Synthesis of Solid Alkaline Lanthanide Carbonates ($AlkLn(CO_3)_2$)*

Violaine Philippini(1)(2), P. Vitorge(1)(2), T. Vercouter(1) and A. Chausse(2)
S. Bosonnet(3), A. Cheniere(4), C. Desgranges(3), M. Tabarant(4)

(1) CEA Saclay (France) - Laboratory for the Speciation of Radionuclides and Molecules
(2) UMR8587 [University of Evry – CEA – CNRS] (France)
(3) CEA Saclay (France) - Laboratory of Non Aqueous Corrosion Studies
(4) CEA Saclay (France) - Laboratory of Surfaces and Interfaces Reactivity

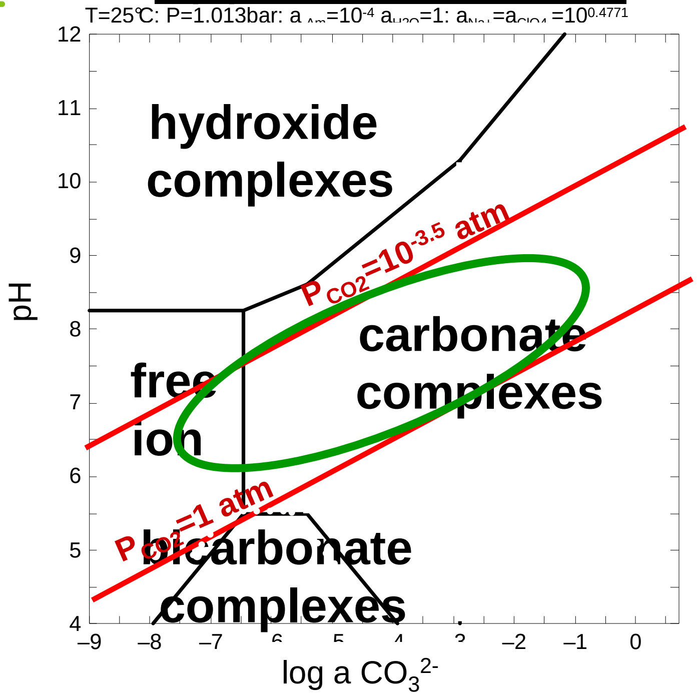
SECR

* This work is part of V. Philippini's PhD thesis

Knowing the stoichiometry of the limiting complex

[92VIT] P. Vitorge, Radiochimica Acta, 1992, 58-59, 105-107.

Simplified predominance diagram for M(III) in carbonate medium



4 different species

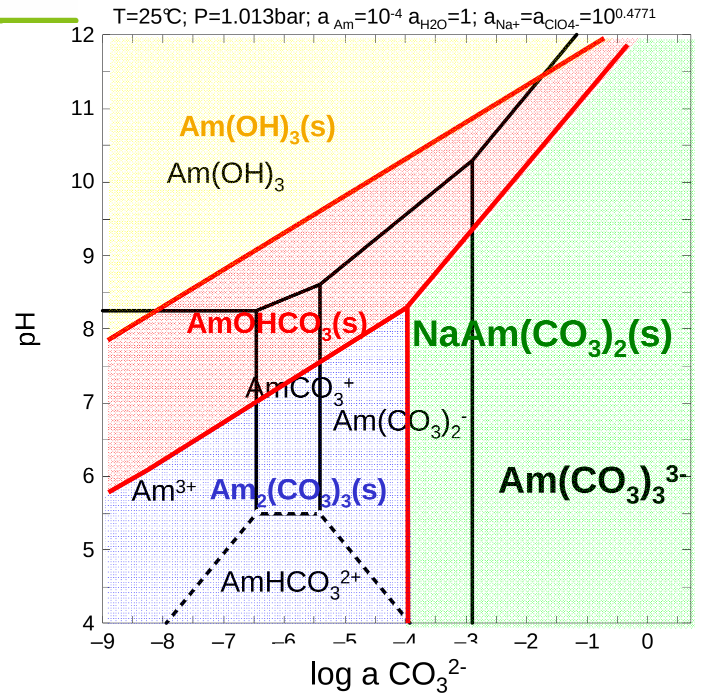
most common experimental conditions

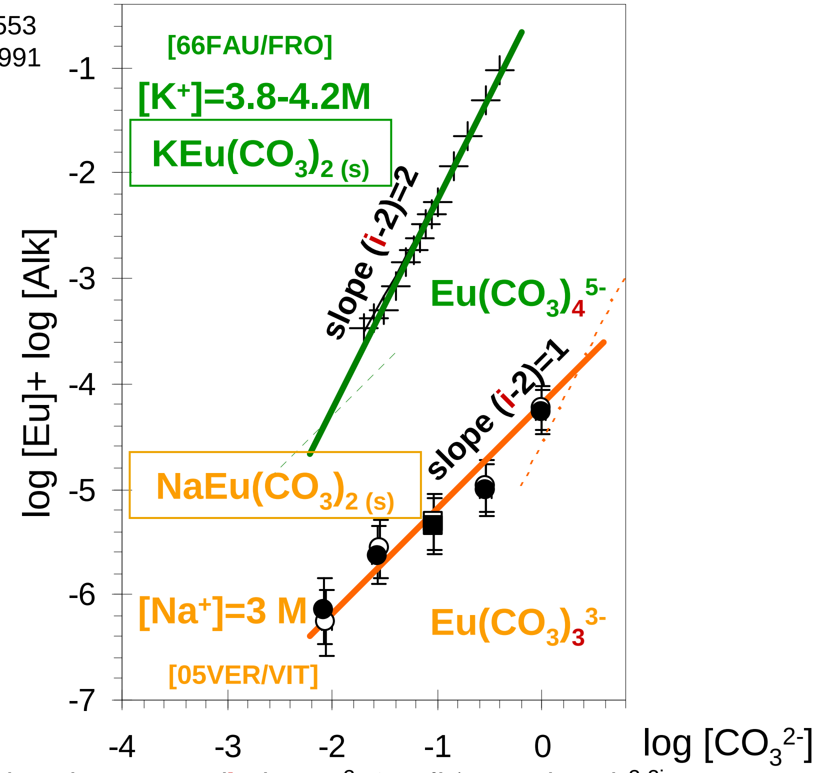
complex aqueous speciation

- ➔ **Stability and mobility of An species in groundwater may govern their long time behaviour**
- ➔ **Potential radioactive waste repository : Callovo-Oxfordian geological formation; anoxic conditions**
  - ➢ ***Pu(III), Am(III), Cm(III)***
  - ➢ ***aqueous speciation dominated by carbonate complexes***
- ➔ **Thorough review of the thermochemical data ⇨ limiting carbonate complex of An(III) still discussed**
- ➔ **Knowing aqueous speciation to determine stability constants**

