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1 Thermodynamics of CeSiO₄: Implications for Actinide Orthosilicates

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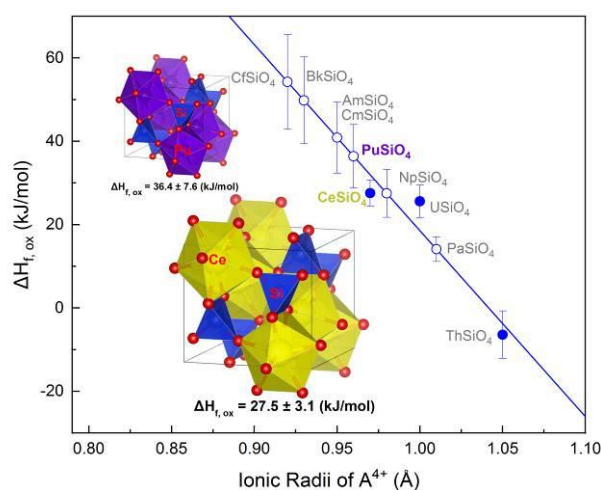
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26 **Abstract:**

27 The mineral zircon (ZrSiO_4 ; $I4_1/amd$) can accommodate natural actinides, such as thorium
 28 and uranium. The zircon structure has also been obtained for **several** of the end member
 29 compositions of other actinides, such as plutonium and neptunium. However, the thermodynamic
 30 properties of these actinide zircon structure-types are largely unknown due to the difficulties in
 31 synthesizing these materials and handling transuranium actinides. Thus, we have completed a
 32 thermodynamic study of cerium orthosilicate, stetindite (CeSiO_4), a surrogate of PuSiO_4 . For the
 33 first time, the standard enthalpy of formation of CeSiO_4 was obtained by high temperature oxide
 34 melt solution calorimetry to be -1971.9 ± 3.6 kJ/mol. Stetindite is energetically metastable with
 35 respect to CeO_2 and SiO_2 by 27.5 ± 3.1 kJ/mol. The metastability explains the rarity of the natural
 36 occurrence of stetindite and the difficulty of its synthesis. Applying the obtained enthalpy of
 37 formation of CeSiO_4 from this work, along with those previously reported for USiO_4 and ThSiO_4 ,
 38 we developed an empirical energetic relation for actinide orthosilicates. The predicted enthalpies
 39 of formation of AnSiO_4 are then made with a discussion of future strategies to efficiently
 40 immobilize Pu or minor actinides in the zircon structure.

41
 42 **Keywords:** cerium orthosilicate; thermodynamics; enthalpy of formation; ceramic waste forms;
 43 rare earth minerals; actinide geochemistry; lanthanide geochemistry; stetindite
 44

45 **TOC:**



46
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49 **Introduction:**

50 The fate of actinides from spent nuclear fuel discharged from a reactors, the actinide-containing
 51 waste separated by chemical processing of nuclear fuels, and of plutonium from dismantled nuclear
 52 weapons has raised several daunting environmental issues¹. Currently, many countries are investigating
 53 solid matrices in order to immobilize the actinides prior to permanent disposal². The immobilization
 54 step is typically accomplished either by vitrification or cementation, while the permanent disposal is
 55 completed either by a deep-mined geologic repository or deep bore-hole³⁻⁵. The main concern with this
 56 strategy, is the long-term safety associated with a disposal system's integrity on time scales that range
 57 from thousands to hundreds of thousands of years⁶. The structural and chemical stability of ceramics
 58 has been ascertained by studies of minerals, such as garnet, pyrochlore, zircon, zirconolite, apatite and
 59 monazite⁷⁻¹⁵ which are all known to be able to incorporate Th and U over geologic time scales that
 60 stretch well beyond a million years¹⁶. Thus, the use of these mineral structure "analogues" as potential
 61 ceramic-based waste hosts for the permanent immobilization of actinides and long lived fission
 62 products have been the subject of considerable research over the past several decades¹⁷⁻²³.

63 Among the single-phase, one of the crystalline ceramic candidates for actinide immobilization is the
 64 mineral zircon (ZrSiO_4 ; $I4_1/amd$).^{13,14,24} This is a direct result of zircon being an extremely durable
 65 mineral with a high loading of actinides and lanthanides²⁵. The durability of zircon is demonstrated
 66 through its high insolubility under a variety of geochemically relevant conditions²⁶⁻²⁸ (*i.e.* high P-T
 67 environments and highly saline brines), even retaining these properties of insolubility as it undergoes
 68 metamictization^{13,23,25}, and a high physical toughness as the mineral grains are shown to endure the
 69 abrasive nature of weathering and erosional processes²⁹.

70 Furthermore, zircon has been reported to readily allow for the substitution of Pu into its structure
 71 and has been identified as a key mineral phase for Pu in the "lavas" at the Chernobyl Nuclear Power
 72 Plant^{21,30-33}. The synthesis of a pure Pu endmember orthosilicate (PuSiO_4) possessing the zircon
 73 structure was reported in the literature by Keller in 1963 through hydrothermal synthetic techniques³⁴,
 74 however questions still remain about the overall purity of this zircon and the extreme difficulty of such
 75 a synthesis³⁵. Also, there could be an miscibility gap within the $(\text{Zr,Pu})\text{SiO}_4$ system, as is evidenced by
 76 the substitution of Pu into zircon becoming increasingly more difficult when exceeding 10 wt%
 77 Pu^{15,36,37}. This is most likely attributed to the thermodynamically unfavorable formation of PuSiO_4 from
 78 its binary oxides, PuO_2 and SiO_2 , which also indicates the instability Pu introduces to the zircon
 79 structure for the following solid-solution reaction: $x \text{Pu}^{4+} + \text{ZrSiO}_4 \rightarrow (\text{Pu}_x\text{Zr}_{1-x})\text{SiO}_4 + x \text{Zr}^{4+}$. This
 80 hypothesis is supported by the recent work by Estevenon *et al.* in 2020, where they found that the

81 hydrothermal conditions under which a pure PuSiO₄ may form are extremely limited, with PuSiO₄ as
82 the minor product and PuO₂ and SiO₂ being the major phases³⁵. Thus, due to the challenge of obtaining
83 pure PuSiO₄ and the safety precautions in handling of transuranium bearing orthosilicates, our
84 experiments were conducted on CeSiO₄. Cerium was selected as the surrogate for Pu, due to the
85 similarity in structure, and the ionic radii of the A-site cations and chemical properties (*i.e.*, multiple
86 valence states)³⁸⁻⁴¹. Ce⁴⁺ in the eight-coordination environment has an ionic radius of 0.97 Å, which is
87 very close to that of eight-coordinated Pu⁴⁺ (0.96 Å)⁴², therefore Ce in the solid-state system can be
88 used to simulate Pu. Pure synthetic CeSiO₄ has been successfully prepared by both direct and indirect
89 hydrothermal methods in 2019^{43,44} and has been used for the thermodynamic study in this paper.

