TCIII- 2020- 02E

ThermoChimie
Technical report

Data selection for Radionuclides and Chemotoxic elements: Supporting document

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The ThermoChimie database was first developed in 1995 by Andra, the French national radioactive waste management agency. They have since been joined by Radioactive Waste Management (RWM) from the UK, and ONDRAF/NIRAS from Belgium.

ThermoChimie provides an accurate and consistent set of data specifically chosen for use in modelling the behaviour of radionuclides in waste packages, engineered barriers, and both the near surface and deep geosphere. The database can be used to model the speciation and solubility of a wide range of stable and radioactive elements, organics, and solid phases including cements, clay minerals and degradation products (such as zeolites). The database is suitable for use within the range of conditions expected in both near-surface and geological disposal facilities: pH 6-14, ionic strength up to SIT, Eh within the stability fields of water, and temperatures from 15 to 80°C.

ThermoChimie is intended for use across the radioactive waste management community, to support repository performance assessment, research and development activities and decision making. To maximise their utility the data are therefore provided in formats suitable for use with common geochemical modelling codes. The database can be viewed and downloaded from the project website: https://www.thermochimie-tdb.com/, where additional information and supporting documents are also available.

The present document provides supporting information for data selection process for radionuclides and toxic elements in ThermoChimie.

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Data selection for Radionuclides and Chemotoxic elements: Supporting document

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1	*2014*	*First version uploaded in ThermoChimie website*

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1. Introduction

The ThermoChimie database contains thermodynamic data for major elements, radionuclides and chemotoxic elements as well as organic ligands and solid phases, including cement hydrates, clay minerals and zeolites. Each of these datasets have different characteristics and thus, different selection procedures are applied. This document summarises the data selection process for radionuclides and chemotoxic elements included in ThermoChimie. It also provides information on quality checks performed.

2. Selection procedure for radionuclides and toxic elements

Each individual datum for the radionuclides and chemotoxic elements included in ThermoChimie is the result of exhaustive literature research, data intercomparison, estimation and, in some cases, development of a focused experimental programme to fill in important data gaps (Grivé et al., 2015b).

The results of the NEA-TDB project (https://www.oecd-nea.org/dbtdb) are used as a primary data source for many radionuclides. However, due to the strict quality standards imposed by the NEA, its selection does not cover all of the elements (Figure 1) and conditions of interest to ThermoChimie. As one of the guiding principles of ThermoChimie is that it must be exhaustive enough to model the systems of interest, additional data must be included in the database. Therefore, the ThermoChimie selection goes beyond the NEA-TDB project.

The data for radioelements and chemotoxic elements included in ThermoChimie are selected by following a structured procedure:

1. When available, aqueous stability constants and solubility equilibria ($\log_{10}K^{\circ}$) are selected.
2. Secondly, enthalpies or entropies are selected, in order to allow calculations to be performed at temperatures other than 25°C (in the range 15 to 80°C).
3. ThermoChimie primarily uses SIT (Specific ion Interaction Theory) for activity corrections of the stability constants to infinite dilution. Therefore, SIT constants are provided for the selected elements to allow these activity corrections to be made.
4. Finally, a range of validation and verification calculations are performed with the data.

The rest of this report provides extended detail on each of these stages of the data selection procedure.

