

# Hydrothermal solution calorimetry and determination of the thermodynamic properties of Nd species in acidic aqueous fluids from 25 to 150 °C.

YERKO FIGUEROA PENARRIETA<sup>1</sup> AND ALEXANDER P  
GYSI<sup>1,2</sup>

<sup>1</sup>New Mexico Institute of Mining and Technology

<sup>2</sup>New Mexico Institute of Mining and Technology, New Mexico  
Bureau of Geology and Mineral Resources

Presenting Author: yerko.figueroapenarrieta@student.nmt.edu

The thermodynamic properties of REE [1] can be used to model their mobilization in hydrothermal-magmatic REE mineral deposits [2,3]. However, the prediction of the stability of many of the aqueous REE complexes are based on Supcrt92 (slop98.dat database), many of which, are based on low temperature experimental data extrapolated to elevated temperature [4-6]. However, calorimetry experiments are needed to accurately determine the properties of REE aqueous species to high temperatures.

In this study, we measured the enthalpy of solution ( $\Delta_{\text{soln}}H^\circ$ ) of synthetic Nd hydroxide ( $\text{Nd}(\text{OH})_3(\text{s})$ ) and Nd chloride ( $\text{NdCl}_3(\text{s})$ ) in aqueous perchloric and hydrochloric acid solutions, respectively. The experiments were performed using solution calorimetry from 25 to 150 °C, with starting pH of 2 and varying ionic strength (0.01 to 0.09 mol/kg  $\text{NaClO}_4$ ; 0.05 to 0.35 mol/kg  $\text{NaCl}$ ). The dissolution of  $\text{Nd}(\text{OH})_3(\text{s})$  is used to retrieve the enthalpy of formation of  $\text{Nd}^{3+}$ , and the dissolution of  $\text{NdCl}_3(\text{s})$  the enthalpy of both  $\text{NdCl}_2^{2+}$  and  $\text{NdCl}_2^+$  species as a function of temperature.

According to the equilibrium reaction  $\text{Nd}(\text{OH})_3(\text{s}) + 3\text{H}^+ \rightleftharpoons \text{Nd}^{3+} + 3\text{H}_2\text{O}(\text{aq})$ , measured  $\Delta_{\text{soln}}H^\circ$  [ $\text{Nd}(\text{OH})_3(\text{s})$ ] values deviate by up to 10 kJ/mol between 25 and 150 °C in comparison to the predicted values from the Supcrt92 database. This results in standard molal enthalpy increment [ $H^\circ(T) - H^\circ(298.15)$ ] deviation for  $\text{Nd}^{3+}$  by up to 12.6 kJ/mol at 150 °C. Similarly, our preliminary results for  $\Delta_{\text{soln}}H^\circ$  [ $\text{NdCl}_3(\text{s})$ ] range from  $-7.66 \pm 1.35$  to  $-15.96 \pm 0.50$  kJ/mol at 25 and 125 °C, respectively. These values are significantly different from the predicted enthalpy values from Supcrt92 based on the dissolution of  $\text{NdCl}_3(\text{s})$  and formation of either  $\text{NdCl}_2^{2+}$  or  $\text{NdCl}_2^+$  species. The obtained thermodynamic properties from this study have important implications for predicting the high temperature stability of aqueous REE in natural hydrothermal fluids.

[1] Migdisov et al. (2016), *Chem. Geol.* 439, 13–42; [2] Gysi and Williams-Jones (2013), *Geochim. Cosmochim. Acta* 122, 324–352; [3] Perry and Gysi (2018), *Geofluids*, Article ID 5382480; [4] Haas et al. (1995), *Geochim. Cosmochim. Acta* 59, 4329–4350; [5] Tanger and Helgeson (1988), *Am. J. Sci.* 288, 19–98; [6] Shock et al. (1997), *Geochim. Cosmochim. Acta* 61, 907–950.