Goal of this study

[05VER/VIT] T. Vercouter *et al.*, New Journal of Chemistry, 2005, 29, 544-553
[66FAU/FRO] J. Faucherre *et al.*, Revue de chimie Minérale, 1966, 3, 953-991





$AlkEu(CO_3)_2,xH_2O + (i\text{-}2)\ CO_3^{2-} \leftrightarrows Alk^+ + Eu(CO_3)_i^{3-2i} + xH_2O$

➔ **$AlkLn(CO_3)_2$ (s): the stable phase in equilibrium with the limiting complex of Am(III) (and their chemical lanthanide analogues) ⇨ $Am(CO_3)_3^{3-}$**

➔ **Using the same methodology, different limiting complex**

- ***Ln radii***
- ***Interactions between Ln and counter-ion***

➔ **$AlkLn(CO_3)_2$ preparation ⇨ solubility measurements; LC, K**

Literature survey of $AlkLn(CO_3)_2$ synthesis

➔ **Ln** ⇨ *check the analogy between them*

La Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu

Li Na K Rb Cs Fr

➔ **counter-ion (Alk)** ⇨ *hydration of ions in solution*

+ NH_4^+

➔ **$AlkLn(CO_3)_2$ of various compositions have been reported in literature**

- ***preparation poorly described***
- ***characterisation not convincing (no XRD analysis)***

➔ **$AlkLn(CO_3)_2$ ways of synthesis**

- ***mixture of Ln^{3+} and Alk_2CO_3 or $AlkHCO_3$ solutions at room temperature***
- ***CO_2 bubbling in $Ln(OH)_3$ solution***
- ***mixtures of Alc_2CO_3 and $Ln_2(C_2O_4)_3$ (500°C-1000, 3000 bar)***

➔ **parameters**

- ***nature of the precipitant***
- ***temperature and pressure***
- ***concentration of metal ion and precipitant***
- ***aging period***

[94IRM] M. Irmler *et al.* Gmelin Handbook of Inorganic and Organometallic Chemistry, C12B 1994 Springer.

Experimental synthesis of $AlkLn(CO_3)_2$

➔ Solid compounds are precipitated at room temperature and atmospheric pressure

➔ Conditions close to those used for solubility measurements

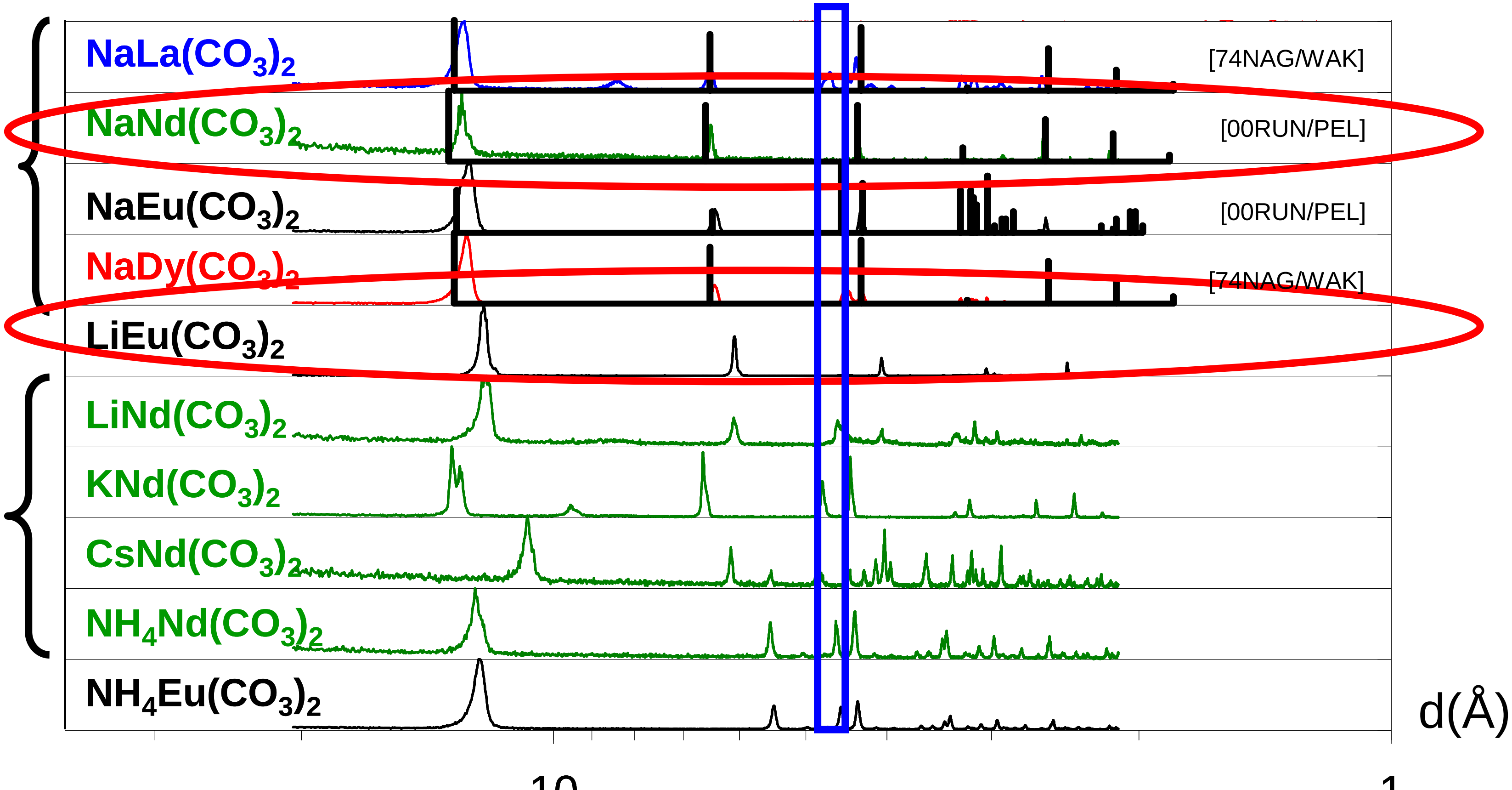
➔ Only solid syntheses will be presented