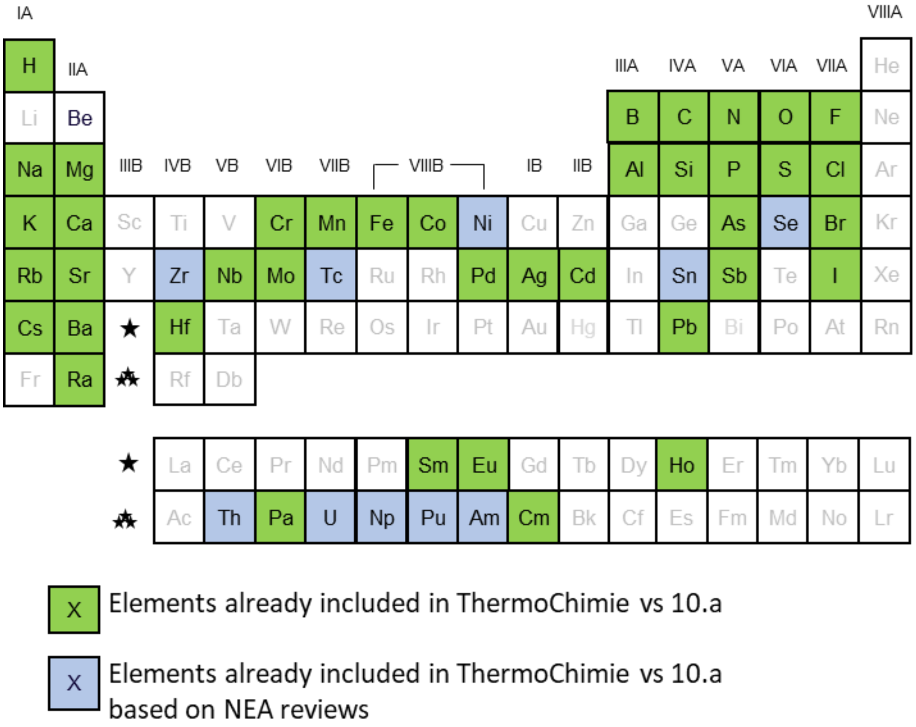

Figure 1. The elements included in ThermoChimie 10a are shown in colour in the periodic table. Those elements for which thermodynamic data are based on the OECD-NEA-TDB publications are highlighted in blue.

2.1 Stability data

The main data required by ThermoChimie are, aqueous stability constants and solubility equilibria ($\log_{10}K°$) for the elements of interest. Figure 2 summarises the process followed when adding new $\log_{10}K°$ values to ThermoChimie. In some cases, these data can be used to calculate the Gibbs free energy of formation of the species under consideration from the free energies of formation of the basic components, if these are known.

