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Pascal E. Reiller, Michaël Descostes

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- 1 **Development and Application of the**
- 2 Thermodynamic Database PRODATA Dedicated to
- **3 the Monitoring of Mining Activities from**
- 4 **Exploration to Remediation.**
- 5 Pascal E. Reiller^{a,*} and Michaël Descostes^b
- 6 ^aDen Service d'Études Analytiques et de Réactivité des Surfaces (SEARS), CEA, Université
- 7 Paris-Saclay, F-91191 Gif-sur-Yvette, France.
- 8 ^bORANO Group Mining R&D Dpt, 125 avenue de Paris, F-92320 Châtillon, France
- 9 * corresponding author : pascal.reiller@cea.fr
- 10

11 Abstract

12 A growing demand exists on the monitoring of both uranium mining activities and their 13 environmental impacts. In order to help understanding and modelling both these aspects, 14 a thermodynamic database dedicated to uranium mining activities is built: the PRODATA 15 database. Relevant species and phases for uranium and radium are chosen from existing 16 compilations of data, complemented with important missing data for the application to 17 mining activities and environmental monitoring. Important major anions and cations 18 chemistry are included, as well as secondary pollutants such as arsenic, lead or nickel. 19 Applications of the PRODATA extracted database file for PhreeqC to theoretical speciation 20 calculations of uranium and radium for actual water compositions — either linked to 21 uranium mining activities, or under monitoring for environmental survey - are 22 presented. Wider applications to other available water compositions from different 23 geochemical concepts are also tested. For the tested cases, the major radium and uranium 24 species obtained using PRODATA are compared with other available thermodynamic 25 database (Thermochimie, LLNL, Wateq4f, Minteq, PSI/NAGRA). The choice of the 26 database file — and of the ionic strength correction — can strongly impact the final 27 speciation results. Sulphate complexes of radium and uranium are of particular 28 importance in mining exploitation context, and carbonate uranium complexes particularly $Ca_n UO_2(CO_3)_3^{(4-2n)-}$ complexes — are crucial for environmental monitoring. 29 30 The latter complexes are key species for the aqueous speciation of uranium even in reducing environment where U(IV) low solubility usually governs uranium mobility. 31

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32 **1. Introduction**

33 Evaluation of environmental impact of anthropic activities, particularly of mining 34 activities, must be considered before any industrial project development. One of the 35 approaches currently developed relies on predictive reactive transport modelling. Such 36 strategy requires, on the one hand, a thorough description of the physico-chemical 37 reactions that govern the mobility of contaminants of concern and, on the other hand, 38 their couplings in order to better constrain the studied system. These approaches allow 39 testing several evolution scenarii on space and time scales beyond the ones probed by 40 laboratory and field experiments (Steefel et al., 2015). This is particularly true for: 41 (i) mining and nuclear industries (Zhu et al., 2001; Curtis et al., 2006) including the 42 management of legacy sites (Drozdzak et al., 2016; Husson et al., 2019); (ii) uranium in 43 the framework of long-term safety assessment of radioactive waste repositories (van der Lee et al., 2003; Montarnal et al., 2007; Claret et al., 2018; Mühr-Ebert et al., 2018); 44 45 (iii) management of polluted soils and aquifers inherited from the use of depleted 46 uranium from armor-piercing ammunition (Chen and Yiacoumi, 2002; Mitsakou et al., 47 2003); (iv) assessment of the ecotoxicological impact of uranium (Paredes et al., 2016, 48 2018; Husson et al., 2019; Lartigue et al., submitted). One may also use such an approach 49 for mining exploration, optimizing mining operations — especially in the case of In Situ 50 Recovery (ISR) mines (Johnson and Tutu, 2016; Lagneau et al., 2019) —, and remediation (Yabusaki et al., 2007). 51

52 Uranium is considered as a trace element that is showing a complex aqueous chemistry, 53 especially in natural environments. Its mobility is generally governed by pH and redox, 54 the presence of inorganic — e.g., CO_3^{2-} , SO_4^{2-} , PO_4^{3-} (Guillaumont et al., 2003) — and - 3 - organic ligands (Hummel et al., 2005), but also adsorption reactions at the mineral water interfaces — see Lartigue et al. (submitted) and references therein. Hence, assessing and understanding the geochemical mechanisms controlling the mobility of uranium in the environment requires also the consideration of the other major elements chemical properties, which are often observed at higher significant concentrations.