➔ After an equilibration period: a fraction is filtered, washed, air-dried over a night:

- *characterised by XRD*
- *[Alk] and [Ln] by ICP-AES*
- *H_2O and CO_3^{2-} thermogravimetric analysis*

CO_3^{2-} / HCO_3^-	Li^+	Na^+	K^+	Cs^+	NH_4^+
La^{3+}	no	yes	no	no	no
Nd^{3+}	yes	yes	yes	yes	yes
Eu^{3+}	yes	yes	no	no	yes
Dy^{3+}		yes	no	no	

XRD powder patterns

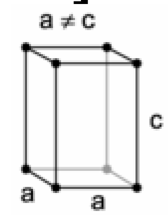


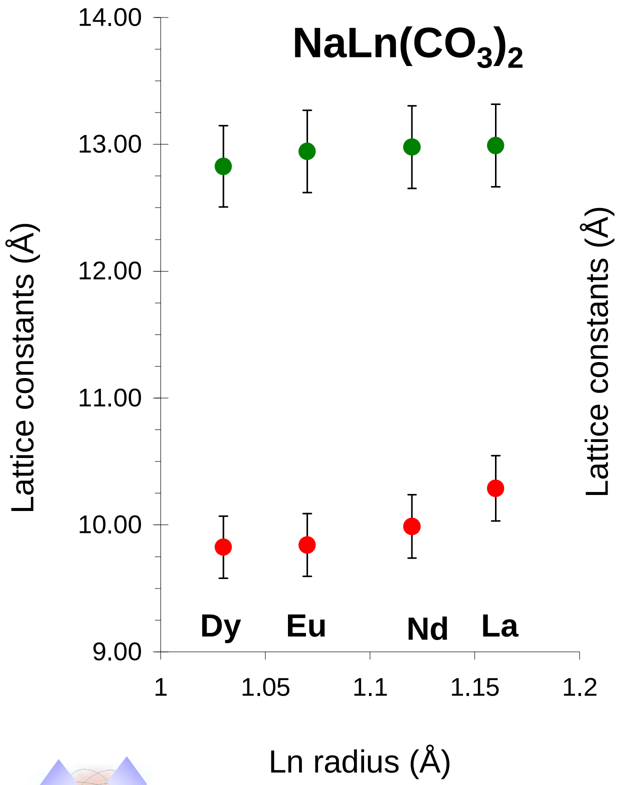
- ➔ **Not explained peaks ⇨ mixture with other minor phases (not identified)**
- ➔ **$LiEu(CO_3)_2$ was obtained with a good purity, after 7 months in its mother liquor**
- ➔ **$NaNd(CO_3)_2$ was obtained with a good purity, after solubility measurements**

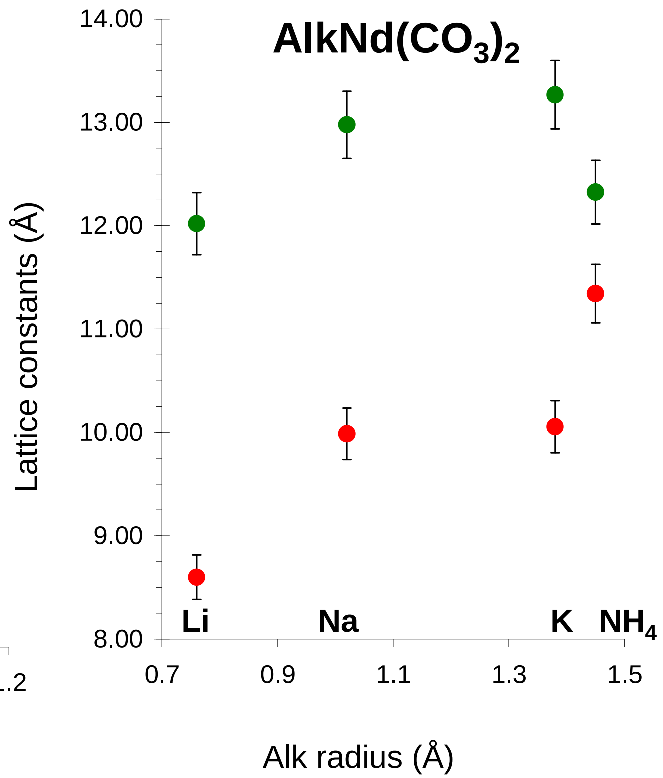
[00RUN/PEL] W. Runde *et al.*, Journal of Alloys and Compounds 2000, 303-304, 182-190
[74NAG/WAK] A. Mochizuki *et al.* Bulletin of the Chemical Society of Japan 1974, 47(3), 755-756

Carbonate lattice parameters

- ➔ calculated with a tetragonal cell [00RUN/PEL] [74NAG/WAK]
- ➔ Miller index values from JCPDS 31-1291 [74NAG/WAK]
- ➔ lattice parameters increase with Ln or Alk radius





