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Reply to comment by Konings and Plyasunov on “First experimental determination of the solubility constant of coffinite” [Geochim. Cosmochim. Acta 181 (2016) 36-53]

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R.J.M. Konings and A. Plyasunov investigated the values of thermodynamic data determined by Szenknect et al. (2016) from solubility experiments performed using a synthetic sample of coffinite. Especially, they focused on the value of the standard molar entropy, which was derived from these solubility data and the calorimetric measurement of the standard molar enthalpy of formation of coffinite published by Guo et al. (2015). The two independent measurements were performed on the same synthetic sample prepared by Mesbah et al. (2015) and fully characterized using complementary techniques by the two teams. We thank Konings and Plyasunov for their comment and the relevant analysis of previously published work. As they concluded, we agree that new experimental data are required to solve the “coffinite issue”. Here, we simply wish to clarify a few points regarding the questions arising from their analysis.

In Szenknect et al. (2016), we determined the standard molar entropy of formation of the coffinite by combining the  $\Delta_f G_m^\circ$  (USiO<sub>4</sub>, coffinite, 298.15 K) = - (1867.6 ± 3.2) kJ.mol<sup>-1</sup> obtained from the  $\Delta_R G_m^\circ$  (298.15 K) of the reaction (1) with the  $\Delta_f H_m^\circ$  (USiO<sub>4</sub>, coffinite, 298.15 K) = - (1970.0 ± 4.2) kJ.mol<sup>-1</sup> determined by Guo et al. (2015) from calorimetric measurements and using the Gibbs energy definition  $\Delta_f G_m^\circ(T) = \Delta_f H_m^\circ(T) - T \times \Delta_f S_m^\circ$ .



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Using the auxiliary data recommended by the OECD/NEA review (Grenthe et al., 1992), the standard molar entropy value obtained was  $S_m^\circ(\text{USiO}_4, \text{coffinite}, 298.15 \text{ K}) = (136 \pm 25) \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ . Konings and Plyasunov noticed that the uncertainty associated with this value was large and that the source of the “extreme” uncertainty was not specified. We estimated the uncertainty by propagating the uncertainties in  $\Delta_f G_m^\circ(\text{USiO}_4, \text{coffinite}, 298.15 \text{ K})$  and  $\Delta_f H_m^\circ(\text{USiO}_4, \text{coffinite}, 298.15 \text{ K})$  values equal to 3.2 and 4.2  $\text{kJ}\cdot\text{mol}^{-1}$ , respectively. Adding these uncertainties and dividing by 298.15 led to an uncertainty of 25  $\text{J}\cdot\text{mol}\cdot\text{K}^{-1}$  for the standard molar entropy. This is also the main contribution to the uncertainty calculated for the  $\Delta_{r,ox} S_m^\circ(298.15 \text{ K})$  that was  $(17 \pm 31) \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ . The uncertainty associated with  $S_m^\circ(\text{USiO}_4, \text{coffinite}, 298.15 \text{ K})$  could be also calculated as the square root of the sum of squares of the uncertainties in  $\Delta_f G_m^\circ(\text{USiO}_4, \text{coffinite}, 298.15 \text{ K})$  and  $\Delta_f H_m^\circ(\text{USiO}_4, \text{coffinite}, 298.15 \text{ K})$ , then dividing by 298.15. In this case, the uncertainty associated with the standard molar entropy of coffinite is equal to 18  $\text{J}\cdot\text{mol}\cdot\text{K}^{-1}$  instead of 25  $\text{J}\cdot\text{mol}\cdot\text{K}^{-1}$ . Whatever the method used to estimate this uncertainty, it is larger than that usually associated with the direct measurement of the standard molar entropy by calorimetry as it resulted from a combination of two different sets of experiments with their associated uncertainties.

The second, and most important concern addressed by Konings and Plyasunov is the value of the standard molar entropy itself:  $S_m^\circ(\text{USiO}_4, \text{coffinite}, 298.15 \text{ K}) = (136 \pm 25) \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ . Konings and Plyasunov judged that this value is exceptionally large as compared with the value of the standard molar entropy of the isostructural thorite,  $\text{ThSiO}_4$ . The starting point for their analysis is the estimation of the standard molar entropy of thorite, which was derived from the calorimetric measurement of the entropy of huttonite made by Konings et al. (2008) and reached  $S_m^\circ(\text{ThSiO}_4, \text{huttonite}, 298.15 \text{ K}) = (104.3 \pm 2.0) \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$  and the value of the entropy of the thorite-huttonite phase transition at 1483 K equal to  $4.5 \pm 1.7 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ , derived from the enthalpy difference for huttonite and thorite determined by Mazeina et al. (2005). Thus, the calculated value for the standard molar entropy of thorite proposed by Konings and Plyasunov was  $S_m^\circ(\text{ThSiO}_4, \text{thorite}, 298.15 \text{ K}) = (99.9 \pm 2.6) \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ . Using our method to propagate errors, the uncertainty on this value reaches 3.7  $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ , which is slightly larger than the estimate made by Konings and Plyasunov. Adding the magnetic contribution of the  $\text{U}^{4+}$  ion to the value obtained for thorite led Konings and Plyasunov to derive  $S_m^\circ(\text{USiO}_4, \text{coffinite}, 298.15 \text{ K}) = (109 \pm 4) \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ , which is indeed smaller than the value reported by Szenknect et al. (2016) ( $S_m^\circ(\text{USiO}_4, \text{coffinite}, 298.15 \text{ K}) = (136 \pm 25) \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ ).