60 The environmental footprint of uranium mines is driven, on the one hand, by the mining 61 extraction process, and, on the other hand, by the composition of the treated ore. The 62 extraction processes generally involve highly concentrated and oxidizing solutions — in 63 sulphuric acid or under alkaline conditions — in order to increase uranium solubility. In addition to ²²⁶Ra — one of the main radioactive decay products of ²³⁸U —, the ores are 64 generally associated to other metals (e.g., Ni, Fe, Mo, Cu...) and metalloids (e.g., As, Se...). 65 These elements are showing different geochemical behaviours than U, and may become 66 67 in turn (secondary) contaminants.

The geochemical behaviour of ²²⁶Ra is particular. Through its radioactive half-life (1 600 68 years) and its high specific activity (36.6 GBq g⁻¹), ²²⁶Ra is always observed at elementary 69 70 concentrations drastically lower than uranium. As an illustration, for a uranium ore older 71 than 1 My, with an average U content of 1‰ (*ca.* 12 500 Bq kg⁻¹), the secular equilibrium 72 will lead to a hypothetical ²²⁶Ra concentration of 342 ppt. The migration of ²²⁶Ra in the 73 environment is mainly governed by adsorption reactions (see e.g., Sajih et al., 2014; 74 Reinoso-Maset and Ly, 2016; Robin et al., 2017; Bordelet et al., 2018), coprecipitation 75 through solid solution formation with other alkaline earth sulphate minerals (Curti et al., 76 2010; Lestini et al., 2019), and carbonate bearing minerals (Jones et al., 2011).

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77 The description of the physico-chemical reactions involved, directly or indirectly, in the 78 fate of contaminants is usually gathered in a thermodynamic database. It includes redox 79 and aqueous complexation formation equilibria, dissolution or formation of solid or 80 gaseous phases; sometimes, coprecipitation or adsorption reactions are also included. To 81 perform the calculation on these intricate systems, several modelling codes are available, 82 from aqueous speciation calculation to reactive transport, even if this approach has 83 inherent limitations (Nordstrom, 1996), particularly concerning uncertainties (Emrén et 84 al., 1999; Ekberg and Ödegaard-Jensen, 2011; May and Filella, 2011)

85 Currently, ORANO Mining, the historic French uranium mining company (former AREVA 86 Mines and Cogema, https://www.orano.group/en/expertise/from-exploration-to-87 recycling/leading-uranium-producer), has to answer to different national regulators and 88 nuclear safety agencies for the exploration, exploitation, and remediation of its sites. This 89 includes the building of Safety Cases, applying Safety Assessment processes, which 90 require evaluation of the chemistry of uranium, radium, and other eventual secondary 91 pollutants, in different contexts, including speciation and transport. Different softwares 92 are usually needed to attain these objectives, which provided databases are generally not 93 built around the same core of data. To provide robust cases, there is a need to have a 94 common database for the different softwares used to perform the calculations. ORANO 95 Mining is using widely available speciation codes, i.e. PhreeqC (Parkhurst and Appelo, 96 1999, 2013), CHESS (http://chess.geosciences.mines-paristech.fr/?set_language=en), 97 and the Geochemists' WorkBench (GWB, http://www.gwb.com), with which 98 thermodynamic database files are provided. However, a thermodynamic database that 99 can be used with several codes, and can be exploited in monitoring of mining activities, is

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seldom found. Besides, thermodynamic databases provided with the different modelling
codes do not systematically share either the same thermodynamic data, the same
traceability, or the same completeness (Hummel et al., 2019). Direct comparison between
modelling codes' results, but also between studied cases, may therefore be limited.

104 Uranium is the central element of the nuclear fuel cycle. Its thermodynamic properties 105 have been the subject of a large body of work. The data selections that are subject of the 106 largest consensus have been commissioned by the Thermochemical DataBase (TDB) 107 project from the Nuclear Energy Agency (NEA) within the Organization for the Economic 108 Co-operation and Development (OECD) (Wanner, 1988; Mompeán and Wanner, 2003; 109 Ragoussi and Brassinnes, 2015). The selection is including inorganic (Grenthe et al., 1992; 110 Guillaumont et al., 2003) and selected organic complexes (Hummel et al., 2005) — a 111 PhreeqC database file has been made available recently (Martinez et al., 2019). The 112 selection criteria being rather strict, it is inevitable that some data are rejected, and cannot 113 be used as is to perform calculations in relevant media for mining activities and 114 environmental monitoring. A recent study suggests that database files that are sit on the 115 NEA-OECD database selection can be more likely recommended to estimate uranium 116 speciation (Wang et al., 2019), but effectively needed some implementations from other 117 sources, even if traceability issues may appear (Hummel et al., 2019).