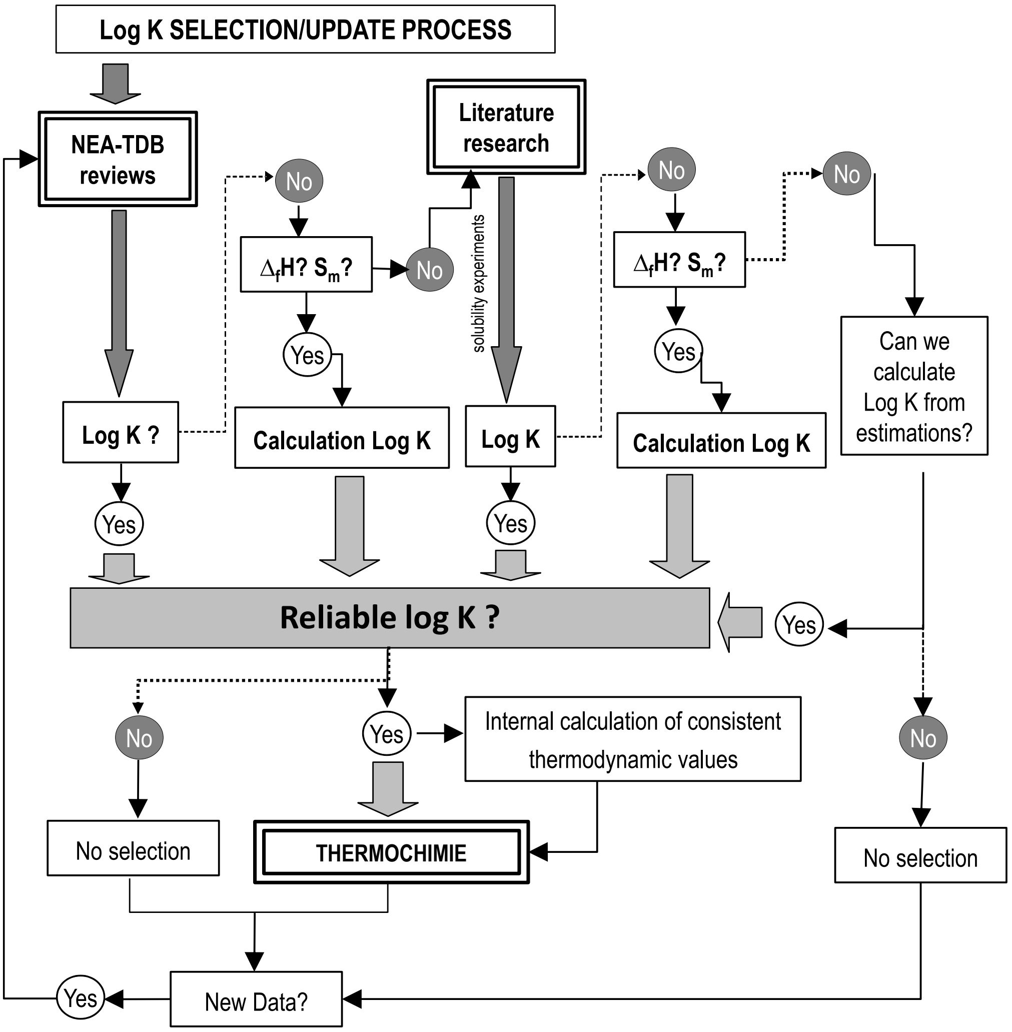

Figure 2. Summary of the selection and update process for log K values of radionuclides and chemotoxic elements in ThermoChimie.

Solubility constants can be either directly measured from solubility experiments or indirectly calculated from enthalpy and entropy data obtained from calorimetric measurements. One of the main uses of ThermoChimie is in calculating solubility limits of radionuclides and chemotoxic elements to support performance assessment. In these calculations the phases usually considered as responsible for the concentration of a given element in solution, the "solubility controlling phases", are these normally present with different degrees of hydration. As detailed calorimetric data is usually only available for crystalline solid phases, preference is given in ThermoChimie to values obtained directly from solubility experiments. These directly measured values are more likely to represent the actual solid-liquid equilibria responsible for the aqueous concentration of the element(s) of interest.

Data from solubility experiments can be used to calculate the solubility product ($\log_{10}K_s°$) of a species from the equilibrium concentrations of its solid and aqueous phases. These calculations require some assumptions to be made about the elements of interest, including their aqueous speciation and the stability of any solution complexes. In any case, the solubility of a solid is always dependent on the aqueous speciation model used. Thus, whenever possible, results from techniques such as spectroscopy, potentiometry, liquid-liquid partitioning, ion exchange, etc that can support the selection of the aqueous species considered in the model are recommended.

Measuring solubility products from experimental redox systems can be particularly difficult. This is because the redox state of the system must be carefully controlled to preserve the true equilibrium. Therefore, it may be necessary to use alternative approaches (e.g., potentiometry) to derive accurate thermodynamic data for redox sensitive elements.

In some cases, due to the lack of data or the inaccuracy of measured values, it is necessary to rely on estimations. The most convenient estimation procedure to use depends on many factors (type of data, availability of the original values, studied element…) and can take different forms (analogies with other elements and complexes, empirical algorithms, correlation with the reciprocal of the ionic radii ($1/r_i$) or with the charge density (z^2/r_i) …).

2.2 Temperature corrections

The repository host rock temperature can be below 25°C, although heat derived from high activity wastes and spent fuel may raise the temperature (up to 90°C) during the thermal phase. Most experimental thermodynamic data are obtained at room temperature (25°C), and the use of temperature corrections to experimental data is needed.

