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### Synthesis of solid alkaline lanthanide carbonates

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Stability and mobility of actinides (An) species in ground-waters may govern their long time behaviour in potential radioactive waste repositories. For this purpose, a Callovo-Oxfordian geological formation is studied in France; it is in anoxic chemical conditions, where Pu, Am and Cm can be stable at the +3 oxidation state, and where their aqueous speciation is often dominated by carbonate complexes.

The stoichiometry of the limiting carbonate complex of An(III) is still discussed, as typically seen in the thorough NEA reviews of published thermochemical data. Robouch evidenced  $\text{Am}(\text{CO}_3)_3^{3-}$  as the limiting complex [2], which was later confirmed by Giffaut [3] and Runde [4]. However,  $\text{M}(\text{CO}_3)_3^{3-}$  [1,2] and  $\text{M}(\text{CO}_3)_4^{5-}$  [1,6-8] stoichiometries have been reported for the limiting complexes of An(III) and their chemical lanthanide analogues (Ln(III)). Vercoouter has recently proposed  $\text{Eu}(\text{CO}_3)_3^{3-}$  as the limiting complex in concentrated sodium carbonate solutions, by studying the solubility of  $\text{NaEu}(\text{CO}_3)_2(\text{s})$ , and this stoichiometry was a key point for sensitive analysis for his SLRT study of the other aqueous complexes[9]; while Faucherre evidenced  $\text{Ln}(\text{CO}_3)_4^{5-}$  in concentrated potassium carbonate solutions using the same methodology [10]. Two parameters can explain this difference: Ln radii and interactions of Ln complexes with aqueous counter-ions. Therefore we decided to systematically study the solubility of  $\text{AlkLn}(\text{CO}_3)_2 \cdot x\text{H}_2\text{O}$  for various elements (Ln = La, Nd, Eu, Dy and Alk = Li, Na, K, Cs (and  $\text{NH}_4$ )) to investigate the stoichiometry of the limiting carbonate complex

Solids  $\text{AlkLn}(\text{CO}_3)_2 \cdot x\text{H}_2\text{O}$  are expected to be the most stable phases in equilibrium with the limiting complex of Ln. We aimed at preparing these solids at room temperature and atmospheric pressure (not in an autoclave). Thus the solid compounds are precipitated under conditions close to those expected during the solubility experiments that will be carried out later on, only the results of solid synthesis are here presented. To check the achievement of equilibrium conditions, it is better studying solubility by precipitation and dissolution; for this reason, we did not specially try to obtain a well characterized solid, since solubility is often controlled by poorly crystallised compounds for this type of solids at room temperature.

Alkaline rare earth carbonates of various compositions have been reported [5, 9 -14]. However, the solid preparation is sometimes poorly described and the characterization not convincing (no X-Ray diffraction -XRD-). We precipitated various solids from different aqueous media, and characterised them by XRD. Moreover, Ln and Alk concentrations were measured by inductively coupled plasma-atomic emission spectrometry (ICP-AES).

The sodium double carbonates  $\text{AlkLn}(\text{CO}_3)_2 \cdot x\text{H}_2\text{O}$  were prepared by precipitation of Ln(III) in  $\text{Alk}_2\text{CO}_3$  or  $\text{AlkHCO}_3$  solutions. The solution was constantly shaken. After an equilibration period, a fraction of the solid was filtered through a 0.45  $\mu\text{m}$  cellulose

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nitrate filter, washed with deionised water, air-dried overnight, and analyzed by XRD. The solids were dissolved in HNO<sub>3</sub> for determining [Ln<sup>3+</sup>] and [Alk<sup>+</sup>] by ICP-AES.

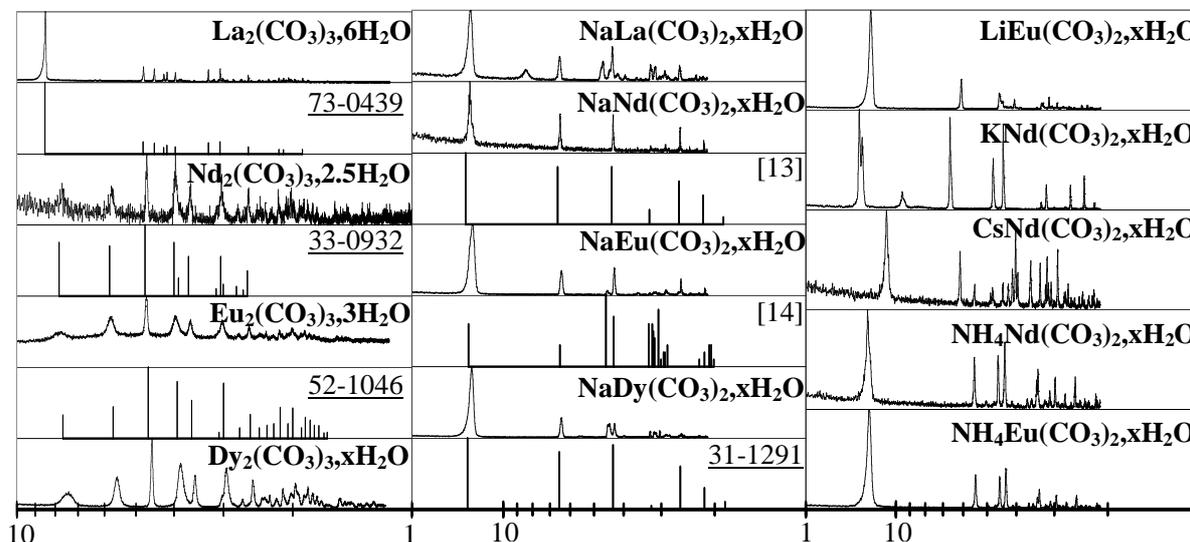


Fig.1: XRD patterns of **synthesized solid phases**, JCPDS references and [from literature].

Most of the AlkLn(CO<sub>3</sub>)<sub>2</sub>·xH<sub>2</sub>O were obtained as mixtures with other minor phases. Only NaNd(CO<sub>3</sub>)<sub>2</sub>·nH<sub>2</sub>O was detected by XRD without impurity. We synthesised hydrated solid phases NaLn(CO<sub>3</sub>)<sub>2</sub> (for Ln = La, Nd, Eu, Dy), AlkNd(CO<sub>3</sub>)<sub>2</sub> (for Alk = Na, K, Cs, NH<sub>4</sub>), LiEu(CO<sub>3</sub>)<sub>2</sub> and NH<sub>4</sub>Eu(CO<sub>3</sub>)<sub>2</sub>. Three compounds were obtained in hydrogencarbonate solutions (NaNd(CO<sub>3</sub>)<sub>2</sub>, NaEu(CO<sub>3</sub>)<sub>2</sub> and NaDy(CO<sub>3</sub>)<sub>2</sub>) and the others in carbonate solutions. Despite Ln(III) are analogues, the solids do not precipitate in the same conditions; however, this could be attributed to kinetics. Ln<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub> compounds were also prepared for Ln = La, Nd, Eu, Dy). Our XRD patterns compare well with published ones, when existing (Fig.1). Some of the synthesised solids had not be previously published -to our knowledge-; for this reason, we found it useful to publish them, it is the aim of the present communication. Solubility experiments are currently in progress using these solid compounds, and may give insight in the variation of the stoichiometries with the nature of the Ln and the Alk ions for limiting carbonate complex.

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