118 Despite of the great interest in the monitoring of mining activities, radium has not been 119 the subject of the same attention. Nevertheless, some data are available, and have 120 sometimes been included in databases.

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121 To perform relevant speciation calculation in actual situations, the database used should 122 be containing the relevant chemical equilibria and species predominant in the system to 123 describe the geochemistry of the site, and should also be as consistent as possible. In 124 addition to uranium, the TDB project from NEA-OECD has commissioned reviews on 125 elements relevant for the management of radioactive wastes that can be directly 126 implemented in a database (e.g., Brown et al., 2005; Gamsjäger et al., 2005; Olin et al., 127 2005; Rand et al., 2009; Lemire et al., 2013). From the strict definition of the selection 128 criteria of the NEA-OECD selection, it can be understood that complementary data must 129 be implemented either on already reviewed elements, or on elements that are necessary 130 for natural or mining systems, such as e.g. Ca, Mg, Al or Si.

Some thermodynamic database files provided with softwares are containing a large body of data on several complexes and phases. But the data within these database files are not always easy to trace, as they are necessarily in the NEA-OECD reviews. There is a pressing demand from nuclear safety authorities to provide evidence that the data used to evaluate a speciation calculation are traceable and retrievable, which if achieved provide a further confidence in the evaluation of a safety case.

From these constraints and legal obligations, there is a need for the building of a thermodynamic database dedicated to uranium mining activities from exploration to remediation: the PRODATA database. This database was thought as a tool in which thermodynamic data (constants and functions) relevant for mining activities and environmental monitoring can be compiled, and database files for the different speciation codes can be exported on demand. Once available, the applicability of the database to specific cases directly linked to uranium mining activities must be verified. These cases

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144 must cover a wide range of applications on uranium and radium: (i) historic impacted 145 sites that either will be submitted to remediation processes, or are in course of 146 remediation (i.e., legacy sites); (ii) sites where mining operations are currently in 147 exploitation; and (iii) sites that are under exploration for future exploitation. These three 148 steps representing the life cycle of a mining site in general, and of uranium mining in 149 particular.

150 To offer a more complete view on the application fields of PRODATA, we have selected a 151 range of water compositions at the boundaries of the uranium mining operations: (i) 152 waters that are not yet impacted either by mining operation or by the nuclear fuel cycle 153 in general; (ii) waters that are impacted by different parts of the nuclear fuel cycle 154 including radioactive waste management; and (iii) waters that are naturally impacted by 155 noticeable natural uranium concentrations. The speciation of these waters will be done 156 on uranium — either using the available amount or in equilibrium with a relevant 157 phase — and radium — if available in the composition.

158 The database file for speciation code PhreeqC extracted from PRODATA will be used to 159 perform uranium and radium speciation calculations for these different water 160 compositions. The results will be compared with other database files that are either 161 provided in the PhreeqC package or provided by the developers of the database. General 162 comportment of uranium and radium will be discussed for the different cases studied. 163 This work can be seen as a benchmark of the PRODATA database, but should not be 164 viewed as a qualitative comparison with the other databases, which are for some of them 165 not developed specifically for the application to monitoring of uranium mining activities.

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166 **2.** Construction of the database and general framework of the modelling exercise.

- 167 *2.1.* Construction of the database
- 168 2.1.1. Database formats required for speciation codes

169 The specific needs from speciation modelling for Orano Mining imply the use of several 170 speciation softwares, i.e. PhreeqC, CHESS, and GWB. As written earlier, several database 171 files are provided with these softwares, but none of them is available for the three codes, 172 at least a database file that would cover the need for mining and environmental 173 monitoring. The need to have the same database in order to obtain coherent calculations 174 using the three speciation codes have been clearly identified. If this work is focused on the 175 PhreeqC database file, a companion study using the CHESS database file is also available 176 in this volume (Lartigue et al., submitted).

- 177 2.1.2. Requirement imposed by the extraction of database files to several codes
- 178 2.1.2.1. General constraints

Building a database that can be extracted to, and used by, several speciation or transport
codes imposes a certain amount of constraints. All of the codes have different ways of
formatting the database files, but some commonalities are existing.