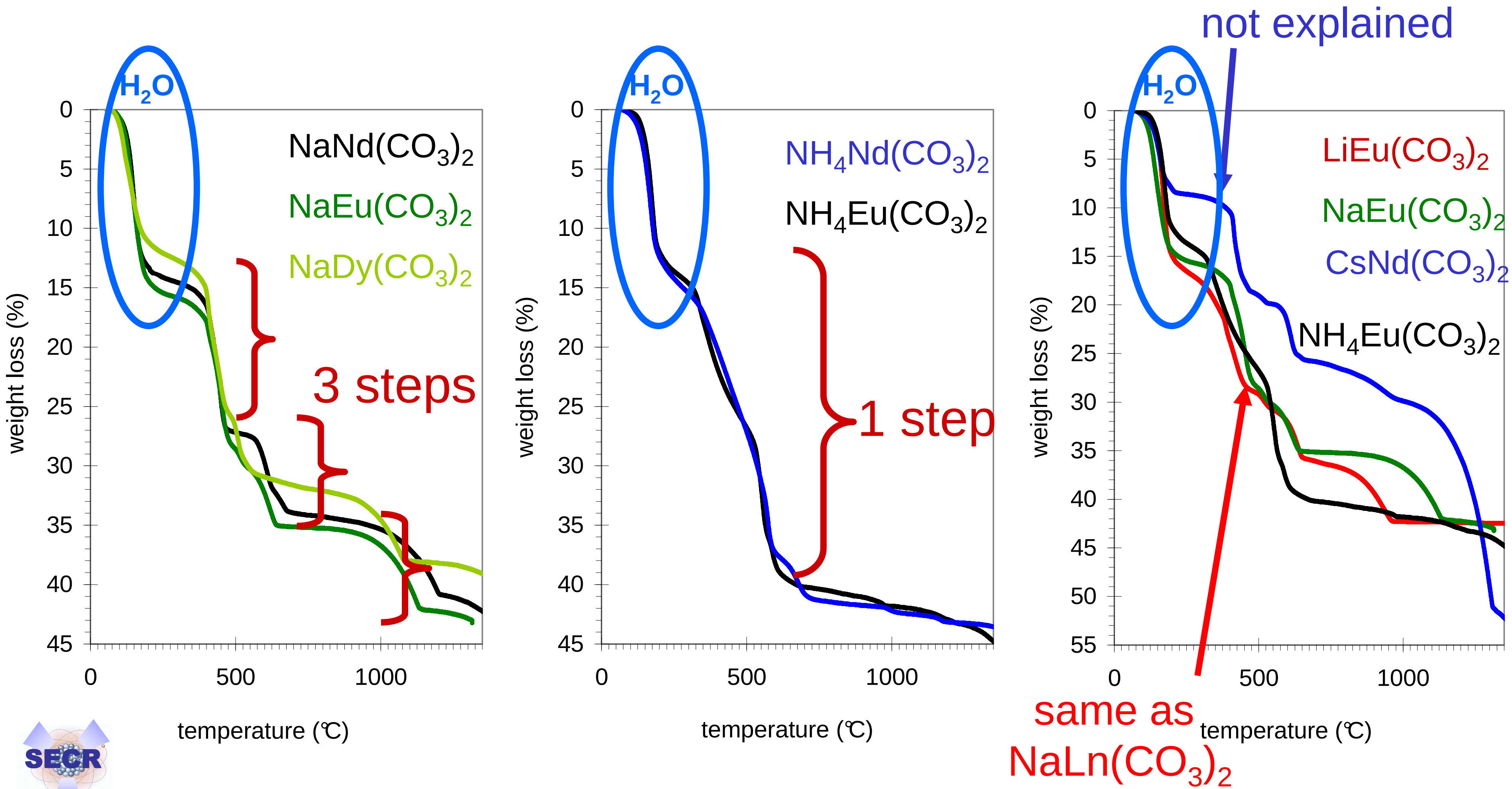


	a	c
$NaLa(CO_3)_2$	12.99	10.29
$NaNd(CO_3)_2$	12.98	9.99
$NaEu(CO_3)_2$	12.91	9.84
$NaDy(CO_3)_2$	12.83	9.83
$LiNd(CO_3)_2$	12.02	8.60
$KNd(CO_3)_2$	13.27	10.06
$NH_4Nd(CO_3)_2$	12.32	11.34

[00RUN/PEL] W. Runde *et al.*, Journal of Alloys and Compounds 2000, 303-304, 182-190
[74NAG/WAK] A. Mochizuki *et al*. Bulletin of the Chemical Society of Japan 1974, 47(3), 755-756

$AlkLn(CO_3)_2,xH_2O$ thermal decomposition

➔ **thermal decomposition studied by TG at 6℃/min under flowing nitrogen**



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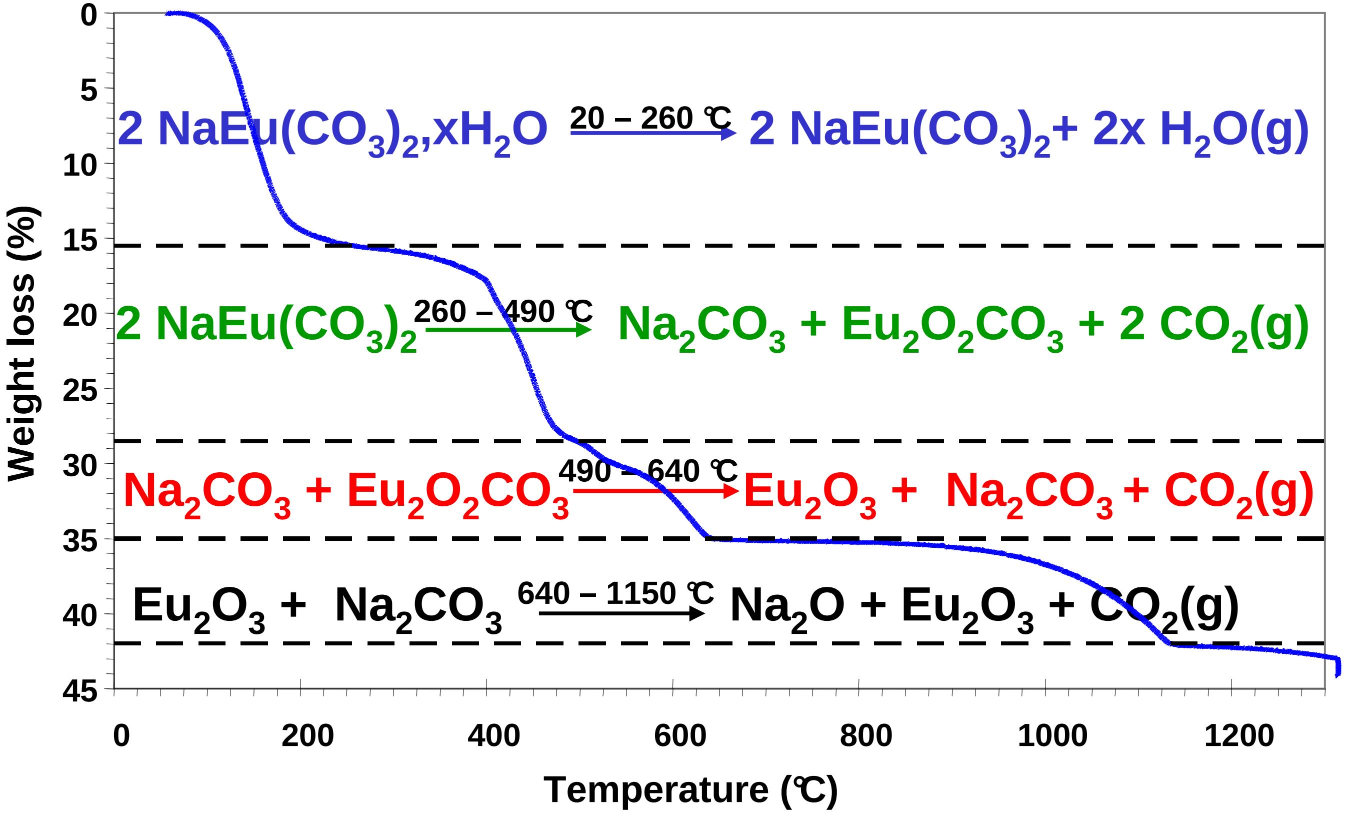
$NaEu(CO_3)_2,xH_2O$ thermal decomposition

