

Experimental Report template

Proposal title: Nd solubility and speciation in hydrothermal fluids: Implications for the transport, segregation and deposition of REE in magmatic-hydrothermal systems.		Proposal number: 30-02-1089
Beamline: BM30-B	Date(s) of experiment: from: 29/04/2015 to: 05/05/2015	Date of report: 10/07/2015
Shifts: 18	Local contact(s): Jean-Louis Hazemann	Date of submission: 01/08/2015

Objective & expected results:

The increasing need of the green energy and high technology sectors for rare metals (REE are HFSE) requires a better understanding of the processes favoring the formation and controlling the grade of rare metal ore deposits. The main aim of our experiments is to provide new constraints on the role of hydrothermal fluids in the formation of rare metals mineralization in large igneous provinces (e.g., Bayan Obo, China, Thor Lake, Canada) by **studying the REE high temperature aqueous chemistry using *in situ* XAS**. To complement previous *in situ* XAS experiments investigating Yb solubility and speciation up to 400 °C (Experimental Report 20140566), we have now determined the effect **the effect of Cl, Si and Na on the speciation and solubility of Gd** from 200 to 500 °C at 80 MPa. The experimental results provide unexpected insights on the role of fluid composition on REE mobilization and transport in hydrothermal systems.

Results and the conclusions of the study:

The experiments were conducted in the high temperature autoclave dedicated to *in situ* X-Ray absorption spectroscopy of hydrothermal fluids available on the BM30-B beamline [1]. XAS spectra collected around the Gd L_{III}-edge (7.243 keV) in transmission and fluorescence modes were used to determine both the speciation and the solubility of Gd in the high temperature fluids, using similar technique as described in [2,3].

First, the effect of increasing Cl concentrations and decreasing pH on Gd solubility and speciation in acidic fluids (pH<3) was investigated loading pieces of synthetic Gd₂O₃, GdPO₄ or Gd₂Si₂O₇ with 0.35-0.75m HCl solutions. As observed for Yb (Experimental Report 20140566)[3], GdPO₄ exhibits significantly lower solubility than Gd₂Si₂O₇ and Gd₂O₃ at T<300 °C (Fig. 1). While all compounds present strongly retrograde solubility, increasing HCl contents appears to delay the solubility decrease to around 350 °C in 0.75m HCl compare to 250 °C in 0.35m HCl. In the 0.35m HCl solution, both Gd₂Si₂O₇ and GdPO₄ solubilities are below the limit of detection (~10-20 ppm) at 450 °C, while Gd concentrations in 0.75m HCl remain above detection limit up to 500 °C.

Although the reported effect of HCl concentrations could just be related to a pH effect (e.g. REE solubility is higher in low pH – 3), XANES and EXAFS spectra suggest that Gd speciation evolves both with increasing temperature and HCl contents. The XANES spectra and EXAFS oscillations of Gd in the

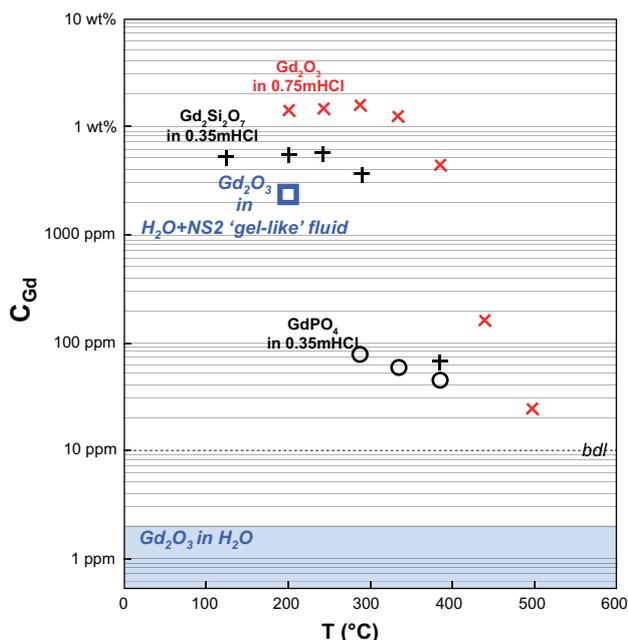


Fig. 1: Effect of temperature on the solubility of Gd compounds in various fluid compositions.