90 We have measured the thermodynamic property of CeSiO₄ for the first time. The significance is
91 two-fold. Firstly, it has been well accepted that an empirical thermodynamic relationship exists within
92 isostructural ceramic materials⁴⁵ that the enthalpy of formation (ΔH_f) for the ceramic phase can be
93 correlated with the ionic radii of metal cations⁴⁶. Thus, given the measured ΔH_f of orthosilicates, one
94 may predict ΔH_f of an unknown phase (*i.e.* PuSiO₄) through linear extrapolations⁴⁷. This methodology
95 enables the evaluation of the impact of Pu and minor actinides to the zircon structure from a
96 thermodynamic perspective. Previously, thermodynamic parameters for coffinite (USiO₄) and thorite
97 (ThSiO₄), isostructural compounds to zircon, have been determined experimentally^{1,8,48}. Coffinite was
98 found to be metastable, as evidenced by its positive enthalpy of formation from oxides ($\Delta H_{f,ox} = 25.6 \pm$
99 3.9 kJ/mol⁴⁸) measured by Guo *et al.* using the high temperature oxide melt solution calorimetry, and
100 the positive Gibbs free energy of formation ($\Delta G_{f,ox} = 20.6 \pm 5.2$ kJ/mol⁴⁹) determined by Szenknect *et*
101 *al.* from solubility studies. The metastability of coffinite directly explains the difficulty associated with
102 its synthesis such that one cannot simply prepare coffinite by a conventional solid-state reaction⁵⁰.
103 However, thorite is relatively easier to synthesize by various solid-state and aqueous-chemistry
104 methods⁵¹⁻⁵⁴, despite of the ionic similarity in Th⁴⁺ (1.05 Å) and U⁴⁺ (1.00 Å)⁴², the less difficult
105 synthesis is consistent with its negative value of $\Delta H_{f,ox}$, -6.4 ± 5.7 kJ/mol⁸. Additionally, Ferriss *et al.* in
106 2010 performed density functional theory (DFT) calculations³⁷ to predict ΔH_f of CeSiO₄, ThSiO₄,
107 USiO₄, and PuSiO₄. The DFT results predict values in good agreement with those of ThSiO₄⁸, USiO₄⁴⁸,
108 and CeSiO₄ from this work.

109 Secondly, the natural mineral occurrence of CeSiO₄, stetindite, was discovered in 2009 in a granitic
110 pegmatite in Norway⁵⁵. However, there are no studies of its thermodynamic stability. Thus, the first
111 determination of ΔH_f for CeSiO₄ provides a basis for understanding the geochemical factors leading to
112 the formation of this relatively rare mineral.

113

114 2. Experimental Methods

115 2.1. Sample synthesis and characterization:

116 CeSiO₄ samples were synthesized by hydrothermal method from Ce(III)-silicate solid
117 precursor according to the protocol described by Estevenon *et al.*⁴⁴. A stoichiometric mixture of
118 CeO₂ (Sigma Aldrich, particle size < 5 μm) and SiO₂ (Sigma Aldrich, 10-20 nm) were
119 mechanically milled (30 Hz, 1 hour) with a Retsch MM 200 vibration mill mixer in a tungsten
120 carbide milling vessel. This mixture was pelletized by uniaxial pressing under 5 MPa at room
121 temperature and then heated at 1350°C under reductive atmosphere (Ar-4% H₂) to prepare
122 A-Ce₂Si₂O₇ (tetragonal system, space group *P4₁*). 200 mg of A-Ce₂Si₂O₇ was placed in contact
123 with 4 mL of a 0.75 M HNO₃ solution (prepared by dilution of ACS grade 70% HNO₃, Sigma
124 Aldrich), the pH of that solution was then adjusted to 7.0 using freshly prepared NaOH solution
125 (from ACS grade NaOH pellets, Sigma Aldrich). This mixture was hydrothermally treated for 7
126 days at 150°C under air atmosphere in a 23 mL Teflon lined Parr autoclaves. The final product
127 was separated from the aqueous solution by centrifugation, washed twice with deionized water
128 and once with ethanol and then dried overnight at 60°C. The final CeSiO₄ powder sample was
129 well characterized by a multitude of different characterization techniques. A summary of the
130 techniques and the resulting data are presented in the supplementary information (SI) to this
131 manuscript, with a more detailed description of the characterization being found in our previous
132 work of Estevenon *et al.* 2019⁴⁴. These techniques included XRD (Figure S1), FTIR (Figure S2),
133 Raman (Figure S3), XANES (Figure S4), EXAFS (Figure S5) and SEM (Figure S6). The results
134 of all of these techniques allows us to confirm that the material which was investigated through
135 the calorimetric techniques utilized and presented in this study to be chemically CeSiO₄, with all
136 the Ce presented being tetravalent, and the overall structure to belong to the space group *I4₁/amd*.

137 2.2. Thermogravimetric analysis coupled with differential thermal analysis (TGA-DTA):

138 The TGA-DTA measurements were performed on a Setaram SetSYS 2400
139 thermogravimetric differential scanning calorimeter, where CeSiO₄ was heated from 28°C to
140 1200°C, with a heating rate of 10°C/min., under a flowing N₂ atmosphere (20 mL/min.). The
141 temperature and sensitivity of the instrument was calibrated by heating indium, tin, lead, zinc, and
142 aluminum across their fusion point repeatedly at the temperature change rates of 5, 10, 15, and
143 20°C/min. The signals of each phase transition were then calibrated against the known heats of
144 fusion for the metals.