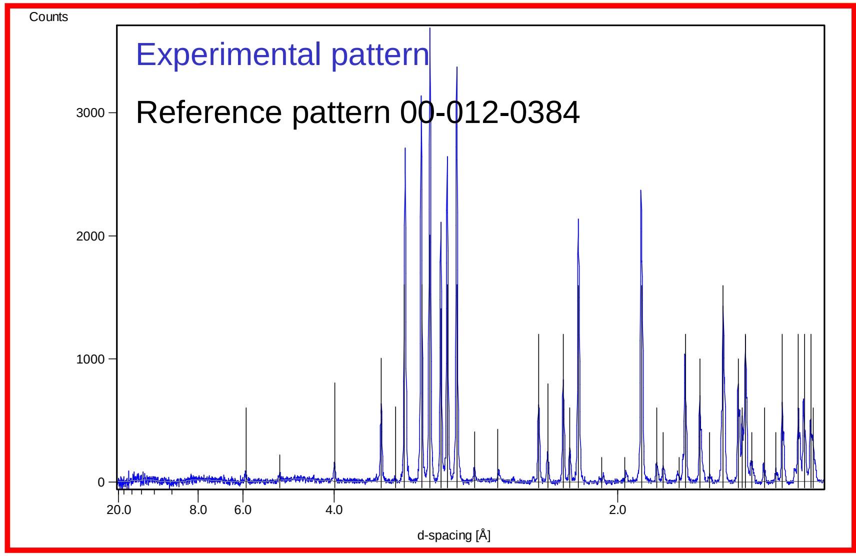
➔ $NaNd(CO_3)_2$, $NaDy(CO_3)_2$, $LiEu(CO_3)_2$ behaviours are the same as $NaEu(CO_3)_2$ one

➔ temperatures of the steps differ slightly for the different carbonates



[81SCH/SEI] H. Schweer *et al*., Zeitschrift fur anorganische und allgemeine chemie 1981, 477, 196-204

$NaEu(CO_3)_2,xH_2O$ thermal decomposition



➔ **Uncertainty in literature for the last step:**

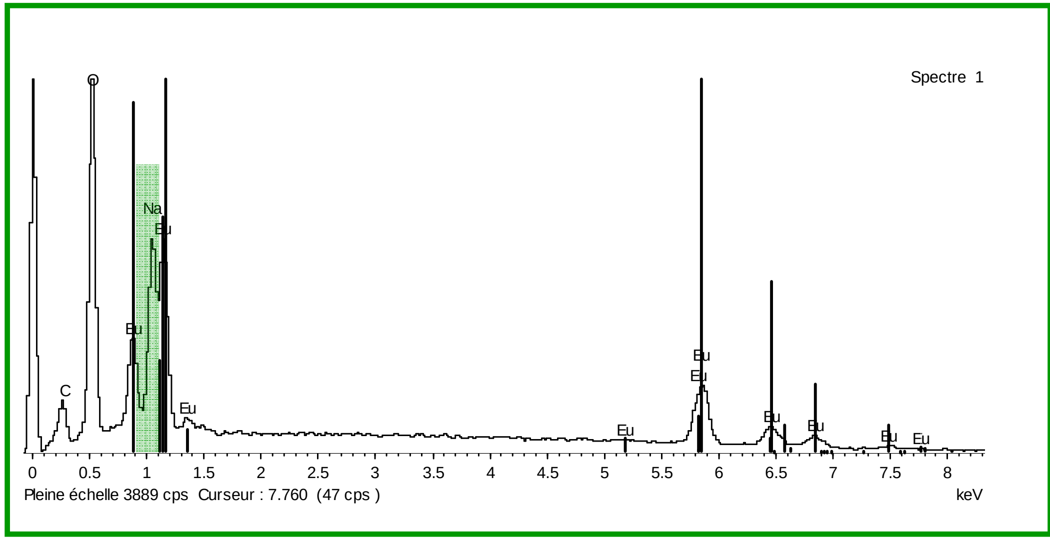
- ***$Eu_2O_3 + Na_2CO_3 \rightarrow Na_2O + Eu_2O_3 + CO_2(g)$***
- ***$Eu_2O_3 + Na_2CO_3 \rightarrow 2\ NaEuO_2 + CO_2(g)$***

➔ **Analysis of the residuum**

XRD analysis

$$Eu_2O_3 + Na_2CO_3 \rightarrow Eu_2O_3 + Na_2O + CO_2(g)$$

SEM/EDS analysis



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$AlkLn(CO_3)_2,xH_2O$ composition

	ICP-AES	Thermogravimetric analysis	
	$\frac{[Alc]}{[Ln]}$	nCO_3^{2-}	nH_2O
$LiNd(CO_3)_2$		Not analysed	
$LiEu(CO_3)_2$	1.04±0.04	1.7±0.2	2.5±0.2
$NaLa(CO_3)_2$		Not analysed	
$NaNd(CO_3)_2$	0.99±0.04	1.9±0.2	2.4±0.2
$NaEu(CO_3)_2$	1.07±0.07	1.9±0.2	2.7±0.2
$NaDy(CO_3)_2$	1.00±0.04	1.8±0.2	2.2±0.2
$KNd(CO_3)_2$		Not analysed	
$CsNd(CO_3)_2$	1.00±0.06	TG curve not examined	
$NH_4Nd(CO_3)_2$	Not analysed	TG curve not examined	
$NH_4Eu(CO_3)_2$		TG curve not examined	

