <i>Table 6</i> )
$0.5(1-x-y)\text{Ln}_{(\text{s},298)} + x\text{Ca}_{(\text{s},298)} + y\text{Th}_{(\text{s},298)} + \text{P}_{(\text{s},298)} + z\text{H}_2_{(\text{g},298)} + (2 + 0.5z)\text{O}_2_{(\text{g},298)} \rightarrow$ $\rightarrow \text{Ln}_{(1-x-y)}\text{Ca}_x\text{Th}_y\text{PO}_4 \cdot z\text{H}_2\text{O}_{(\text{rh},298)}$	$\Delta\text{H}_{\text{f el},298}^{\text{rh}}$ (see <i>Table 6</i> )
$0.5(1-x-y)\text{Ln}_{(\text{s},298)} + x\text{Ca}_{(\text{s},298)} + y\text{Th}_{(\text{s},298)} + \text{P}_{(\text{s},298)} + 2\text{O}_2_{(\text{g},298)} \rightarrow$ $\rightarrow \text{Ln}_{(1-x-y)}\text{Ca}_x\text{Th}_y\text{PO}_4_{(\text{ch},298)}$	$\Delta\text{H}_{\text{f el},298}^{\text{ch}}$ (see <i>Table 6</i> )
$\text{Ln}_{(1-x-y)}\text{Ca}_x\text{Th}_y\text{PO}_4 \cdot z\text{H}_2\text{O}_{(\text{rh},298)} \rightarrow \text{Ln}_{(1-x-y)}\text{Ca}_x\text{Th}_y\text{PO}_4_{(\text{ch},298)} + z\text{H}_2\text{O}_{(\text{l},298)}$	$\Delta\text{H}_{\text{rh} \rightarrow \text{ch} + \text{H}_2\text{O}}$ (see <i>Table 5</i> )
$\Delta\text{H}_{\text{f ox},298}^{\text{rh}} = -\Delta\text{H}_{\text{ds},1073}^{\text{rh}} + 0.5 \times (1-x-y) \times \Delta\text{H}_1 + x \times \Delta\text{H}_2 + y \times \Delta\text{H}_3 + 0.5 \times \Delta\text{H}_4 + z \times \Delta\text{H}_5$	
$\Delta\text{H}_{\text{f ox},298}^{\text{ch}} = -\Delta\text{H}_{\text{ds},1073}^{\text{ch}} + 0.5 \times (1-x-y) \times \Delta\text{H}_1 + x \times \Delta\text{H}_2 + y \times \Delta\text{H}_3 + 0.5 \times \Delta\text{H}_4$	
$\Delta\text{H}_{\text{f el},298}^{\text{rh}} = \Delta\text{H}_{\text{f ox},298}^{\text{rh}} + 0.5 \times (1-x-y) \times \Delta\text{H}_6 + 0.5 \times \Delta\text{H}_7 + x \times \Delta\text{H}_8 + y \times \Delta\text{H}_9 + z \times \Delta\text{H}_{10}$	
$\Delta\text{H}_{\text{f el},298}^{\text{ch}} = \Delta\text{H}_{\text{f ox},298}^{\text{ch}} + 0.5 \times (1-x-y) \times \Delta\text{H}_6 + 0.5 \times \Delta\text{H}_7 + x \times \Delta\text{H}_8 + y \times \Delta\text{H}_9$	
$\Delta\text{H}_{\text{rh} \rightarrow \text{ch} + \text{H}_2\text{O}} = \Delta\text{H}_{\text{ds},1073}^{\text{rh}} - \Delta\text{H}_{\text{ds},1073}^{\text{ch}} - z \times \Delta\text{H}_5$	

The found values are plotted against ionic radius and compared to the results obtained for the rhabdophane end-member in Shelyug et al., (2018) (see **Figure 5**). For all samples in the current