145 *2.3. High temperature oxide melt solution calorimetry:*

146 The enthalpy of drop solution (ΔH_{ds}) was directly measured by a Setaram AlexSYS-1000
147 Calvet-type calorimeter. The calibration of the instrument was conducted by performing transpose
148 temperature drops using solid pieces of α -Al₂O₃ and Pt. Powdered samples were hand pressed into
149 pellets, with masses between 3-5 mg, and dropped from room temperature into a molten solvent of
150 sodium molybdate (Na₂O·MoO₃) contained in a Pt crucible at 700°C. The calorimeter chambers
151 were continuously flushed with O₂ gas at a rate of ~100 mL/min in order to facilitate a constant
152 gas environment above the solvent. The Na₂O·MoO₃ melt is slightly oxidative^{56,57} and will
153 maintain a redox environment which will keep all of the dissolved Ce in melt as Ce⁴⁺.⁵⁸⁻⁶⁰
154 Flushing of O₂ gas above the solvent also further aids in maintaining an oxidative solvent
155 environment, by oxidizing any low-valence Mo to Mo⁺⁶. Further, the Na₂O·MoO₃ solvent
156 dissolves refractory elements, such as Ce, but is relatively chemically inert to silicon (Si)^{48,58,60,61}.
157 Therefore, the solvent saturation method⁶² was used for correctly accounting for the energy
158 associated with the all Si in the stetitindite. This was accomplished by saturating 15g of
159 Na₂O·MoO₃ with 100 mg of silica gel prior to the experiments as the solvent will no longer
160 dissolve any SiO₂, but instead will precipitate out as cristobalite at 700°C. All of the calibration
161 and methodology employed in this study are further described in more detail in previous reports
162 ^{11,48,58,62-65}. Associated

163
164 **3. Results & Discussion**

165 *3.1. Thermogravimetric analysis coupled with differential thermal analysis (TGA-DTA):*

166 Thermogravimetric analysis (TGA) of CeSiO₄ showed two mass losses (Figure 1). The
167 first mass loss of 3.20% occurs from room temperature to 900°C and is associated with the
168 removal of surface water and structural water. The water content of the synthetic CeSiO₄ was
169 quantified from the TGA result leading to the chemical formula: CeSiO₄·0.43H₂O, which also
170 resembles the hydrated form of synthetic USiO₄ prepared by hydrothermal methods⁴⁸. The origins
171 and location of water within zircon structural materials has been highly debated in the
172 literature^{17,52,66-71}. The observation of a continual mass till 900°C, shows that majority of the water
173 associated with CeSiO₄ is energetically strongly associated with the material, for merely adsorbed
174 surficial water would leave the sample below 200°C. This conclusion of strongly associated water
175 is consistent with the previous observations of excess water associated with both natural and
176 synthetic coffinite samples (USiO₄).^{17,48} However, the origins of such excess water in coffinite is

177 not simple and still subject to debate as both infrared spectroscopic and X-ray diffraction studies
178 have ruled out the water being structural^{17,52,66-70}. One prevailing theory of how water is
179 associated with natural zircons is in form of OH- and various Zr or Si related vacancies⁷¹. Such
180 OH- groups would be evident in the 3000-3500cm⁻¹ IR region⁷² of which was not detected by
181 FTIR (Figure S2) and would further require a charge substitution of Ce⁴⁺ to Ce³⁺, which was not
182 present in the XANES spectra (Figure S4). Lastly, the EXAFS (Figure S5) of the material
183 elucidates that the coordination environment of the elements is that of a zircon structural material,
184 with no vacancies or OH- being found to contribute. A potential origin of water which is
185 energetically strongly associated, but non-structural, and is not readily visible through FTIR or
186 XRD could be as confined molecular water inside channels along the [001] in the zircon
187 structure^{17,70,73}. This hypothesis offers an explanation for why the water is observed as molecular
188 and not structural⁶⁹.

189 The second mass loss (2.17%) from 980 - 1110°C corresponds to ¼ of a mole of O₂ being
190 released in association with the reduction of Ce⁴⁺ to Ce³⁺ resulting in the cerium (III) disilicate
191 phase, A-Ce₂Si₂O₇ under the inert atmosphere. This is further supported by the corresponding
192 endothermic heat flow indicated by DTA. The decomposition temperature is much higher than
193 700°C at which the oxide melt solution calorimetry was conducted. Thus, we conclude that the
194 decomposition has no bearing to the final thermochemical results.

195 3.2. Enthalpy of formation of CeSiO₄:

196 The hydrothermally prepared CeSiO₄ sample used in this study exhibits a similar hydrated
197 composition to that of the analogous synthetic USiO₄ prepared by similar hydrothermal
198 techniques^{48,74}. To ensure the quality of the obtained enthalpy of formation, we followed the
199 previously developed methodology for hydrated minerals (*e.g.*, coffinite⁴⁸) and performed two sets
200 of high-temperature oxide melt solution calorimetry experiments. The first set of these
201 experiments were performed using the sample as is, with a chemical formula of CeSiO₄·0.43H₂O.
202 Through these experiments the enthalpy of drop solution (ΔH_{ds}) of CeSiO₄·0.43H₂O was found to
203 be 95.36 ± 3.52 kJ/mol (Table 1). The second set of experiments was done after the sample was
204 fully dehydrated. The dehydration of the sample was accomplished by heating pelletized samples
205 (3-5 mg) for two hours under an inert atmosphere of N₂ to 800°C. Samples were then stored at
206 room temperature under a N₂ atmosphere prior to being dropped in order to avoid any potential
207 water re-adsorption. All of the experimental parameters and materials exactly mirrored those
208 utilized for the hydrated sample outlined above in the methods sections. The resulting enthalpy of

209 drop solutions determined by these experiments was $\Delta H_{\text{ds}} = 92.88 \pm 3.40$ kJ/mol (Table 1),
 210 slightly less endothermic than that from the first experiment. This is reasonable because the
 211 thermal dehydration leads to the positive contribution to the ΔH_{ds} value. However, the difference,
 212 2.48 kJ/mol, is unexpectedly small. The small hydration enthalpic value could be due to the partial
 213 dehydration of $\text{CeSiO}_4 \cdot 0.43\text{H}_2\text{O}$ during dropping before it reached the reaction chamber where the
 214 measurements were taken. AlexSYS-1000 has an inhomogeneous temperature profile, with over
 215 60 cm above the reaction chamber maintaining at around 650°C. Rapid dehydration could
 216 occur,^{75,76} and the composition of the resulting sample detected by the thermopiles was estimated
 217 from the TGA result to be $\text{CeSiO}_4 \cdot 0.025\text{H}_2\text{O}$.