ThermoChimie currently uses the Van't Hoff[1] equation (Eq. 1) to perform temperature corrections of the stability constants to temperatures other than 25 °C (298.15 K). This approach assumes that the enthalpy of reaction ($\Delta_r H_m°$) is independent of the temperature.

$$\log K_T = \log K_{Tr} + \frac{\Delta_r H_m^0}{Rln10}\left(\frac{1}{T_r} - \frac{1}{T}\right) \qquad \textbf{Eq. 1}$$

Where K_T stands for the stability constant at the temperature of interest (T) or the reference temperature (T_r, 298.15 K), $\Delta_r H_m^0$ is the molar entalphy of the reaction, and R is the molar gas constant.

The influence of temperature on radionuclide behaviour can be directly studied by calorimetric techniques, potentiometry at different temperatures and other experimental approaches.

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[1] The use of other approaches requires information other parameters besides enthalpy (e.g. heat capacity). Unfortunately, the information on those parameters is nearly inexistent for radionuclides and for several toxic elements. This is the reason why the Van't Hoff approach is currently used in ThermoChimie.

Nevertheless, reliable experimental data remains scarce due to the inherent difficulties involved in designing and interpreting these experiments. To overcome this limitation, estimation methods are commonly applied.

Several methods are available in the literature to estimate entropy (or enthalpy) values. Part of the ongoing ThermoChimie development work is focused on reviewing the applicability of these estimation methods and updating ThermoChimie to improve data at temperatures other than 25°C.

Most of the available temperature correction methods for aqueous species rely on correlations between entropies of chemically similar complexes and properties of the constituent elements, such as crystallographic radii, molar volumes and mass, electrical charge, etc.

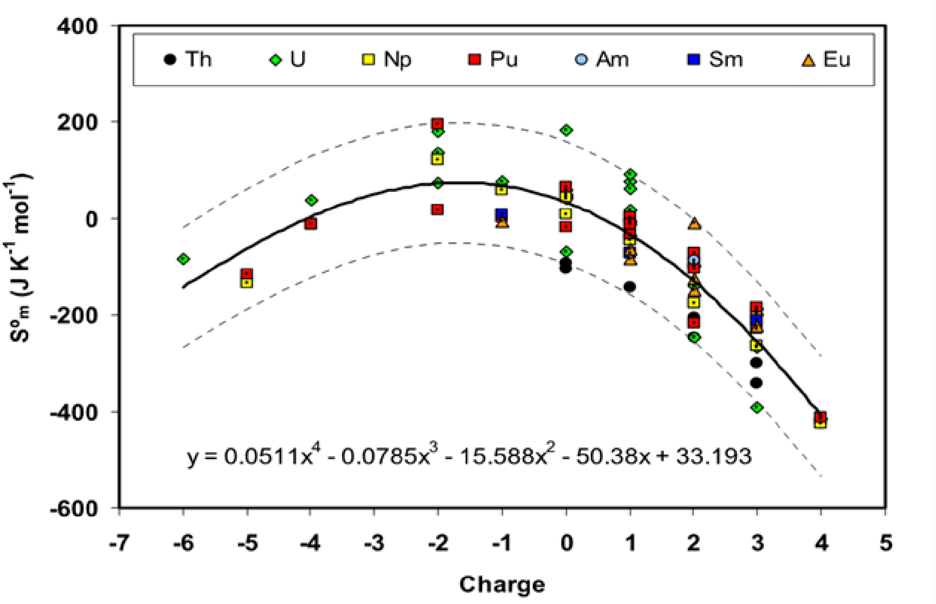

Figure 3. Relationship between experimental entropies for lanthanide and actinide aqueous complexes and the charge of the complex, from Duro et al. (2011).