478 study, enthalpies of drop solution are compatible to that of the  $\text{PrPO}_4$  monazite-type end-member  
 479 determined in the previous work (Shelyug et al., 2018). Nevertheless, the enthalpy of drop solution  
 480 of the  $\text{Ca}_{0.5}\text{Th}_{0.5}\text{PO}_4$  end-member determined by Popa et al., (2008) was  $(127.65 \pm 4.4) \text{ kJ mol}^{-1}$ .  
 481 This value is 30 to 40  $\text{kJ mol}^{-1}$  lower than the enthalpies of drop dissolution of the  $\text{Pr}_{1-2x}\text{Ca}_x\text{Th}_x\text{PO}_4$   
 482 samples measured in this work. Additionally, a linear correlation between the enthalpies of drop  
 483 solution and the ionic radius of cations was observed, where the ionic radii in the monazite-  
 484 cheralites were the weighted averages of those of  $\text{Ca}^{2+}$ ,  $\text{Th}^{4+}$ , and  $\text{Pr}^{3+}$  (**Table S4 of Supporting**  
 485 **Information**). A similar linear correlation was also observed for corresponding Th-rhabdophane  
 486  $\text{Pr}_{1-2x}\text{Ca}_x\text{Th}_x\text{PO}_4 \cdot n\text{H}_2\text{O}$ , while their enthalpies of dissolution in the molten salt were more  
 487 endothermic than those of the monazite-cheralite because of the evaporation of water.

488



489

490

491 **Figure 5.** Evolution of enthalpies as a function of ionic radius: enthalpies of drop solution  
 492  $\Delta H_{\text{ds},1073} \text{ K}$  (a), enthalpies of formation from oxides  $\Delta H_{\text{f,ox},298} \text{ K}$  (b), and enthalpies of  
 493 formation from elements  $\Delta H_{\text{f,el},298} \text{ K}$  (c) and enthalpies of reaction of rhabdophane to  
 494 cheralite-monazite plus water (d). The data of rhabdophanes are presented as open  
 495 symbols and those of monazite-cheralite are closed symbols. The data of  $\text{LnPO}_4$  and  
 496  $\text{Ca}_{0.5}\text{Th}_{0.5}\text{PO}_4$  end-members are from (Shelyug et al., 2018) and (Popa et al., 2008),  
 497 respectively.

498

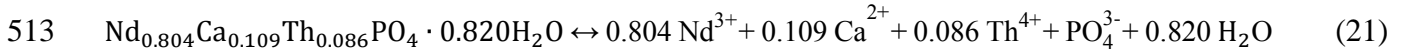
499 Likewise, the enthalpies of formation from oxides or from elements of monazite-cheralite  
 500  $\text{Pr}_{1-2x}\text{Ca}_x\text{Th}_x\text{PO}_4$  are in good agreement with those of monazite end-members  $\text{PrPO}_4$ , but lower than  
 501 the enthalpy of formation of  $\text{Ca}_{0.5}\text{Th}_{0.5}\text{PO}_4$ . This result suggested the as-synthesized monazite-  
 502 cheralite  $\text{Pr}_{1-2x}\text{Ca}_x\text{Th}_x\text{PO}_4$  might be an ideal solid solution, but data obtained for samples at higher  
 503 Th mole fractions are required to conclude definitely. On the contrary, the enthalpies of formation

504 from oxides of Th-rhabdophanes do not follow the trend of  $\text{LnPO}_4 \cdot n\text{H}_2\text{O}$  series which might be the  
 505 consequence of some additional interaction that should be taken into account.

506

507 **3.3 Calculations on Gibbs free energy and entropies of formation associated with**  
 508  **$\text{Nd}_{0.8}\text{Ca}_{0.10}\text{Th}_{0.10}\text{PO}_4 \cdot n\text{H}_2\text{O}$  and respective  $\text{Nd}_{0.8}\text{Ca}_{0.10}\text{Th}_{0.10}\text{PO}_4$ . Energetics of reaction of**  
 509 **rhabdophane to cheralite-monazite plus water**

510 The  $\lg K_{s,0}^\circ$  value associated with reaction (21) was obtained from the solubility experiments  
 511 and then was used to calculate the corresponding variation of Gibbs free energy,  $\Delta G_r^\circ$  at 298 K,  
 512 according to equation (22):



$$514 \Delta G_r^\circ = -R \times T \times \ln K_{s,0}^\circ \quad (22)$$

515 where R is the gas constant and T the absolute temperature. Since  $\lg K_{s,0}^\circ(\text{Th-rhabdophane}) \simeq$   
 516  $\lg K_{s,0}^\circ(\text{monazite-cheralite})$ , then  $\Delta G_r^{\text{rh}} = \Delta G_r^{\text{ch}} = \Delta G_r^\circ = 178 \pm 2 \text{ kJ mol}^{-1}$ .