218 The ΔH_{ds} for such partially hydrated sample must be then corrected in order to account for
 219 the additional energetics related with the associated water. As it was stated above, it is reasonable
 220 to assume that a portion of water is strongly bonded to CeSiO_4 as the TGA data showed an
 221 extended mass loss till 900°C. Using an integral adsorption enthalpy of -80 kJ/mol per mol of H_2O
 222 (-44 kJ/mol for “free water”) for the adsorbed water, which was observed in the alumina and
 223 titania⁷⁷⁻⁷⁹ and used for estimating hydration energy of coffinite⁴⁸, one may derive the corrected
 224 ΔH_{ds} for anhydrous CeSiO_4 to be 88.7 ± 3.4 kJ/mol and $\Delta H_{\text{f, ox}}$ to be 29.2 ± 3.5 kJ/mol (Table 1).
 225 While the direct measurement of anhydrous CeSiO_4 yields $\Delta H_{\text{f, ox}}$ of 25.0 ± 3.5 kJ/mol (Table 1),
 226 by averaging the results of the two experiments, $\Delta H_{\text{f, ox}}$ of CeSiO_4 reaches 27.5 ± 3.1 kJ/mol
 227 (Table S1), which is in excellent agreement with the DFT predicted value, 23.8 kJ/mol^{37,63}. With
 228 all of the evidence supporting that water is energetically strongly associated with stetindite, we
 229 report that $\Delta H_{\text{f}}^\circ = -1971.9 \pm 3.6$ kJ/mol, which is first reported standard enthalpy of formation data of
 230 stetindite (Table S1).

231 3.3. Energetic Landscape of End-Member Actinide orthosilicates:

232 Several empirical methodologies were developed for the prediction thermodynamic
 233 parameters of ceramic compounds. For instance, Chen *et al.* discovered that both the Gibbs free
 234 energies (ΔG_{f}) and enthalpies of formation (ΔH_{f}) of hexavalent uranium minerals could be
 235 predicted through the structural-summation technique.⁸⁰ Whereas, Sverjensky and Molling⁴⁵
 236 established an empirical linear relationship between the free energy of isostructural inorganic
 237 solids and the ionic radii of aqueous metal cations. While this model was originally developed for
 238 divalent cations the model has been expanded to include tetravalent cations and its application
 239 allowed for the free energies of crystalline solids to be estimated by only having experimental data
 240 on a few samples.^{81,82} A very similar empirical linear relationship has been recognized for

241 isostructural inorganic compounds which links the enthalpies of formation with the ionic radii of
 242 metal cations.⁴⁶ Many lanthanide and actinide bearing isostructural ceramic materials follow this
 243 empirical trend and it has been applied numerous times in the literature^{47,64,83–85}.

244 By using the experimentally determined $\Delta H_{f, \text{ox}}$ of CeSiO_4 (27.5 ± 3.1 kJ/mol), USiO_4 (25.6
 245 ± 3.9 kJ/mol⁴⁸) and ThSiO_4 (-6.4 ± 5.7 kJ/mol⁸) and the ionic radii (\AA) of metal cations in an eight-fold
 246 coordination environment⁴², a near linear trend is found between $\Delta H_{f, \text{ox}}$ and the ionic radius r (\AA), $\Delta H_{f, \text{ox}}$
 247 $\text{ox} = (-446.3 \pm 152.5) r - (464.9 \pm 153.6)$, with an adjusted $R^2 = 0.79096$. From the obtained linear
 248 regression, we obtained the $\Delta H_{f, \text{ox}}$ for the other actinide (Pa, Np, Pu, Am, Cm, Bk, Cf)
 249 orthosilicates (Figure 2). The heavier transuranic elements (Am, Cm, Bk, and Cf) show more
 250 lanthanide-like characteristics, thus prefer having a trivalent oxidation state^{86–88}. The trivalent oxidation
 251 would result in different ionic radii and preferred coordination chemistry^{89,90}. In order for such trivalent
 252 cations to be introduced into the zircon structure a charge-coupled substitution would be required.
 253 Nonetheless, the tetravalent states of all the aforementioned elements are possible through either a
 254 transient state as a result of radiation-induced radiolysis^{91–93} or a steady state being stabilized by either
 255 ligands or electrochemical methods^{88,94–96}. Each of these states, the transient state and steady state
 256 conditions, are achievable in the unlikely event of a failure of the geological repository and breach in
 257 radiological waste canister. Each of these states could be observed under such a hypothetical scenario,
 258 if said geological repository is located in a geologic setting where the host lithology is also rich with
 259 mineral halides (*i.e.* halite), such as what is observed at the Waste Isolation Pilot Plant (WIPP) located
 260 in New Mexico, U.S.A.^{97,98}, then there would be a supply of radiation, heat, high ionic-strength aqueous
 261 solutions⁹⁹, and silica source from the bentonite backfill¹⁰⁰. This could cause for the dissolution of
 262 another ceramic waste form and allow for the formation of an actinide orthosilicate, with such
 263 hypothetical conditions being similar to those used in synthesizing PuSiO_4 ³⁵. These actinide
 264 orthosilicate could form as colloid allowing for them to be transported immense distances^{101–103}. Thus,
 265 here we consider the possible tetravalent states of these heavy transuranic elements and their potential
 266 impact to the structural stability.

267 As the thermodynamic stability of any given material is dictated by ΔG_f , one needs $\Delta G_f = \Delta H_f -$
 268 $T\Delta S_f$, with knowing the appropriate entropy (ΔS_f) value besides ΔH_f , in order to evaluate the
 269 overall stability. However, under the standard condition ($T = 25^\circ\text{C}$, $P = 1\text{Bar}$), the entropic term is
 270 small. This is evidenced taking coffinite as an example. ΔG_f of coffinite was determined through
 271 solubility studies to be -1867.6 ± 3.2 kJ/mol⁴⁹ and its ΔH_f was determined by high temperature
 272 drop oxide melt calorimetry to be -1970.0 ± 4.2 kJ/mol⁴⁸. At 25°C , $T\Delta S_f$ equal to -0.344