We agree that the comparison of the standard molar entropy of coffinite with the isostructural thorite is of great interest. Thus, we estimated the value of  $S_m^\circ(\text{ThSiO}_4, \text{thorite}, 298.15 \text{ K})$  by using exactly the same method as for the coffinite. Indeed, Szenknect et al. (2013) reported solubility data for thorite and derived the value for  $\Delta_f G_m^\circ(\text{ThSiO}_4, \text{thorite}, 298.15 \text{ K}) = -(2044 \pm 11) \text{ kJ}\cdot\text{mol}^{-1}$ . However, in this study, the LLNL database (Johnson et al., 1992) was used to determine the activity of  $\text{Th}^{4+}$  and  $\text{H}_4\text{SiO}_4$  in the 0.1 M HCl solution at equilibrium with the synthetic sample of thorite. Following the same methodology as for the solubility experiments performed with coffinite, we used the Thermochemie database (Giffaut et al., 2014) and auxiliary data recommended by the OECD/NEA review (Rand et al., 2009) to calculate the standard free energy of formation of thorite. We obtained  $\Delta_f G_m^\circ(\text{ThSiO}_4, \text{thorite}, 298.15 \text{ K}) = -(2049.3 \pm 7.1) \text{ kJ}\cdot\text{mol}^{-1}$ . This value is not significantly different from the value previously published and in very good agreement with the value reported earlier by Schuiling et al. (1976):  $\Delta_f G_m^\circ(\text{ThSiO}_4, \text{thorite}, 298.15 \text{ K}) = -(2050.15 \pm 4.35) \text{ kJ}\cdot\text{mol}^{-1}$ . The standard enthalpy of formation of thorite was measured by Mazeina et al. (2005) and was  $\Delta_f H_m^\circ(\text{ThSiO}_4, \text{thorite}, 298.15 \text{ K}) = -(2117.6 \pm 4.2) \text{ kJ}\cdot\text{mol}^{-1}$ . More recently, Guo et al. (2016) reported the value  $\Delta_f H_m^\circ(\text{ThSiO}_4, \text{thorite}, 298.15 \text{ K}) = -(2143.5 \pm 6.8) \text{ kJ}\cdot\text{mol}^{-1}$ . This value was derived from calorimetric measurement performed with the thorite sample used by Szenknect et al. (2013). Using the Gibbs energy definition

and the values of Guo et al. (2016) for  $\Delta_f H_m^\circ$  (ThSiO<sub>4</sub>, thorite, 298.15 K) and  $\Delta_f G_m^\circ$  (ThSiO<sub>4</sub>, thorite, 298.15 K) = - (2049.3 ± 7.1) kJ.mol<sup>-1</sup> led to  $S_m^\circ$  (ThSiO<sub>4</sub>, thorite, 298.15 K) = (166 ± 47) J.mol<sup>-1</sup>.K<sup>-1</sup>. This value is even larger than the standard molar entropy estimated using the same methodology for coffinite.

Unlike coffinite, thorite is stable relative to the mixture of the oxides. Thus, in that case, high temperature calorimetry could not have been affected by the metastability of thorite, as suggested for coffinite by Konings and Plyasunov. In the case of coffinite, the sample was essentially at room temperature when it reached the calorimetric sensors, so any reaction was seen by the calorimeter. As enthalpy is a state function, whether coffinite decomposed then dissolved, or dissolved directly in the oxide melt solution should neither affect the value of the enthalpy of drop solution, nor the enthalpy of formation from binary oxides calculated from thermochemical cycles.

The discrepancy between the two values proposed for the standard molar entropy of thorite (99.9 ± 2.6) and (166 ± 47) J.mol<sup>-1</sup>.K<sup>-1</sup>, respectively raises questions about the appropriate way to estimate entropy, which are not limited to the case of the coffinite. As already discussed by Chen and Ewing (2003) based on a review of crystallographic and thermodynamic data published for various uranyl phases, there are some contributions to the entropy that cannot be determined by calorimetric measurements solely. These contributions, called residual entropy could be related to structural disorder (especially linked to the presence of structural water molecules), site-mixing, isotopic mixing, disorder in magnetic spin and nuclear spin disorder, and are only accessible by combining calorimetric data with solubility data. These contributions are not expected to cause considerable residual entropy in thorite or coffinite, which were found to be anhydrous, pure and homogeneous end-member phases. However, both thorite and coffinite were synthesized hydrothermally, forming grains 200-400 nm in size. The polycrystalline nature of these grains was evidenced from X-ray peaks broadening that corresponded to a crystallite size of 20 nm and 80 nm, for thorite and coffinite, respectively. On the other hand, the standard entropy value of huttonite determined by Konings et al. (2008) corresponded to a sample synthesized by solid-state reaction. The huttonite sample used was obtained by heating at 1873 K during 50 h a mixture of ThO<sub>2</sub> and SiO<sub>2</sub>, which probably led to the formation a larger crystals of huttonite. The crystallite size may affect the thermodynamic properties of the phase (Hochella et al., 2008; Navrotsky et al., 2008), especially by increasing the contribution of the structural disorder. This might explain why the values obtained for the entropy of coffinite and thorite by combining solubility and calorimetric data are higher than the values deduced by Konings and Plyasunov from the direct measurement of the standard molar entropy of a well crystallized sample of huttonite.

Nevertheless, we agree that further investigations of the thermodynamic properties of the coffinite are necessary, especially low-temperature heat capacity and standard molar entropy measurements performed with the same synthetic sample, which is available in sufficient amount and whose particle size is representative of most “real world” situations (natural coffinite and that produced by the corrosion of spent nuclear fuel). It is of primary interest to know if the three independently derived thermodynamic properties for coffinite form a consistent set of data, and to identify the more reliable method to determine the thermodynamic properties of fine-grained and polycrystalline phases, which are widespread in the geosphere.

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