517 Further, the variation of the standard Gibbs energy associated with the formation from the  
 518 constitutive elements,  $\Delta G_{f,\text{el}}$ , was determined by applying the Hess's law and data from **Table S5** as  
 519 follows:

$$520 \Delta G_{f,\text{el}}^{\text{rh}} = -\Delta G_r^\circ + 0.804 \times \Delta G_f^\circ(\text{Nd}^{3+}) + 0.109 \times \Delta G_f^\circ(\text{Ca}^{2+}) + 0.086 \times \Delta G_f^\circ(\text{Th}^{4+}) + \Delta G_f^\circ(\text{PO}_4^{3-}) + \\ + 0.82 \times \Delta G_f^\circ(\text{H}_2\text{O}) \quad (23)$$

$$521 \Delta G_{f,\text{el}}^{\text{ch}} = \Delta G_r^\circ + 0.804 \times \Delta G_f^\circ(\text{Nd}^{3+}) + 0.109 \times \Delta G_f^\circ(\text{Ca}^{2+}) + 0.086 \times \Delta G_f^\circ(\text{Th}^{4+}) + \Delta G_f^\circ(\text{PO}_4^{3-}) \quad (24)$$

522 Thus, the standard free energy of formation of the two phases differs by the value for water  
 523  $0.820 \times \Delta G_{f,\text{el}}(\text{H}_2\text{O}) = -194.45 \pm 0.04 \text{ kJ mol}^{-1}$ .

524 The entropies of formation from elements at 298 K were then calculated from:

$$525 \Delta S_{f,\text{el}} = \frac{\Delta H_{f,\text{el}} - \Delta G_{f,\text{el}}}{T} \quad (25)$$

527 Finally, the standard molar entropy,  $S_m^\circ$ , could be expressed as follows:

$$528 S_m^\circ(\text{rh}) = \Delta S_{f,\text{el}}^{\text{rh}} + 0.804 \times S_m^\circ(\text{Nd}_{\text{cr}}) + 0.109 \times S_m^\circ(\text{Ca}_{\text{cr}}) + 0.086 \times S_m^\circ(\text{Th}_{\text{cr}}) + S_m^\circ(\text{P}_{\text{cr}}) + \\ + 2 \times S_m^\circ(\text{O}_{2\text{g}}) + 0.820 \times [0.5 \times S_m^\circ(\text{O}_{2\text{g}}) + S_m^\circ(\text{H}_{2\text{g}})] \quad (26)$$

$$529 S_m^\circ(\text{ch}) = \Delta S_{f,\text{el}}^{\text{ch}} + 0.804 \times S_m^\circ(\text{Nd}_{\text{cr}}) + 0.109 \times S_m^\circ(\text{Ca}_{\text{cr}}) + 0.086 \times S_m^\circ(\text{Th}_{\text{cr}}) + S_m^\circ(\text{P}_{\text{cr}}) + \\ + 2 \times S_m^\circ(\text{O}_{2\text{g}}) \quad (27)$$

530

531 Using the values listed in **Table S6** and the results of drop solution calorimetry from the  
 532 previous section, the thermodynamic data for the rhabdophane and monazite-cheralite were  
 533 calculated and summarized in **Table 8**.