273 kJ/mol·K × 298.15 K = 102.6 kJ/mol. Hence, under the standard condition enthalpy alone can be
 274 used to approximately discuss the stability of actinide orthosilicates and represent the energetic
 275 landscape (Figure 2). The regression of measured $\Delta H_{f, ox}$ leads to an almost linear trend. The
 276 extrapolated results based on such linear trend are in good agreement with those reported in a previous
 277 computational study³⁷. The result of the linear regression is summarized in Table 2 and plotted in
 278 Figure 2. Only ThSiO₄ has a negative formation enthalpy (-6.4 ± 5.7 kJ/mol)⁸, while all others are
 279 expected to be thermodynamically metastable with respect to their binary oxides (AnO₂ and SiO₂).
 280 The favorable formation of ThSiO₄ could be a result of its lowest ionic potential (Z/r) of 3.81 that
 281 allows Th⁴⁺ to be stabilized in the zircon structure. Whereas, USiO₄, CeSiO₄, and PuSiO₄ having
 282 larger ionic potentials of 4.00, 4.12, and 4.17, respectively, and thus can destabilize the zircon
 283 structure. Said that, $\Delta H_{f,ox}$ of ThSiO₄ does follow the linear trend established in this work and does
 284 not exhibit as an exception to the general rule.

285 The prediction in Figure 2 are consistent with the reported difficulty in synthesizing pure
 286 PuSiO₄³⁵, which has a predicted $\Delta H_{f, ox}$ value of 36.4 ± 7.6 kJ/mol. These results indicate that if one
 287 plans to use the zircon structure for immobilizing Pu or other minor actinides, they need to target
 288 synthesis strategies which disfavor the formation of binary oxides. As both coffinite and stetindite are
 289 found to have positive $\Delta H_{f, ox}$, the synthetic conditions of their formations could be highly informative
 290 for such strategies. Both of them have been discovered in nature under hydrothermal conditions and
 291 their synthetic analogs have been prepared by tailoring synthetic routes to avoid the formation of
 292 thermodynamically more favorable binary oxides^{43,44,50,53,104}. In particular the formation of stetindite
 293 under laboratory conditions^{43,44}, as the kinetics needed in order to oxidize either the Ce³⁺
 294 intermediate complex⁴³ or Ce³⁺ solid⁴⁴, into the Ce⁴⁺ solid were only stable under hydrothermal
 295 conditions. In addition, taking the $\Delta H_{f, ox}$ calculated through the linear regression, we also report the
 296 predicted ΔH_f° values for PaSiO₄, NpSiO₄, PuSiO₄, AmSiO₄ and etc. (Table 2) by using ΔH_f° of the
 297 respected AnO₂¹⁰⁵ as the auxiliary data. The overall $\Delta H_{f, ox}$ is shown to be thermodynamically
 298 unfavorable for the major transuranic elements, Np, Pu, Am, and Cm. Nevertheless, Am-orthosilicate
 299 has been successfully synthesized and reported by Keller in 1963,³⁴ which make CmSiO₄ also highly
 300 possible to exist because of their almost identical predicted formation enthalpies.

301 The zircon structure-type includes other crystalline ceramics and mineral orthosilicates. The
 302 lanthanide orthovanadate (LnVO₄) minerals wakefieldite and dreyerite, the heavy rare earth
 303 orthophosphate (HREEPO₄) mineral xenotime, and the lanthanide orthoarsenate (LnAsO₄) mineral
 304 chernovite all share the zircon structure¹⁷. As the orthophosphate and orthovanadate materials

305 enthalpies of formation have been reported in the literature^{59,106}, they were also included in Figure 2 in
 306 order to detect any other trends across the isostructural family. This led to another important
 307 observation of the energetic landscape of orthosilicates in that both zircon and hafnon (HfSiO₄) are
 308 “outliers” of the predicted trend. We hypothesize that there could be a separate trend for transitional
 309 metal orthosilicates due to the structural difference that both of Zr⁴⁺ and Hf⁴⁺ are smaller cations (0.84 Å
 310 and 0.83 Å, respectively). This is further supported by both of these materials following the
 311 orthovanadate trend line, which are comparable in both energetics and unit cell volume to ScVO₄. This
 312 observation, however, does not exclude the possibility of zircon and hafnon being outliers as a result
 313 of the fundamental bonding difference in *d*-orbitals vs. *f*-orbitals¹⁰⁷. Lastly, these two trends for
 314 transition metal and lanthanide/actinide orthosilicates disagree with the previously reported actinide
 315 orthosilicate energetic landscape¹⁰⁸. The discrepancy is attributed to an inaccuracy of ΔH_{ds} for thorite
 316 as a result of incomplete dissolution of the single crystal sample and the inconclusive ΔH_{ds} for
 317 coffinite in the early experiments, which we have discussed in a previous work⁴⁸. The
 318 experimentally derived energetic trend fully agrees with the calculated values reported by the DFT-
 319 LDA study³⁷ (Figure 2), which likewise shows that both zircon and hafnon deviate from the linear
 320 trend.

321 3.4. Strategic analysis of immobilizing Pu or other actinides in zircon structure:

322 Although the pure actinide orthosilicate endmembers were calculated to have a positive $\Delta H_{f,ox}$,
 323 it should be investigated whether any intermediate compositions from MSiO₄ (M = Zr, Hf) and
 324 AnSiO₄ (An = Th, U, Np, Pu, etc.) endmembers can lead to thermodynamically favorable solid
 325 solutions for waste form applications. Using MSiO₄-based solid solutions to strategically
 326 accommodate actinides has advantages in two different ways. Firstly, it may allow for easier
 327 synthesis of actinide-containing orthosilicates, as there could be a potential for short-range cation
 328 ordering that could significantly lower the enthalpic penalty for introducing An⁴⁺ into ZrSiO₄.
 329 Such a phenomenon has already been demonstrated in uranothorite solid solution (Th_{1-x}U_xSiO₄),
 330 where the intermediate compositions are stabilized by a negative heat effect of -118.7 kJ/mol⁸.
 331 Secondly, the application of HfSiO₄ as the endmember, instead of ZrSiO₄, can offer an additional
 332 benefit to the waste form as hafnium is a neutron absorber^{14,19}. The soft hydrothermal synthesis of
 333 hafnon could easily be modified to incorporate tetravalent actinides¹⁰⁹. This soft hydrothermal
 334 synthetic technique could also be scalable for industrial application¹¹⁰. Unfortunately, the
 335 introduction of hafnium as a neutron absorber does not imply a reduction in the susceptibility to
 336 radiation damage²¹, a topic that has been extensively studied in the past^{31,111–116} and is still one of

337 the greatest challenges to the utilization of zircon-based ceramic as a nuclear waste host.
338 However, the introduction of hafnium could allow the incorporation of higher loadings of
339 radionuclides with high specific activity (e.g. plutonium and americium isotopes) in the waste
340 form without any worry of possible criticality¹⁵.