182 The main constraint comes from the definition of the basic species and how equilibria are 183 written. PhreeqC imposes definition of MASTER the species 184 (SOLUTION_MASTER_SPECIES keyword), gives the possibility to define secondary redox 185 species, and then allows the definition of complexes in a very flexible way. The more 186 illustrative example is the definition of phosphate complexes, where complexes relative to PO_4^{3-} , HPO_4^{2-} , $H_2PO_4^{-}$, or $H_3PO_4(aq)$ can coexist as long as all equilibria between species 187

are defined in the database. In Guillaumont et al. (2003) the $\log_{10}\beta^{\circ}$ values of the $UO_2PO_4^$ and $UO_2HPO_4(aq)$ complexes are defined relative to PO_4^{3-} and HPO_4^{2-} , respectively, as

190
$$PO_4^{3-} + UO_2^{2+} \rightleftharpoons UO_2PO_4^{-}$$
 $\log_{10}\beta^\circ = 12.23 \pm 0.15$

191 and

192 $HPO_4^{2-} + UO_2^{2+} \rightleftharpoons UO_2 HPO_4(aq) \quad \log_{10}\beta^\circ = 7.24 \pm 0.26$

that can coexist in a PhreeqC database file, associated with the acidity constants forphosphate species.

These definitions will not be recognized either by CHESS or GWB that impose the definition of a single ligand species implied in reactions beyond the redox definition. Depending on the choice of the "basis-species" definition in CHESS or GWB, preceding equilibria must be written relative to only one phosphate species.

Hence, for the sake of adaptability, a common choice of a single basic species for a ligand is done, and the $\log_{10}\beta^{\circ}$ values are recalculated from the stoichiometry of the reactions, and using the thermodynamic functions, whenever available.

In PRODATA, the choice of PO_4^{3-} is done, and for the $UO_2HPO_4(aq)$ complex it comes,

203
$$PO_4^{3-} + H^+ + UO_2^{2+} \rightleftharpoons UO_2 HPO_4(aq)$$
 $\log_{10}\beta^\circ = 19.59 \pm 0.26$

which assures the compatibility for the three codes. The definition relative to sulphate and carbonate complexes are done relative to SO_4^{2-} and CO_3^{2-} — even if the swap between CO_3^{2-} and HCO_3^{-} is possible.

207 2.1.2.2. Definition of redox equilibria

Another constraint is the definition of redox equilibria. If all the redox equilibria can be defined relative to the electron in PhreeqC, they have to be defined relative to $O_2(aq)$ in CHESS and GWB — even if GWB requires the definition of e⁻. But in PhreeqC, both the oxidation of H₂O and reduction of H⁺ have to be defined relative to e⁻. The choice of the definitions of the other redox equilibria relative to $O_2(aq)$ are then done for the sake of compatibility of the different equilibrium reactions and export to CHESS and GWB.

As for the swap between CO_3^{2-} and HCO_3^{-} , some redox swaps are possible, as e.g., SO_4^{2-}/HS^- , SeO_4^{2-}/HSe^- , $AsO_4^{3-}/H_2AsO_3^-$, Fe^{3+}/Fe^{2+} , MnO_4^-/Mn^{2+} , or UO_2^{2+}/U^{4+} .

216 2.1.2.3. Use of metastable species

217 The particular cases of metastable species is particularly difficult to handle in 218 thermodynamically based speciation codes — particularly in PhreeqC, CHESS, and GWB. The most illustrative example is the formation of perchlorate ion ClO_4^- , which is 219 220 metastable in water, but is the basis of the complexation studies in indifferent background 221 electrolyte media. The other would be the account of organic ligands that are 222 thermodynamically metastable in the water stability domain. The most convenient way 223 to handle this is through the definition of independent species to circumvent 224 thermodynamically driven decomposition of molecules during the calculation, which 225 would "remove" a ligand from, or change a background electrolyte in, the solution. Both 226 PhreeqC and CHESS allow defining these kinds of species, but the constraints of GWB 227 basis-species, made of elements with only two letters, is more difficult. Hence, the 228 definition of species that are not composed of elements from the periodic table is done in

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both PhreeqC and CHESS — e.g., for PhreeqC, a species name "Perchlorate-" for ClO₄,
"Thiocyanate-" for SCN⁻, or "Selenocyanate-" for SeCN⁻ —, but is not yet available in GWB
version of PRODATA. Another possibility would be to handle the metastability through
kinetic reactions. But a kinetic database for uranium speciation, or for other elements, is
not available. It is noteworthy that other softwares allow validating or devalidating
specific reactions (e.g., CHNOSZ http://chnosz.net/) to handle metastability.