534

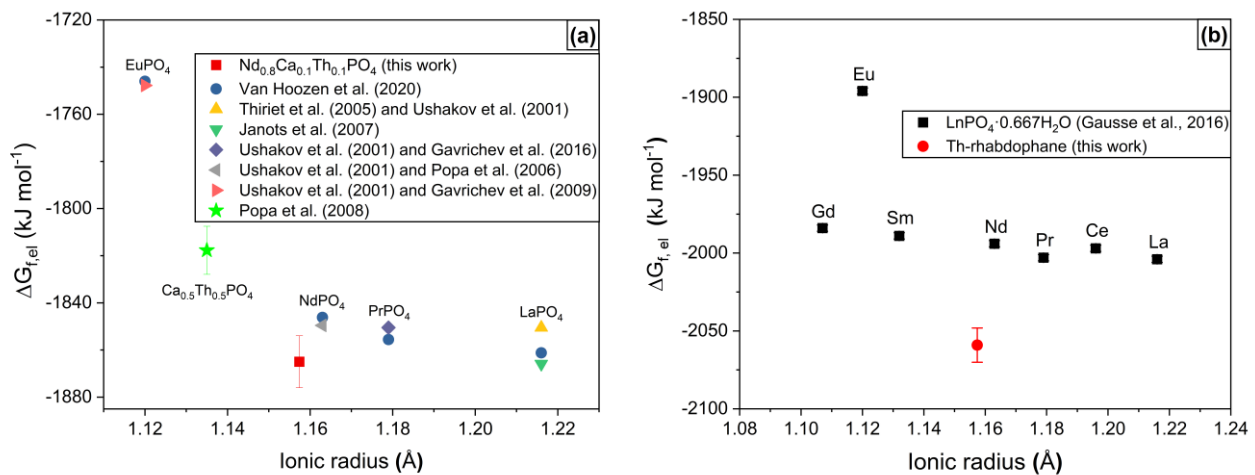
535 **Table 8.** Thermodynamic data for  $\text{Nd}_{0.8}\text{Ca}_{0.10}\text{Th}_{0.10}\text{PO}_4$  and  $\text{Nd}_{0.8}\text{Ca}_{0.10}\text{Th}_{0.10}\text{PO}_4 \cdot 0.82\text{H}_2\text{O}$   
 536 (T = 298 K).

	$\Delta G_{f,el}$ [kJ mol <sup>-1</sup> ]	$\Delta S_{f,el}$ [J mol <sup>-1</sup> K <sup>-1</sup> ]	$S_m^\circ$ [J mol <sup>-1</sup> K <sup>-1</sup> ]
$\text{Nd}_{0.804}\text{Ca}_{0.109}\text{Th}_{0.086}\text{PO}_4 \cdot 0.82 \text{H}_2\text{O}$	$-2059 \pm 11$	$-413 \pm 8$	$295 \pm 9$
$\text{Nd}_{0.804}\text{Ca}_{0.109}\text{Th}_{0.086}\text{PO}_4$	$-1865 \pm 11$	$-357 \pm 7$	$161 \pm 8$

537

538 The Gibbs free energies of formation of some monazite end-members were determined before  
 539 (Gavrichev et al., 2016; Gavrichev et al., 2009; Janots et al., 2007; Popa et al., 2006; Popa et al.,  
 540 2008; Thiriet et al., 2005; Ushakov et al., 2001; Van Hoozen et al., 2020). The data obtained in the  
 541 current study and the literature available data are provided in **Figure 6a** as a function of ionic radius.  
 542 Similarly, **Figure 6b** presents the value of  $\Delta G_{f,el}^{rh}$  determined in this work and those of rhabdophane  
 543 end-members  $\text{LnPO}_4 \cdot 0.667\text{H}_2\text{O}$ , determined by Gausse et al., (2016) for the whole light lanthanide  
 544 series. The difference between  $\Delta G_{f,el}$  values of monazite compounds is smaller than that between  
 545 those of rhabdophanes, nevertheless the coupled substitution of Nd by Th and Ca seems to stabilize  
 546 both structures. The results depicted in **Figure S2** and **Figure S3** of *Supporting Information*,  
 547 suggest that monazite-cheralite and Th-rhabdophane solid solutions are stabilized by the  
 548 configurational entropy term.

549



550

551 **Figure 6.** Evolution of Gibbs free energy of formation at 298 K as a function of ionic radius:  
 552 monazite end-members/monazite-cheralite (a), rhabdophane end-members/Th-  
 553 rhabdophane (b). Data from literature were cited from references (Gausse et al., 2016;  
 554 Gavrichev et al., 2016; Gavrichev et al., 2009; Janots et al., 2007; Popa et al., 2006;  
 555 Popa et al., 2008; Thiriet et al., 2005; Ushakov et al., 2001; Van Hoozen et al., 2020).