341

342 **5. Conclusions**

343 Through thermogravimetric analysis, differential thermal analysis (TGA-DTA), and high
344 temperature oxide melt solution calorimetry, the thermodynamic parameters of stetindite (CeSiO₄)
345 were determined. The results of the TGA-DTA show that CeSiO₄ is hydrated, similar to that of
346 USiO₄⁴⁸. By performing high temperature oxide melt solution calorimetry on CeSiO₄, we
347 determined its enthalpy of formation to be $\Delta H_{f,ox} = 27.5 \pm 3.1$ kJ/mol, confirming its metastability
348 with respect to its binary oxides. The strong endothermic heat of formation accounts for the
349 difficulty in synthesizing this phase in addition to the overall rarity of stetindite in nature. The
350 overall enthalpy of formation was found to be thermodynamically favorable: $\Delta H^{\circ}_f = -1971.9 \pm 3.6$
351 kJ/mol. Exploiting the empirically derived linear trend between the enthalpy of formation and the
352 ionic cation radius enabled the prediction of ΔH°_f of some unknown actinide silicates AnSiO₄ (An
353 = Np, Pu, Am, Cm, Bk, and Cf). These high endothermic formation enthalpies provide an
354 explanation for the difficulties in their synthesis, particularly the attempts to obtain pure PuSiO₄,
355 which was encountered by Estevenon *et al.*³⁵ using hydrothermal methods. Indeed, it appears to be
356 difficult according to a predicted value of $\Delta H_{f,ox} = 36.4 \pm 7.6$ kJ/mol. Furthermore, the synthesis
357 of minor actinides possessing the zircon structure, such as AmSiO₄, should be even more difficult
358 to synthesize as they are all found to be more energetically uphill than PuSiO₄, with all being
359 estimated to have $\Delta H_{f,ox} > 40$ kJ/mol. Lastly, we propose that some Zr-An or Hf-An orthosilicate
360 systems may be thermodynamically favored by possible negative mixing enthalpies due to the
361 short-range ordering of the two metal cations that can be engineered to increase the loadings of
362 actinides in the zircon or hafnon structure-type, which have a relatively large stability field.

363

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371 Technology Institute.

372 **Tables**

373

374 **Table 1** Thermochemical cycles used for calculations of the enthalpy of formation from binary
 375 oxides and the standard enthalpy of formation of stetindite based on the data of drop solution
 376 calorimetry in molten sodium molybdate saturated with amorphous silica at 25°C.

Reaction	ΔH (kJ/mol)
(1) $\text{CeSiO}_4 \cdot 0.43\text{H}_2\text{O}_{(s, 25^\circ\text{C})} \rightarrow \text{CeO}_{2(\text{sln}, 700^\circ\text{C})} + \text{SiO}_{2(\text{cristobalite}, 700^\circ\text{C})} + 0.43 \text{H}_2\text{O}_{(\text{g}, 700^\circ\text{C})}$	$\Delta H_1 = 95.36^* \pm 3.52^\ddagger (3)^\ddagger$
(2) $\text{CeSiO}_4 (s, 25^\circ\text{C}) \rightarrow \text{CeO}_{2(\text{sln}, 700^\circ\text{C})} + \text{SiO}_{2(\text{cristobalite}, 700^\circ\text{C})}$	$\Delta H_2 = 92.88 \pm 3.40 (2)$
(3) $\text{CeO}_{2(s, 25^\circ\text{C})} \rightarrow \text{CeO}_{2(\text{sln}, 700^\circ\text{C})}$	$\Delta H_3 = 74.37 \pm 0.75^{58} (66)$
(4) $\text{SiO}_{2(\text{quartz}, 25^\circ\text{C})} \rightarrow \text{SiO}_{2(\text{cristobalite}, 700^\circ\text{C})}$	$\Delta H_4 = 43.54 \pm 0.60^{58} (3)$
(5) $\text{Ce}_{(s, 25^\circ\text{C})} + \text{O}_{2(\text{g}, 25^\circ\text{C})} \rightarrow \text{CeO}_{2(s, 25^\circ\text{C})}$	$\Delta H_5 = -1088.7 \pm 1.5^{117}$
(6) $\text{Si}_{(s, 25^\circ\text{C})} + \text{O}_{2(\text{g}, 25^\circ\text{C})} \rightarrow \text{SiO}_{2(\text{quartz}, 25^\circ\text{C})}$	$\Delta H_6 = -910.7 \pm 1.0^{117}$
(7) $\text{H}_2\text{O}_{(l, 25^\circ\text{C})} \rightarrow \text{H}_2\text{O}_{(\text{g}, 700^\circ\text{C})}$	$\Delta H_7 = 69.0^{117}$
(8) $\text{H}_2\text{O}_{(l, 25^\circ\text{C})} \rightarrow \text{H}_2\text{O}_{(\text{cr}, 25^\circ\text{C})}$	$\Delta H_8 = -80.0^{48}$
Enthalpy of drop solution corrected for proper molar mass of the partially hydrated sample:	
(9) $\text{CeSiO}_4 \cdot 0.025\text{H}_2\text{O}_{(s, 25^\circ\text{C})} \rightarrow \text{CeO}_{2(\text{sln}, 700^\circ\text{C})} + \text{SiO}_{2(\text{cristobalite}, 700^\circ\text{C})} + 0.025 \text{H}_2\text{O}_{(\text{g}, 700^\circ\text{C})}$	$\Delta H_9 = -92.48 \pm 3.42 (3)$
Corrected enthalpy of drop solution value assuming water is strongly bonded:	
(10) $\Delta H_{\text{ds}}(\text{CeSiO}_4) = \Delta H_{10} = \Delta H_9 - 0.025 \cdot (\Delta H_6 + \Delta H_7)$	$\Delta H_{\text{ds}} = 88.7 \pm 3.4$
Enthalpy of formation of stetindite from CeO_2 and SiO_2 (quartz) assuming water is strongly bonded:	
(11) $\Delta H_{\text{f,ox}}(\text{CeSiO}_4) = \Delta H_{11} = -\Delta H_{10} + \Delta H_3 + \Delta H_4$	$\Delta H_{\text{f,ox}} = 29.2 \pm 3.5$
Standard enthalpy of formation of stetindite assuming water is strongly bonded	
(12) $\Delta H^\circ_{\text{f}}(\text{CeSiO}_4) = \Delta H_{11} + \Delta H_4 + \Delta H_5$	$\Delta H^\circ_{\text{f}} = -1970.2 \pm 4.0$
Enthalpy of formation of dehydrated stetindite from CeO_2 and SiO_2 (quartz):	
(13) $\Delta H_{\text{f,ox}}(\text{CeSiO}_4) = \Delta H_{13} = -\Delta H_2 + \Delta H_3 + \Delta H_4$	$\Delta H_{\text{f,ox}} = 25.0 \pm 3.5$
Standard enthalpy of formation of stetindite:	
(14) $\Delta H^\circ_{\text{f}}(\text{CeSiO}_4) = \Delta H_{13} + \Delta H_4 + \Delta H_5$	$\Delta H^\circ_{\text{f}} = -1974.2 \pm 4.0$