0.75m HCl are flatter and shifted to higher position compare to the 0.35m HCl (Fig. 2). There are also significant changes of the XANES spectra in 0.75m HCl with increasing temperature, including a strong increase of the white line amplitude at $T > 300$ °C that is attributed to a complete change of the local geometry around Gd.

Preliminary EXAFS modeling confirms the significant change of Gd local environment with increasing temperature and Cl contents. In the 0.35m HCl solution Gd coordination number decreases slightly from 9 to 8 while increasing temperature from 125 to 242 °C. The Gd-O bond distance remains constant around 2.41 ± 0.02 Å within this temperature range. The dissolution of Gd as $\text{Gd}(\text{H}_2\text{O})_{9.8}^+$ is in good agreement with solubility models that suggest the high stability of REE aqua ions at low temperature and low Cl contents [4]. At 287 °C, the hydration number further decrease towards 6, while Gd-O bond distance increases to ~ 2.45 Å. For similar Cl contents, [5] reported a reduction of Gd hydration shell associated with the onset of chlorination (involving ~ 1 Cl atom) at 300 °C. Such low number of Gd-Cl association could not be included in our fits. It is only at 385 °C that we monitor a significant speciation change that is modeled by a structure involving about 6 O and 2 Cl atoms located at 2.38 Å and 2.67 Å, respectively. We note that the incorporation of Cl in Gd local-environment is not associated to significant changes of the EXAFS oscillations shape and position (Fig. 2). A similar observation can be made from experiments by [5].

At higher Cl contents (0.75mHCl), the fits suggest that Gd hydration shell only involves 5-6 oxygens located at ~ 2.43 Å at 200 and 242 °C. The hydration number further decreases to about 4 at 287 and 334 °C, though no obvious Gd-Cl association could be modeled. At 385 °C and 439 °C, the quality of the fits are significantly improved by adding 4 and 3 Cl atoms around Gd. Both structures provide similar Gd-O and Gd-Cl bond distances, which makes it for now unclear whether $\text{GdCl}_3(\text{H}_2\text{O})_3^0$ or $\text{GdCl}_4(\text{H}_2\text{O})_4^-$ is the dominant specie at $T \geq 385$ °C. While REECl_2^{2+} and REECl_2^+ are generally considered the most stable chloride complexes in hydrothermal fluids [4], calculations by [6] predicted that at $T > 200$ °C, the formation of high-order chloro-complexes involving 3-4 Cl should be significantly more favorable for Gd (and Dy) than Yb. Our preliminary results suggest that such complexes could in fact dominate Gd speciation in Cl-bearing fluids and should hence be further considered in future solubility models. We also note that such high-order Gd complexes have recently been invoked to explain extreme Gd enrichment in volcanic fumarolles [7].

In a second part of our experiments, we tested a new hypothesis regarding the nature of hydrothermal fluids involved in REE transport and deposition in magmatic-hydrothermal environment. In a previous study, [8,9] suggested that the formation of alkali-silicate complexes could significantly enhance HFSE solubility and favor their transport in Si,Na-rich high-temperature fluids. While such fluids have not yet been reported in rare metal deposits, HFSE-REE-rich hydrosilicate liquids (HSL – ‘gel-like’ fluids rich in silicates and alkalis) have been identified in pegmatites [10]. Furthermore, Si,Na-rich single-phase fluids containing between 20 and 70 wt% dissolved Si and Na are known to be stable over a wide P-T range in the $\text{H}_2\text{O}-\text{Na}_2\text{Si}_2\text{O}_5$ system [11], and could hence be expected to form in fluorine and phosphorus-rich highly peralkaline systems such as some reported in association with REE mineralization (e.g., Dubbo/Toongi, Australia). Therefore, we investigated the potential of Si,Na-rich to mobilize and transport REE, loading Gd_2O_3 with H_2O and a piece of synthetic $\text{Na}_2\text{Si}_2\text{O}_5$ glass (NS2). At 200 °C, Gd_2O_3 solubility in pure H_2O is well-below our detection limit, we report up to 2500 ppm Gd in the $\text{H}_2\text{O}-\text{NS}_2$ system (Fig. 1), a solubility almost as high as in the 0.35m HCl solution. At 287 °C, we report systematic precipitation of Gd_2O_3 , which is due to unmixing of the $\text{H}_2\text{O}-\text{NS}_2$ ‘gel-like’ fluid to form an H_2O -rich aqueous fluid and a NS2 melt [11]. Upon quench, a REE-rich sodium silicate melt globules was recovered, confirming