One promising approach is that taken by Langmuir (1978). He found that, for a given element, the entropies of its aqueous complexes reasonably correlate with the charge (z) of the complexes, following a 4th degree polynomial equation. This correlation was able to provide rough estimates for monomeric complexes of uranium (Langmuir, 1978) and Th (Langmuir and Herman, 1980). The approach proposed by Langmuir was later applied by Lemire and Tremaine (1980), Lemire (1984) and Lemire and Garisto (1989) (among others) to estimate the entropies of some Pu and Np hydroxides. Figure 3 shows that all the available experimental entropies for the aqueous complexes of lanthanide and actinide species appear to follow this parabolic trend (Duro et al. 2011). Therefore, it may be possible to use this approach to provide more reliable data in ThermoChimie for radionuclides at temperatures above 25°C. This approach is currently being tested as part of ongoing work to develop the database.

Only a limited number of methods exist to estimate the enthalpy or entropy data of solid compounds, most of them based on empirical observations.

One of the most widely used approaches for estimating solid entropies is that developed by Latimer (Latimer, 1951; Latimer, 1952). In Latimer's approach, the entropy of a ionic solid is estimated by combining the apparent entropy contribution of its constitutive ions. The apparent entropy contribution of a given anion is related to the charge of the cation in the solid. In this way, Latimer proposed entropy contributions of cations, anions, and hydration water.

Latimer's method was updated by Mills (Mills, 1974) using experimental data for ca. 300 compounds. Although Latimer initially devised the method for ionic compounds, Mills demonstrated its applicability to non-ionic compounds. This approach was later applied to estimate entropies for a range of solid compounds, including those containing UO_2^{2+} (Naumov et al. (1974), Langmuir (1978) and Grenthe et al. (1992)).

Latimer's method is simple to apply and can be easily extended to other elements and ligands not considered in the initial publication, given that the calculation of missing ion contributions is relatively easy. The method provides accurate estimations for a large number of (crystalline) phases, although it has not been extensively applied to ternary compounds or amorphous solid phases.

2.3 Ionic strength corrections

In accordance with the NEA guidelines (Grenthe et al. 2013), ThermoChimie primes the SIT (specific ion interaction theory) approach for ionic strength activity corrections. The SIT approach (described in Grenthe et al. 1997) takes into account short-range non-electrostatic interactions by adding terms to the Debye-Hückel expression, as shown in Eq. 2.

$$\log(\gamma_i) = -z_i^2 \underbrace{\boxed{\left(\frac{A\sqrt{I_m}}{1+Ba_i\sqrt{I_m}}\right)}}_{\substack{\text{Debye-Hückel term, accounts for} \\ \text{long-range electrostatic interactions}}} + \underbrace{\boxed{\sum_k \varepsilon(i,k,I_m)m_k}}_{\substack{\text{Ion interaction coefficient term, accounts} \\ \text{for various short-range forces}}} \tag{Eq. 2}$$

In Eq. 2, the charge (z_i) of the ion (i) and the ion interaction coefficient $\varepsilon(i, k, I_m)$ ($kg \cdot mol^{-1}$) is specific for each aqueous species i which interacts with a counterion k at a given ionic strength I_m for the molality of the counterion m_k. Parameter A (which is temperature dependent) is 0.51 $kg^{1/2} \cdot mol^{-1/2}$ at 298.15 K and 1 atm (Grenthe et al., 2013). Grenthe et al., 1997 proposed a value of 1.5 $kg^{1/2} \cdot mol^{-1/2}$ for the product Ba_i (where a_i is the effective ion diameter) in the

Debye-Hückel term at 298.15 K and 1 atm. According to the Brøntesd (1922) principle of specific-ion interactions, the ion interaction coefficients $\varepsilon(i, k, I_m)$ are expected to be small for ions with the same charge as well as for interactions between uncharged species and electrically neutral combinations of ions. For this reason, ThermoChimie only includes interaction coefficients between species of opposite charge.

The Debye-Hückel term (circled in blue), which is the dominant term in the expression for the activity coefficients in dilute solutions, accounts for long-range electrostatic interactions. In concentrated solutions, the ion interaction coefficient term (circled in red) accounts for the short range, non-electrostatic interactions. The range of ionic strength covered by the SIT approach depends on the particular system and the ionic media considered; in NaCl systems, it may be applicable up to 6 $\mathrm{mol \cdot kg^{-1}}$.