377 * Average. † Two standard deviations of the average value. ‡ Number of measurements.

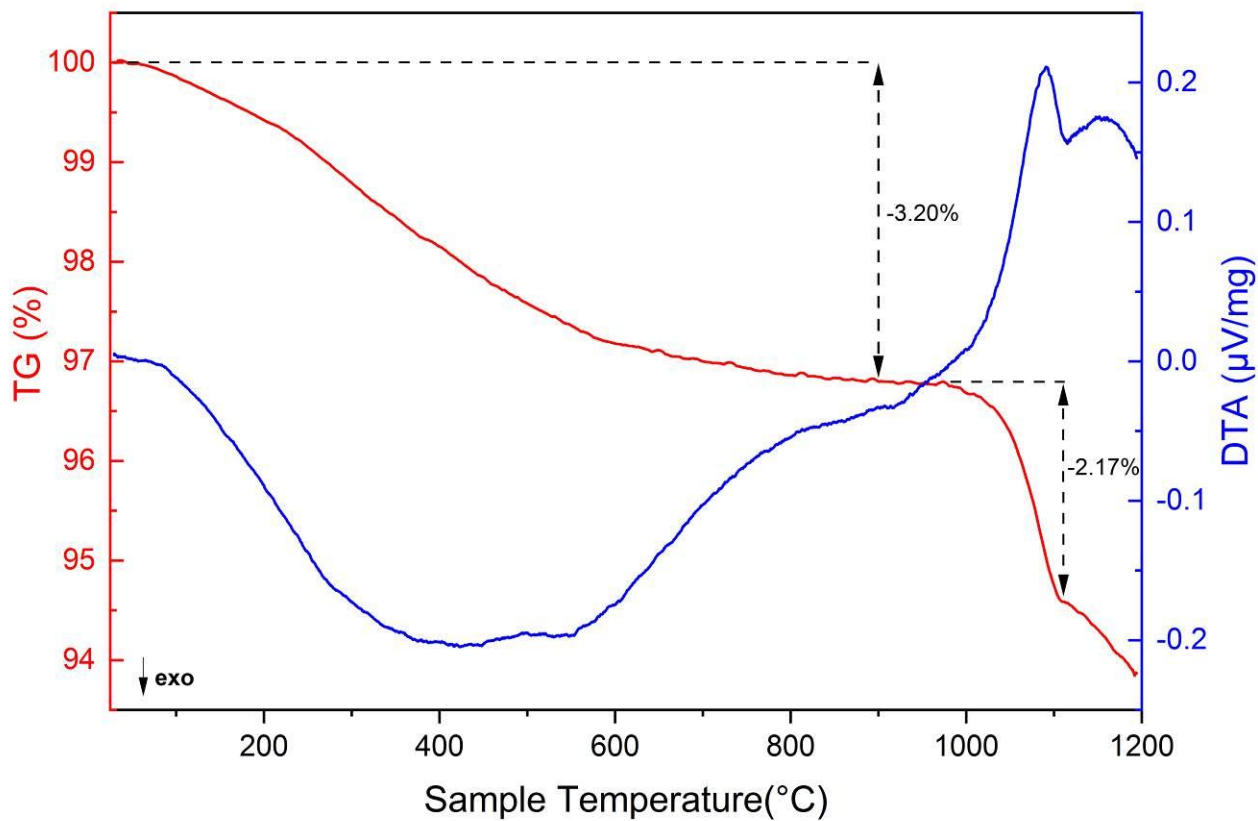
378

379 **Table 2** Enthalpy of formation from oxides for orthosilicate end-members, coming from
 380 experiments and calculations at 25°C.