556

557 Finally, the entropy and Gibbs free energy of reaction (18) were calculated as follows:

$$\Delta S_{\text{rh} \rightarrow \text{ch} + \text{H}_2\text{O}} = -S_{\text{m}}^{\text{rh}} + S_{\text{m}}^{\text{ch}} + z \times S_{\text{m}}^{\circ}(\text{H}_2\text{O}) = -77 \pm 12 \text{ J mol K}^{-1} \quad (37)$$

$$\Delta G_{\text{rh} \rightarrow \text{ch} + \text{H}_2\text{O}} = \Delta H_{\text{rh} \rightarrow \text{ch} + \text{H}_2\text{O}} - 298.15 \times \Delta S_{\text{rh} \rightarrow \text{ch} + \text{H}_2\text{O}} = 0 \pm 5 \text{ kJ mol}^{-1} \quad (38)$$

These values imply that rhabdophane coexists with cheralite-monazite when it comes in contact with water at low temperature. Therefore, Th-rhabdophane  $\text{Nd}_{0.8}\text{Ca}_{0.10}\text{Th}_{0.10}\text{PO}_4 \cdot n\text{H}_2\text{O}$  is the more probable solubility-controlling phase in this study, although the solubility products of the two phases were not significantly different considering the experimental uncertainty. Gausse et al., (2018) and Gausse et al., (2016) also concluded that rhabdophane was the solubility-controlling phase during the leaching of monazite end-members at low temperature ( $T < 383 \text{ K}$ ).

## 4 CONCLUSION

This work aimed to evaluate the chemical durability of monazite-cheralite  $\text{Ln}_{1-2x}\text{Ca}_x\text{Th}_x\text{PO}_4$  ( $\text{Ln} = \text{Pr}, \text{Nd}; x = 0 - 0.15$ ) converted from corresponding Th-rhabdophane  $\text{Ln}_{1-2x}\text{Ca}_x\text{Th}_x\text{PO}_4 \cdot n\text{H}_2\text{O}$ , which was prepared through wet chemistry synthesis.

Solubility experiments starting from under-saturated conditions were performed with  $\text{Nd}_{0.8}\text{Ca}_{0.1}\text{Th}_{0.1}\text{PO}_4$  sample as an example of the series. When saturation conditions were reached, the associated standard solubility product was found as  $\lg K_{\text{s},0}^{\circ} = -31.2 \pm 0.3$ , which implies virtually no Th release in solution at near neutral pH condition.

With the application of high temperature oxide melt solution calorimetry, the enthalpies of Th-rhabdophane and corresponding monazite-cheralite solid solutions were measured and thermodynamic parameters ( $\Delta H_{\text{ds}}$ ,  $\Delta H_{\text{f,ox}}$ , and  $\Delta H_{\text{f,el}}$ ) were calculated. Combining these results with those of solubility experiments, the thermodynamic data associated with the formation of both phases from elements,  $\Delta G_{\text{f}}^{\circ}$ ,  $\Delta H_{\text{f}}^{\circ}$  and  $\Delta S_{\text{f}}^{\circ}$ , were determined. Compared to the reported thermodynamic data of rhabdophane and monazite end-members, Th-rhabdophane  $\text{Nd}_{0.8}\text{Ca}_{0.10}\text{Th}_{0.10}\text{PO}_4 \cdot n\text{H}_2\text{O}$  was found to be the more probable solubility-controlling phase at low temperature. Calculation of the thermodynamic data on reaction of Th-rhabdophane to cheralite-monazite plus water also supported the stability of the Th-rhabdophane phase.

This thermodynamic study of the Th-rhabdophane/monazite-cheralite system supports the high chemical durability of these solid solutions and confirm its potential as a specific conditioning matrix for the long-term immobilization of tetravalent actinides.

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744

## 745 Data availability

746 The research data is available upon request. To request the data, contact the corresponding author of  
747 the article.