➔ **A few solids are not analysed yet**

- *$LiNd(CO_3)_2$*
- *$NaLa(CO_3)_2$*
- *$KNd(CO_3)_2$*

➔ **NH_4 can not be quantified by ICP-AES, since the matrix is HNO_3**

➔ **$CsNd(CO_3)_2$ TG curve is too different from the others to be analysed**

➔ **for $NH_4Nd(CO_3)_2$ and $NH_4Nd(CO_3)_2$ H_2O, NH_3 and CO_2 are lost simultaneously ⇨ TG curves are not analysed**

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Conclusion and future works

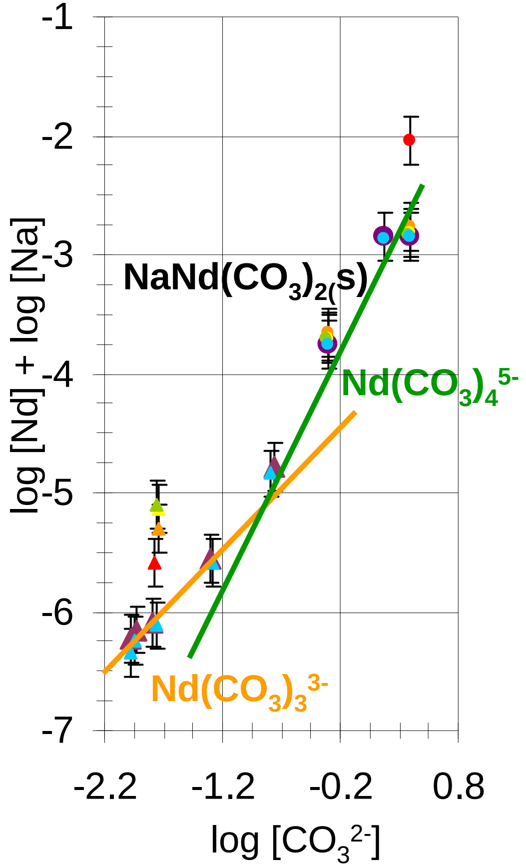
Conclusions

➔ Numerous published data on syntheses

- *empirical*
- *slight differences in AlkLn(CO_3)$_2$ syntheses*

➔ Solid compounds are precipitated at room temperature and atmospheric pressure ⇨ mixture with other minor phases, two pure solids

➔ Characterisation by XRD, optic spectrometry and thermogravimetry



Future works

➔ Solubility measurements on sodium lanthanide carbonates (in progress)

➔ Solubility measurements on alkaline neodymium carbonates ⇨ the first pure phase NaNd(CO_3)$_2$

➔ Partition measurements with radioactive tracers

➔ Same study with Th(IV)

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I would like to acknowledge:

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- **CEA for financial support**
- **The scientific committee**