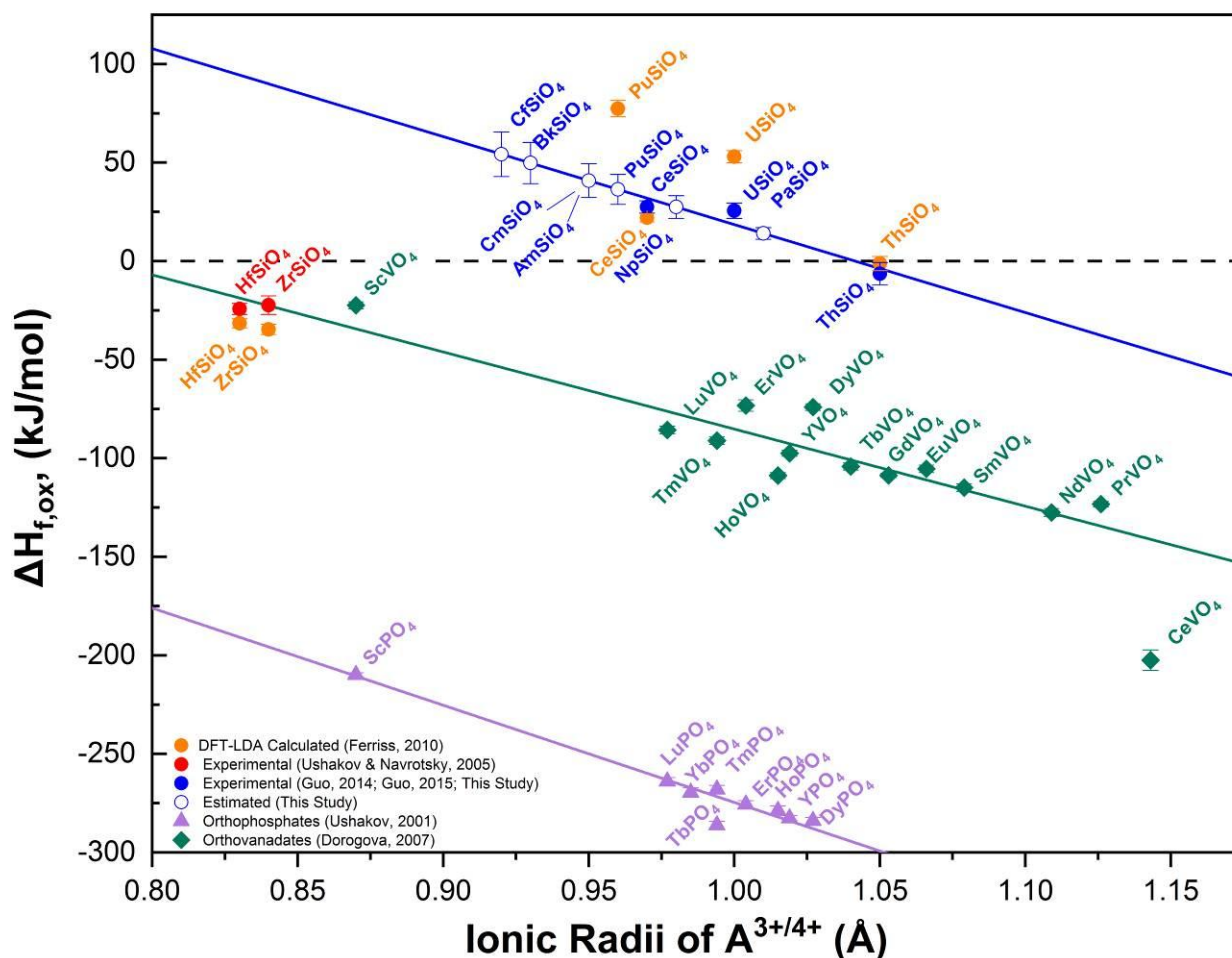
	8 CN A⁴⁺ Ionic Radii (Å)	$\Delta H^\circ_f \text{AO}_2$ (kJ/mol)	$\Delta H^\circ_f \text{ASiO}_4$ (kJ/mol)	$\Delta H_{f, \text{ox}, 25^\circ\text{C}}$ ASiO₄ (kJ/mol)
zircon	0.83	-1100.6 ± 1.7 ^a	-2035.5 ± 3.4 ^a	-24.2 ± 2.8 ^a
hafnon	0.84	-1117.6 ± 1.6 ^a	-2050.3 ± 5.1 ^a	-22.3 ± 4.7 ^a
stetindite	0.97	-1090.4 ± 1.0 ^b	-1971.9 ± 3.6 ^c	27.5 ± 3.1 ^e
thorite	1.05	-1226.4 ± 3.5 ^b	-2143.5 ± 6.8 ^c	-6.4 ± 5.7 ^c
PaSiO₄	1.01	-1107.0 ± 15.0 ^b	-2003.6 ± 15.1 ^f	14.1 ± 2.9 ^f
coffinite	1.00	-1085.0 ± 1.0 ^b	-1970.0 ± 4.2 ^d	25.6 ± 3.9 ^d
NpSiO₄	0.98	-1078.5 ± 2.7 ^b	-1961.7 ± 4.1 ^f	27.5 ± 5.7 ^f
PuSiO₄	0.96	-1055.8 ± 1.0 ^b	-1930.1 ± 4.1 ^f	36.4 ± 7.6 ^f
AmSiO₄	0.95	-932.2 ± 3.0 ^b	-1802.0 ± 5.3 ^f	40.9 ± 8.5 ^f
CmSiO₄	0.95	Not Available	Not Available	40.9 ± 8.5 ^f
BkSiO₄	0.93	Not Available	Not Available	49.8 ± 10.4 ^f
CfSiO₄	0.92	Not Available	Not Available	54.3 ± 11.3 ^f

381 ^a. Navrotsky and Ushakov (2005)¹¹⁸; ^b. Konings *et al.* (2014)¹⁰⁵; ^c. Guo *et al.* (2016)⁸; ^d. Guo *et al.*
 382 (2015)⁴⁸; ^e. Experimentally derived in this study; ^f. Calculated in this study.

383 **Figures**



384
385 **Figure 1.** TGA-DTA curve obtained from $\text{CeSiO}_4 \cdot 0.43\text{H}_2\text{O}$ (sample mass: 4.5220 ± 0.0005 mg)
386 when heating up to 1200°C under N_2 atmosphere.



387
 388 **Figure 2.** Enthalpy of formation from binary oxides obtained for orthosilicates ($ASiO_4$),
 389 orthovanadates (AVO_4), and orthophosphates (APO_4) that crystallize with the zircon structure
 390 ($I4_1/amd$) as a function of ionic radius of a metal cation (A^{4+} or A^{3+}) in the eightfold coordination.
 391 Data shown as *filled blue circles* were used in order to estimate the values for the *empty blue*
 392 *circles* by means of linear regression. The equation which describes the *blue line* is $\Delta H_{f,ox} = (-$
 393 $446.3 \pm 152.5) r - (464.9 \pm 153.6)$, with an adjusted $R^2 = 0.79096$. Data denoted with *orange circles*
 394 was derived by utilizing the DFT-LDA results for the enthalpy of formation of orthosilicate
 395 materials at -273°C reported by Ferriss *et al.*³⁷, in conjunction with the standard enthalpy of
 396 formation of quartz¹¹⁷ and AO_2 ¹⁰⁵ ($A = \text{Ce, U, Th, Pu}$). This assumes that the energetic
 397 contributions from the respective heat capacities are negligible to the overall calculation, so the
 398 enthalpy of formation data reported by Ferriss *et al.* can be treated as approximately equal to
 399 standard state conditions. Data points as *purple triangles* and *green diamonds* are for
 400 orthophosphates⁵⁹ and orthovanadates¹⁰⁶, respectively.

401

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