Two approaches suggested by the NEA reviews to deal with metal-ion interactions within SIT framework are being used in ThermoChimie. For weak complexes of low charge, the ionic strength correction is handled using only the appropriate ion interaction coefficients. For example, $NaClO_4°$ is not included in the ThermoChimie SIT database and only the ion interaction coefficient $\varepsilon(Na^+/ClO_4^-)$ is taken into account, as the complex is considered an ion pair. In other cases (such as thorium interaction with nitrate) it is necessary to include the complex $ThNO_3^{3+}$ and consistent SIT interaction coefficients $\varepsilon(Th^{4+}/NO_3^-)$ and $\varepsilon(ThNO_3^{3+}/NO_3^-)$.

Ion interaction coefficients $\varepsilon(i, k, I_m)$ can be obtained from the NEA compilations or from open literature data. If individual, reliable and consistent interaction coefficients are available, it is possible to calculate SIT coefficient values accordingly. When no reliable data are available in the literature, SIT interaction coefficients can be calculated with estimations based on correlations between different parameters, as described below.

Linear correlations between SIT parameters in different ionic media can be used to estimate unknown interaction parameters and to test the reliability of available data (Grenthe et al., 1997; Neck et al., 2006). For example:

- Linear correlations between SIT interaction parameters and the ion Z/r value, where “Z” is the charge and “r” is the crystallographic ion radius in Angstroms (Å) (Grenthe et al., 1997; Neck et al., 2006).
- Linear correlations between SIT interaction parameters in chloride and perchlorate media, or chloride and nitrate media (Grenthe et al., 1997).

When no reliable literature data for the SIT coefficients are available and estimations do not prove successful, the extended Debye-Hückel equation is used for activity corrections.

2.4 Verification and validation

The reliability of a thermodynamic database is often judged by its ability to model independent experimental data gathered from either laboratory experiments or field observations. Verification and validation of the selected thermodynamic data are therefore essential parts of the database development and provide important information on the consistency and accuracy of the database.

Verification refers to the process of determining whether the database has been properly implemented as intended by the developer. Verification refers to all the processes used to check that the data are correctly stored and correctly extracted into formats for use with the different geochemical codes.

Examples of verification tests include: benchmarking exercises (where a geochemical model is run several times using different geochemical codes but the same version of the database); modelling of experimental data already used in the data selection process; or direct comparison between values present in different versions of the database (to check for unintended differences).

Figure 4 shows example outputs from a verification exercise. In this case, the solubilities of different solids in a generic clay porewater at 25°C are calculated with different versions of the ThermoChimie database. The results are compared to identify any data gaps or values that need to be modified. For example, due to a typographical error, erroneous thermodynamic values for SnO_2(am) were included in version 9a of the database. This error was detected during the verification process and corrected in ThermoChimie version 9b (Grivé et al., 2015a).