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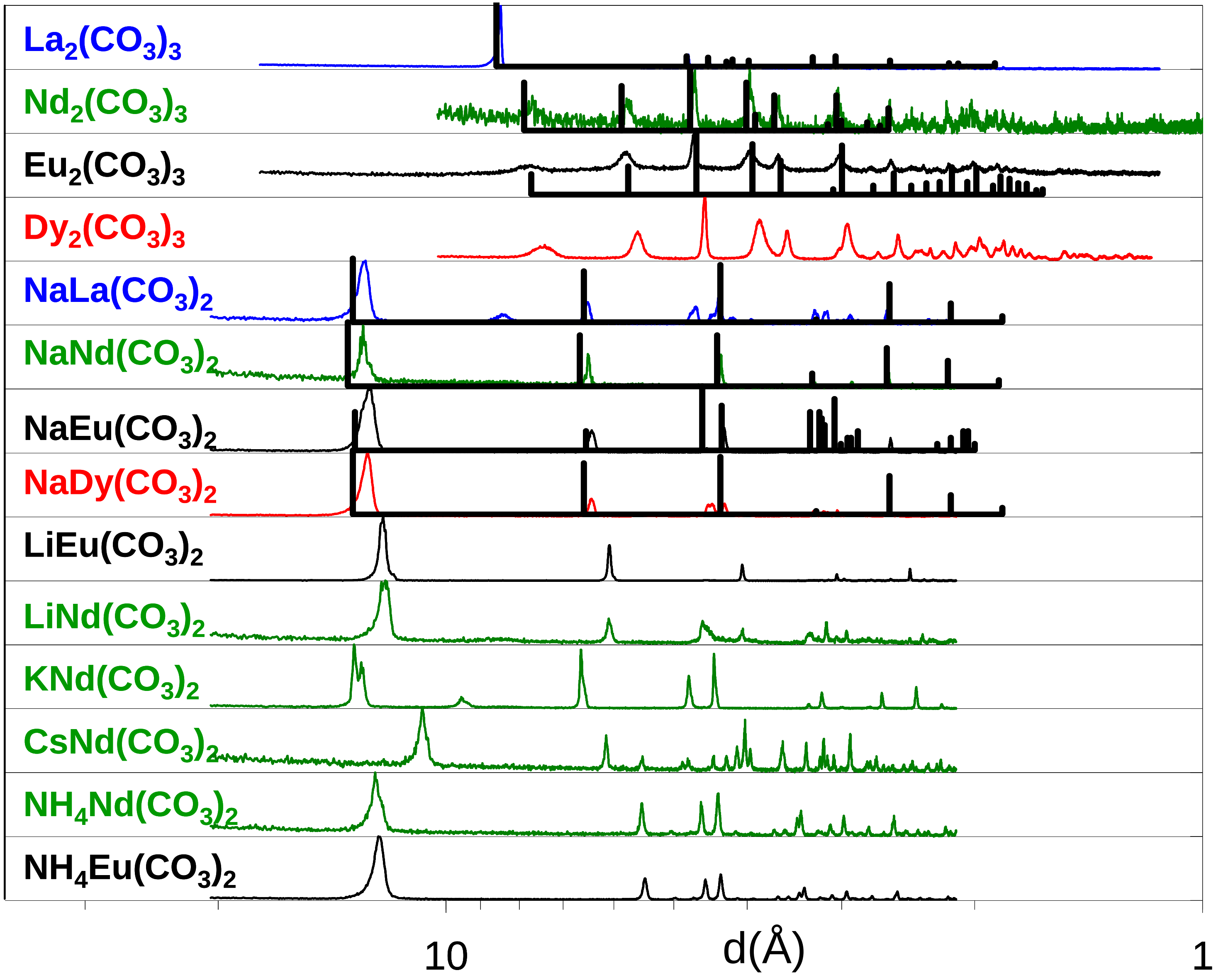
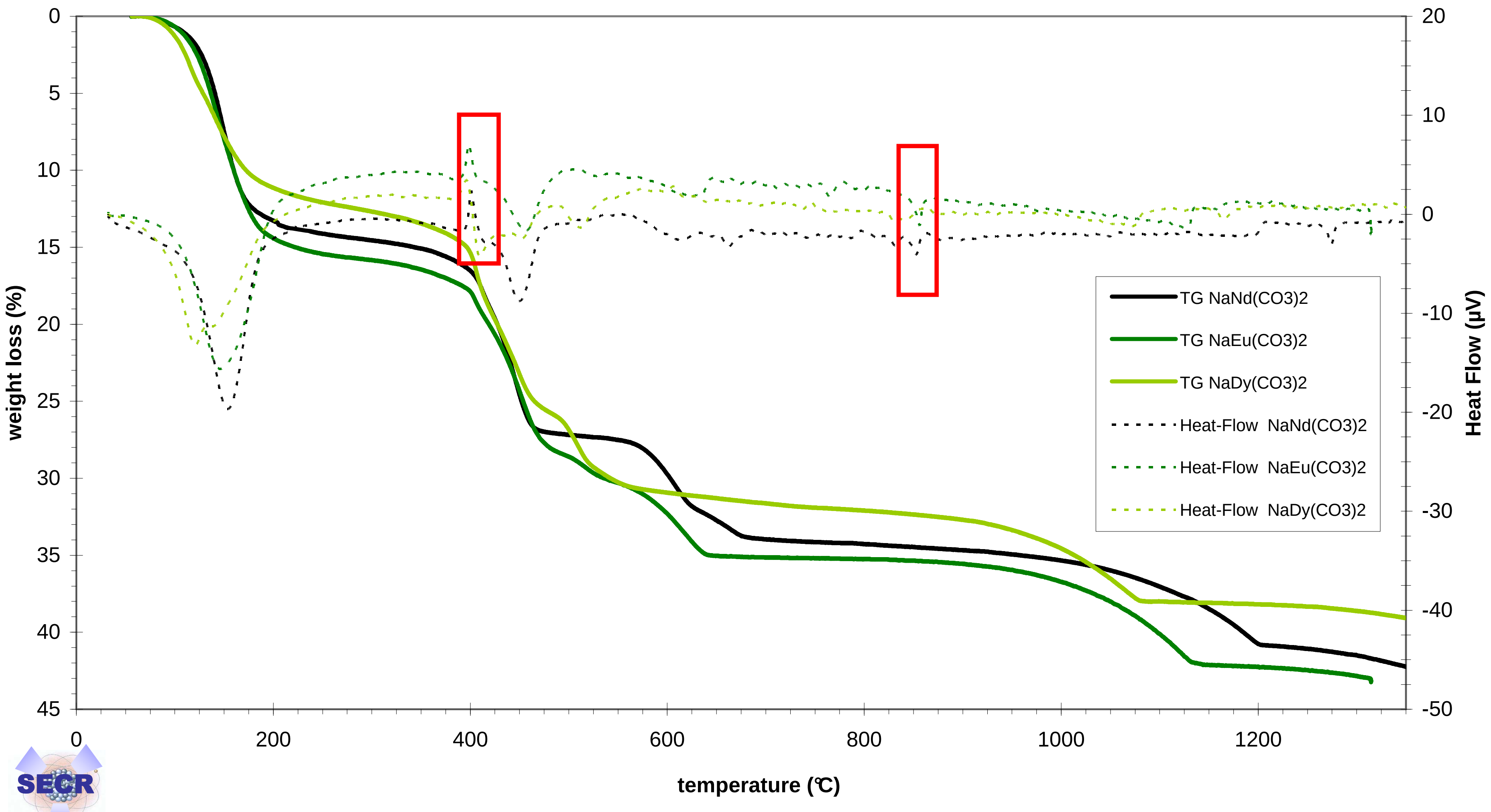
XRD powder patterns