235 2.1.3. Physical constants and atomic weight of the elements

The physical constants are the one used in the NEA-OECD database (Guillaumont et al.,
2003), and the atomic weight of the elements, and eventual isotopes, are taken from
Wieser (2006).

239 2.1.4. Thermodynamic Data

From the constraints already exposed (vide ante), whenever possible, the thermodynamic functions of formation on the molal scale of the species (i.e., $\Delta_f G_m^o, \Delta_f H_m^o, S_{f,m}^o$, and $C_{p,m}^o$) are used within the database. The thermodynamic functions of reaction (i.e., $\Delta_r G_m^o, \Delta_r H_m^o$) are calculated from the formation reaction of a species, or the dissolution reaction of a phase, then the thermodynamic constant at 25°C is calculated.

$$\log_{10} K^{\circ} = -\frac{\Delta_r G_m^{\circ}}{RT \ln(10)} \tag{1}$$

The uncertainties for the formation or dissolution of species are calculated from thepropagation of errors and are given as comments.

At other temperature, the $log_{10}K(T)$ are calculated from - 12 -

$$\log_{10} K^{\circ}(T) = \log_{10} K^{\circ}(T_0) - \frac{\Delta_r H_m^{o}(T_0)}{RT \ln(10)} \left(\frac{1}{T} - \frac{1}{T_0}\right)$$
(2)

248 neglecting the effect of $\Delta_r C_{p,m}^o$ in a first approximation, which is reasonable is view of the 249 application domain of this database.

250 Due to the necessary heterogeneous provenance of the data included in PRODATA, the 251 homogeneity of the thermodynamic functions of formation is not assured a priori. 252 Consistency checks, as done otherwise (Wagman et al., 1982; Guillaumont et al., 2003) are 253 not assured for the moment. Some sources are providing thermodynamic functions 254 (Wagman et al., 1982; Cox et al., 1989; Robie and Hemingway, 1995; Chase, 1998), others 255 are providing thermodynamic constants (Smith et al., 2004), and other give both types of 256 data (Grenthe et al., 1992; Guillaumont et al., 2003; Brown and Ekberg, 2016). It is also 257 noteworthy to recall that not all these databases do share the same level of traceability 258 (Hummel et al., 2019).

The primary data for the characterisation of a reaction is the $log_{10}K^{\circ}$ value, from which 259 260 $\Delta_r G_m^o$ is calculated (eq. 1). Then $\Delta_f G_m^o$ is obtained using other Gibbs energies of formation from the implied reactants and products. In PRODATA exported database files, as $\log_{10} K^\circ$ 261 are calculated from the $\Delta_r G_m^o$ — with the exception detailed later (vide infra) — it was 262 263 decided, whenever possible, to recalculate the $\Delta_f G_m^o$ of the species. This implies an 264 essential choice on the origin of the Gibbs energies of formation. This is surely not a 265 consistency check, but to our vision this allows limiting some inconsistency problems, as those evidenced otherwise (Endrizzi et al., 2016). 266

As it will be detailed later in the text, the choice of the works from CODATA (Cox et al., 267 268 1989) was made because it forms the foundation of the thermodynamic data selection for 269 uranium by the TDB Project from NEA-OECD. As an example, we will explain the particular 270 case of copper, which data are barely available with the NEA-OECD selection of data, but 271 can be important for mining and environmental monitoring (Cretaz et al., 2013). The thermodynamic functions of formation for Cu²⁺ are available in NEA-OECD (Guillaumont 272 et al., 2003) — selected from CODATA (Cox et al., 1989) —, but the data from $Cu(SO_4)(aq)$ 273 274 are available in the United States National Bureau of Standard (NBS) thermodynamic selection of data (Wagman et al., 1982) with slightly different $\Delta_f G_m^o$ for both Cu²⁺ and 275 SO_4^{2-} . Within PRODATA, the thermodynamic functions of formation for $Cu(SO_4)(aq)$ are 276 calculated as shown, taking $\Delta_f G_m^o$ as an example. 277