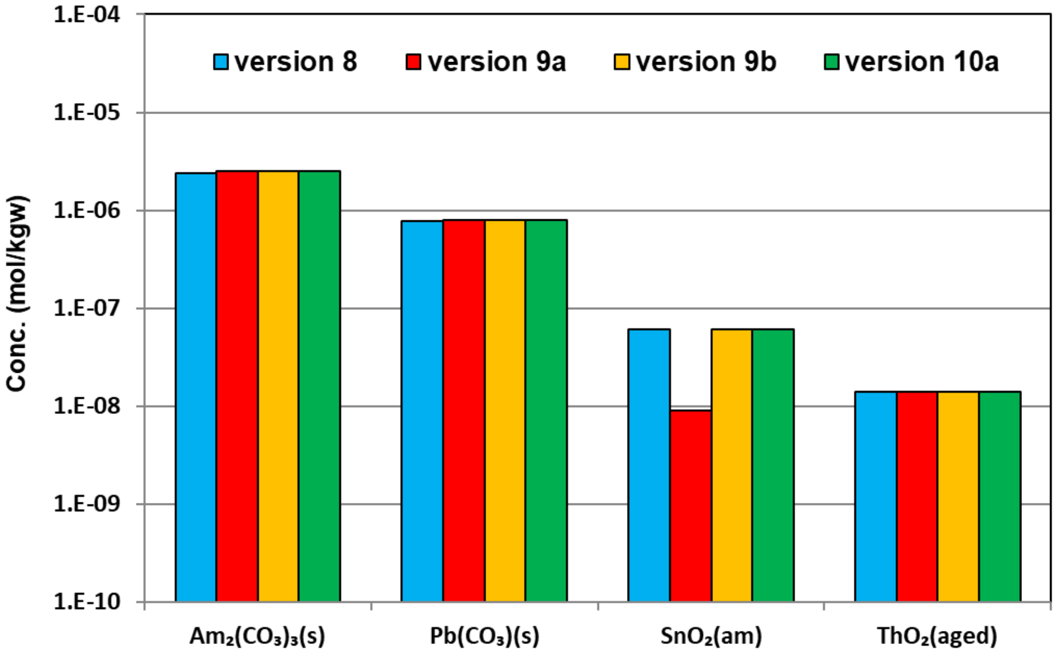

Figure 4. Comparison of the solubility of different solids in generic clay groundwaters calculated with ThermoChimie version 8 (blue bars), 9a (red bars), 9b0 (yellow bars) and 10a (green bars).

Validation exercises are used to determine the ability of the database to describe an experimental or natural system (within its intended limits of application). Different types of validation exercises can be performed, including direct comparison between values in ThermoChimie and other thermodynamic databases, benchmarking exercises (where a geochemical model is run several times with different thermodynamic databases), or modelling to test the ability of ThermoChimie to reproduce reliable experimental data not previously used to update the database.

One example of a validation exercise, which has been performed previously, is modelling the stability of the $CaUO_2(CO_3)_3^{2-}$ and $Ca_2UO_2(CO_3)_3(aq)$ complexes included in ThermoChimie. The current values included in the database are based on the results obtained by Dong and Brooks (2006). Since these results were published, the chemical behaviour of Ca–U(VI)–carbonate species has been further investigated by other authors (Lee and Yun, 2013; Endrizzi and Rao, 2014; Maia, 2018; Shang and Reiller, 2020). Therefore, these alternative datasets can be used for validating ThermoChimie. The results of this comparison are shown in Figure 5, and suggest ThermoChimie can adequately reproduce the more recent results.

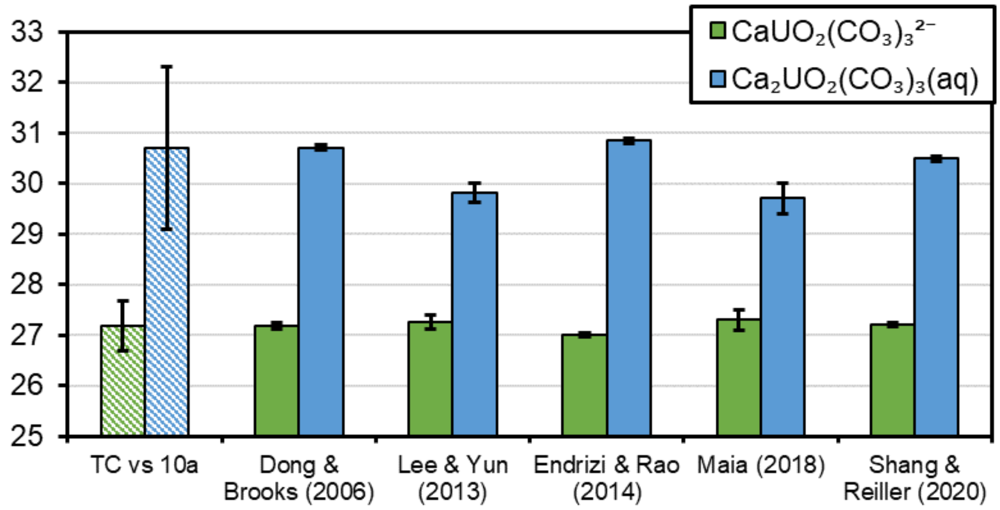

Figure 5. Comparison among log β° stability constants for $CaUO_2(CO_3)_3^{2-}$ (green bars) and $Ca_2UO_2(CO_3)_3(aq)$ (blue bars) by different authors. Data in ThermoChimie version 10a is also shown.