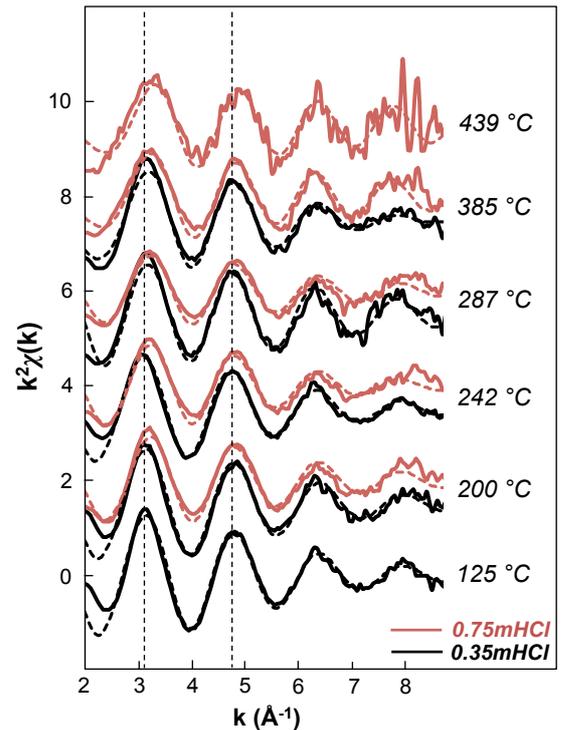


Fig.2: EXAFS oscillations of Gd in 0.35m and 0.75m HCl solutions with increasing temperature. Fits are reported as dashed lines on top of the experimental spectra.

the complete mixing of NS₂ and H₂O at high T. Those results provide evidence for a potential role of Si,Na-rich 'gel-like' fluids in the formation of rare metals deposits that we expect to further test in an upcoming experiment.

Justification and comments about the use of beam time:

The BM30-B beamline provides a unique environment for the *in situ* study of aqueous fluids at the P-T relevant to the hydrothermal precipitation of economic minerals in shallow crustal environments (200 < T < 600 °C and P < 200 MPa). The unpredicted formation of high-order Gd chloro-complexes and the enhanced Gd solubility in Si,Na-rich fluids both confirm the critical inputs of the *in situ* approach to provide new insights on the REE aqueous chemistry and the potential effect of fluid composition on the formation of rare metals ore deposits.

In comparison to previous experiments at the Yb L_{III}-edge (*Experimental Report 20140566*), the use of thinner Be high pressure windows (1.5mm) enable to significantly decrease the limit of detection for REE (*i.e.*, now ~10-20 ppm for Gd, while it was close to 100 ppm with thicker Be windows). Recourse to this design should now facilitate future measurements at the Nd L_{III}-edge.

Unfortunately, different experimental and optical problems have been encountered during the allocated beamtime: the beam became increasingly defocused several times and critical parts of the high pressure vessel had to be replaced, most probably due to normal wear. Overall, we estimate that those problems resulted in the loss of at least 5 shifts and significantly compromised the interpretation of solubility in many runs. Furthermore, most of these troubles occurred at the beginning of experiments, *i.e.*, at T<300 °C, well below the most interesting temperature conditions for our study. Therefore, a follow-up proposal will be submitted in September 2015, with the aim to complete our actual data-set on the Nd, Gd and Yb solubility and speciation in high temperature fluids.

Publication(s):

[1] Testemale et al., 2005. *Reviews of Scientific Instruments* 76, 043905-1-5. [2] Pokrovski et al., 2005. *Chemical Geology* 217, 127-145. [3] Louvel et al. *in press* *Chemical Geology*. [4] Migdisov and Williams-Jones 2014. *Mineralium Deposita* 49, 987-997. [5] Mayanovic et al., 2007. *Chemical Geology* 239, 266-283. [6] Haas et al., 1995. *Geochim. Cosmochim. Acta* 59, 4329-4350. [7] Falcone et al., 2014. *Conf. Abstract. Congresso SGI-SIMP, Milan, Italy*. [8] Louvel et al., 2013. *Geochimica et Cosmochimica Acta*, 204, 281-299. [9] Louvel et al., 2014. *American Mineralogist* 99, 1616-1625. [10] Touret et al., 2007. *Conf. Abstract. Granitic Pegmatites: The State of the Art, Porto*. [11] Mustart, 1972. PhD thesis, Stanford University.