0
5
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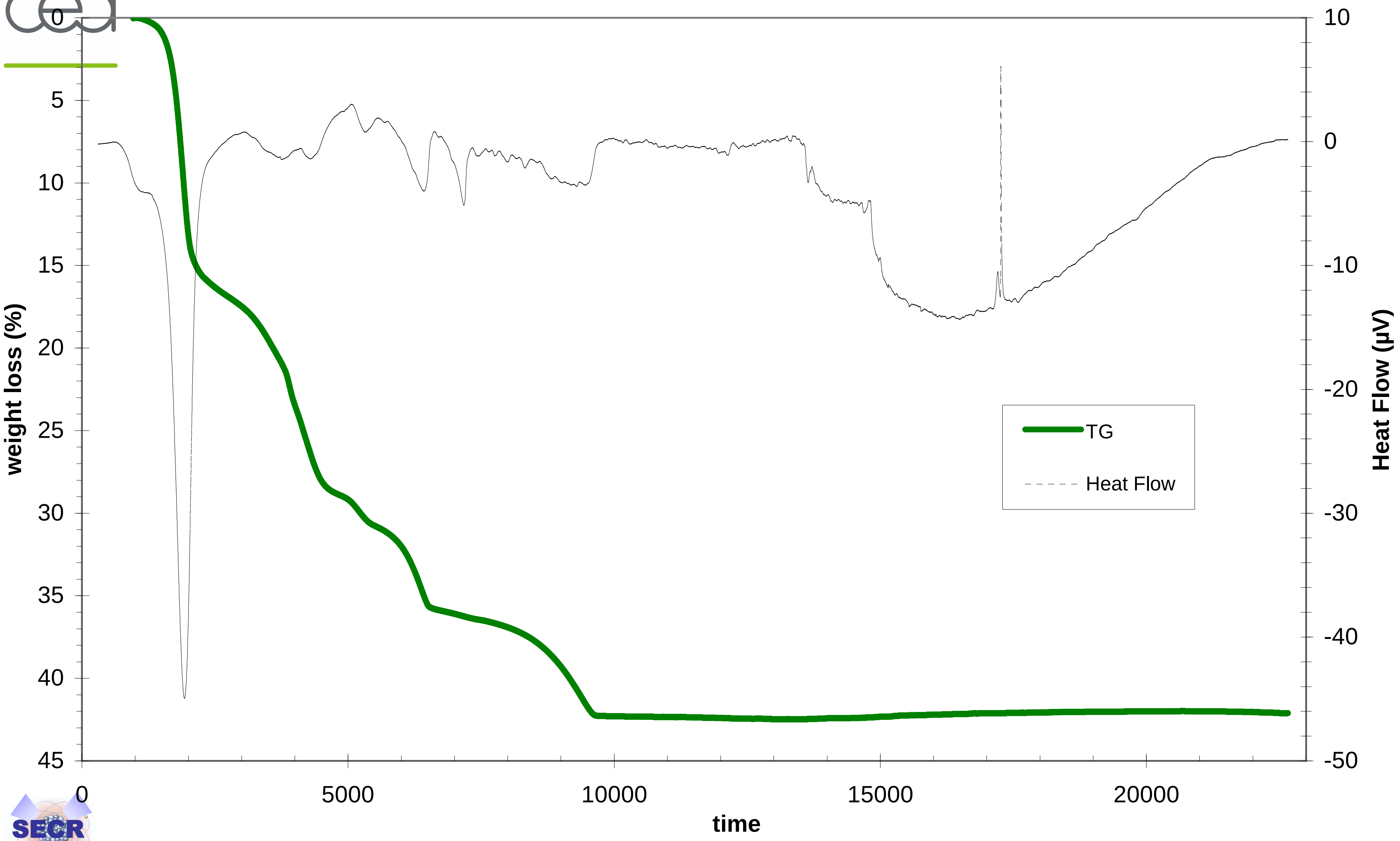
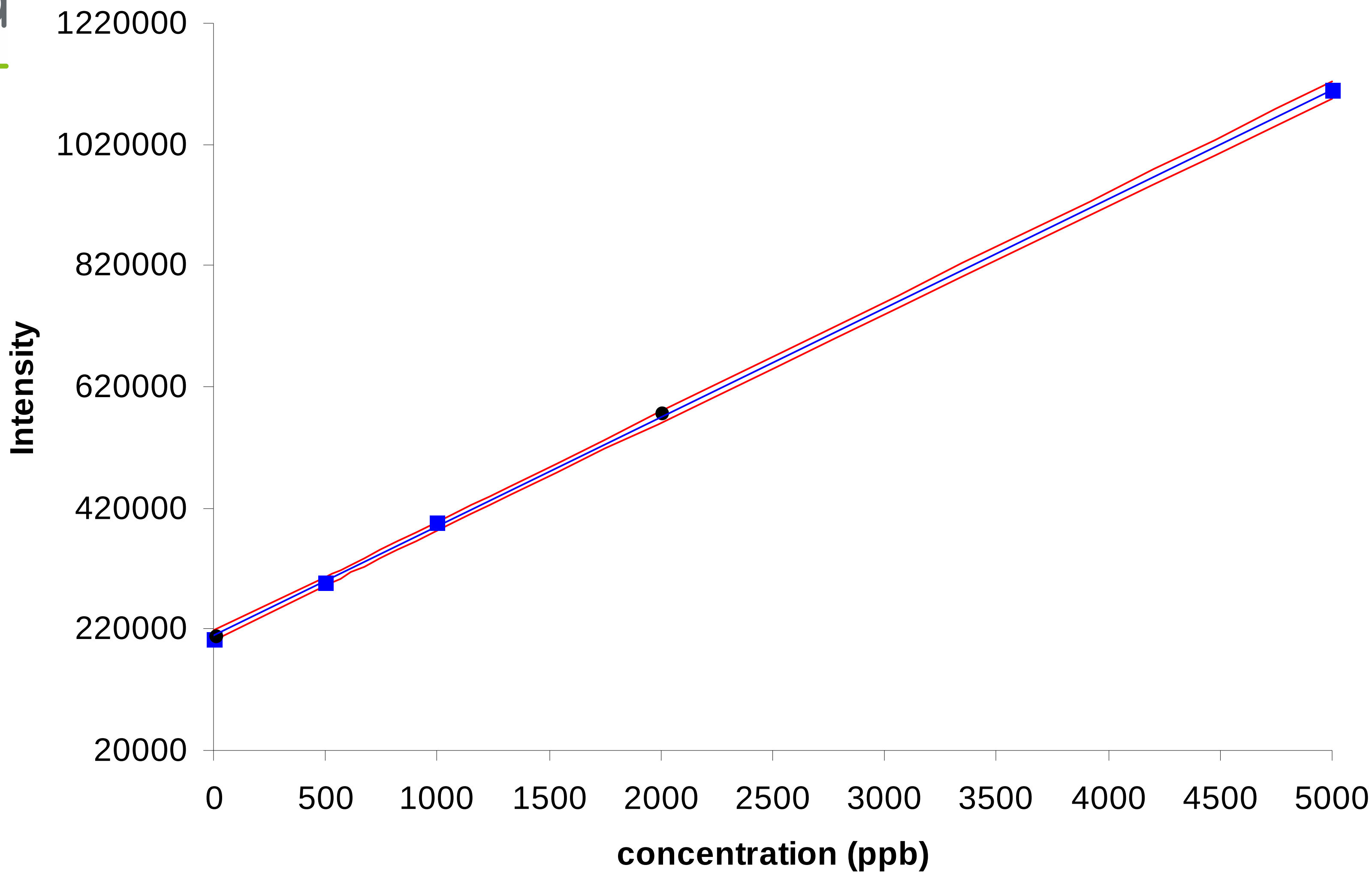
25
30
35
40
45
weight loss (%)
20
10
0
-10
-20
-30
-40
-50
Heat Flow (µV)
0
200
400
600
800
1000
1200
temperature (°C)
TG NaNd(CO3)2
TG NaEu(CO3)2
TG NaDy(CO3)2
Heat-Flow NaNd(CO3)2
Heat-Flow NaEu(CO3)2
Heat-Flow NaDy(CO3)2


0
5
10
15
20
25
30
35
40
45
weight loss (%)
10
0
-10
-20
-30
-40
-50
Heat Flow (µV)
0
5000
10000
15000
20000
time
TG
Heat Flow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620000
420000
220000
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Intensity
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1500
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2500
3000
3500
4000
4500
5000
concentration (ppb)