$$Cu^{2+} + SO_{4}^{2-} \rightleftharpoons Cu(SO_{4})(aq)$$

$$\Delta_{r}G_{m,Wagman}^{o} = \Delta_{f}G_{m,Wagman}^{o}(Cu(SO_{4})(aq)) - \Delta_{f}G_{m,Wagman}^{o}(Cu^{2+})$$

$$-\Delta_{f}G_{m,Wagman}^{o}(SO_{4}^{2-})$$
(3)
$$\Delta_{r}G_{m,Wagman}^{o} = -692.18 - (65.49 - 744.53) = -13.40 \text{ kJ. mol}^{-1}$$

$$\Delta_{f}G_{m,Prodata}^{o}(Cu(SO_{4})(aq))$$

$$= \Delta_{r}G_{m,Wagman}^{o} + \Delta_{f}G_{m,Prodata}^{o}(Cu^{2+}) + \Delta_{f}G_{m,Prodata}^{o}(SO_{4}^{2-})$$

$$\Delta_{f}G_{m,Prodata}^{o}(Cu(SO_{4})(aq)) = -13.40 + 65.046 - 744.004$$
(4)

$$\Delta_f G^o_{m,Prodata} (\operatorname{Cu}(\operatorname{SO}_4)(\operatorname{aq})) = -692.098 \text{ kJ. mol}^{-1}$$

Through this calculation, the obtained $\log_{10} K^\circ = 2.30$ in PRODATA is coherent with its initial value obtained using Wagman et al. (1982). Not assuring this conversion can lead to great discrepancies and inconsistencies, if origins of the data are not controlled. As an example, one can check the differences between the published solubility constants of the phases from the liebigite group — $IM_{2n} IIM_m IIM'_{(2-n-m)}UO_2(CO_3)_3$: xH₂O where IM is an alkaline metal, and IIM and IIM' are alkaline earth metals — and those recalculated using improper thermodynamic functions — see analyses and discussion in Endrizzi et al. (2016).

In some cases, the thermodynamic functions of formation may not be available — e.g., for amorphous solids, which hydration numbers are not known — or for species whose extrapolation of formation constant to infinite dilution is not yet assessed. In these particular cases, the $log_{10}K^{\circ}$ for the formation or dissolution reactions is given explicitly in a different section within the respective keyword section. If the $\Delta_r H_m^o$ is available, then it is either exported to the PhreeqC database file, or the $log_{10}K(T)$ are calculated from eq. 2 for CHESS and GWB database files.

All the data within the database are traced to the original publications, or duly commented if the origin is at stake. It is the case for some clayey phases included in other software databases, which are nice-to-have data, but not directly or easily traceable.

296 2.1.5. Uncertainties

In the majority of cases, speciation softwares do not offer uncertainty estimations of the final results, with noticeable exceptions (Ödegaard-Jensen et al., 2004; Ekberg and Ödegaard-Jensen, 2011; MCPhreeqc, 2011). When the uncertainties of the thermodynamic functions and constants are given — e.g., Cox et al. (1989) and Guillaumont et al. (2003) —, they are directly implemented in PRODATA. The other -15302 available uncertainties are re-estimated by propagation of errors when $\Delta_f G^o_{m,Prodata}$ are 303 recalculated.

In the case of $Cu(SO_4)(aq)$, the uncertainty given by the NBS (Wagman et al., 1982) is between 8 to 80 times the last digit of the data. Choosing 8 times, it comes,

$$\sigma \left(\Delta_f G^o_{m,Prodata} (\operatorname{Cu}(\operatorname{SO}_4)(\operatorname{aq})) \right)^2$$

$$= \sigma \left(\Delta_r G^o_{m,Wagman} \right)^2 + \sigma \left(\Delta_f G^o_{m,Prodata} (\operatorname{Cu}^{2+}) \right)^2$$

$$+ \sigma \left(\Delta_f G^o_{m,Prodata} (\operatorname{SO}_4^{2-}) \right)^2$$
(5)

$$\sigma \left(\Delta_f G^o_{m,Prodata} (\operatorname{Cu}(\operatorname{SO}_4)(\operatorname{aq})) \right)^2 = (0.408)^2 + (1.557)^2 + (0.418)^2$$
(6)

$$\sigma\left(\Delta_f G^o_{m,Prodata}(\operatorname{Cu}(\operatorname{SO}_4)(\operatorname{aq}))\right) = 1.663 \text{ kJ. mol}^{-1}$$
(7)