Besides the validation tests using data from laboratory experiments, described above, natural analogues offer an excellent opportunity to test not only the thermodynamic databases, but also the conceptual geochemical models and the numerical codes required to describe radionuclide migration under repository conditions. Poços de Caldas (Brazil), Cigar Lake (Canada), Maqarin (Jordan), El Berrocal (Spain), Oklo (Gabon) or Palmottu (Finland) are some of the natural analogues used to test different aspects of the ThermoChimie thermodynamic database (Bruno et al., 2002). The results obtained from analyses of trace metals and mineralogical characterisation in the natural analogue studies can be used to validate the database and providing further confidence in the selected values included in ThermoChimie.

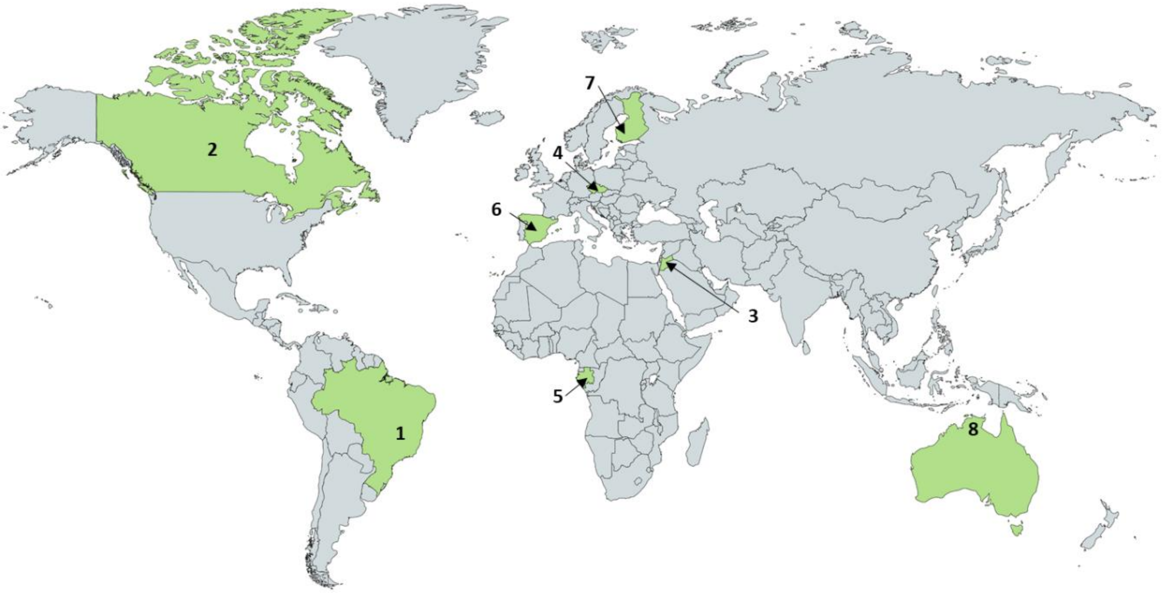

Figure 6. Some of the Natural Analogues studies. 1: Poços de Caldas (Brazil). 2: Cigar Lake (Canada). 3: Maqarin (Jordan). 4: Ruprechtov (Czech Republic). 5: Oklo (Gabon). 6: El Berrocal (Spain). 7: Palmottu (Finland). 8: Alligators River (Australia).

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