306 which finally gives

307
$$\Delta_f G^o_{m,Prodata} (Cu(SO_4)(aq)) = -(692.098 \pm 1.663) \text{ kJ. mol}^{-1}$$

308 and

$$\log_{10} K^{\circ} = 2.30 \pm 0.07$$

310 2.1.6. Deviation from ideality – Ionic strength correction

311 Ionic strength correction can be a serious issue to tackle — see Grenthe et al. (1997) for 312 detailed analysis. Concerning the monitoring of mining activity, impacted natural water 313 can show a large span of salinity, and rather high concentrations of sulphuric acid are used 314 to extract the uranium ore. The theoretical calculation of speciation cannot only rely on Davies (1962) relationship
that allow calculating the mean activity coefficient of a species j of charge z_j,

$$\log_{10}\gamma^{\pm} = -z_{j}^{2}A\left(\frac{\sqrt{I_{m}}}{1+\sqrt{I_{m}}} - 0.3 I_{m}\right)$$
(8)

where *A* is a temperature dependant constant (Helgeson and Kirkham, 1974; Grenthe et al., 1992; Guillaumont et al., 2003), and I_m is the ionic strength on the molal scale (mol kg_{water}-1).

320 Furthermore, as several ions are forming the composition of water, the use of more 321 advance relationship, as the one from e.g. Kielland (1937), does not allow calculating the 322 global ionic strength influence of the mixture. In agreement with the selection from NEA-323 OECD (Grenthe et al., 1992; Grenthe and Puigdomènech, 1997; Guillaumont et al., 2003), 324 and for ionic strength typically lower than 3 mol kg_{water}-1, the specific ion interaction 325 theory (SIT) can be used with PRODATA database when the ion specific parameters $\varepsilon(M^+, X^-) - M^+$ and X^- being the cation and anion from the background electrolyte, 326 327 respectively — are available or can be estimated for the j ion

$$\log_{10}\gamma_{j} = -\frac{z_{j}^{2}A\sqrt{I_{m}}}{1+1.5\sqrt{I_{m}}} + \sum_{k}\varepsilon(j,k,I_{m})$$
⁽⁹⁾

328 where *k* represented the opposite charged ion of the background electrolyte.

Based on the possibility to define metastable species (cf. § 2.1.2.3) all specific ion interaction coefficient relative to ClO_4^- in NEA-OECD selections are given relative to the Perchlorate- species in the PhreeqC database file from PRODATA. The database file for PhreeqC is available for two different ionic strengths correction: Davies (1962), and specific interaction theory (SIT) calculations. The CHESS — as the one used in Lartigue et al. (submitted) — and GWB files are available for Debye-Hückel ionic strength corrections. In the following exercise, we will only discuss the use of the PhreeqC file exported from the PRODATA database for SIT calculations.

337 2.1.7. Oxygen and hydrogen

The basic properties of water are taken from CODATA (Cox et al., 1989) and NBS (Wagman et al., 1982). It is noteworthy that the thermodynamic data for the dissolution of $H_2(g)$ and $O_2(g)$ in water are not yet reported in the NEA-OECD selection. As these data are required for the building of the softwares' database files, the data for $H_2(aq)$ and $O_2(aq)$ were taken from NBS (Wagman et al., 1982).

343 2.1.8. Uranium

344 Uranium has received a consequent interest on its thermodynamic properties. A large 345 body of work has been documented in the reviews commissioned by the Thermodynamic 346 Database project of the NEA-OECD. Out of these volumes, uranium has been the subject of 347 the first volume of the series (Grenthe et al., 1992), one addenda in the second volume 348 (Silva et al., 1995), an update (Guillaumont et al., 2003), and the particular case of selected 349 organic complexes (Hummel et al., 2005). All the fundamental thermodynamic functions 350 on uranium from these reviews are coherent with the work from CODATA (Cox et al., 351 1989). The majority of the data recommended in these reviews are used in PRODATA, 352 with the exception of data outside the scope of its application field - i.e., organic 353 complexes, for the time being.

Some important phases were not selected in NEA-OECD compilations. For instance, phosphate (Muto, 1965; Van Haverbeke et al., 1996), or alkaline earth carbonate (Alwan and Williams, 1980; O'Brien and Williams, 1983). Nevertheless, the data from Muto (1965) on ningyoite (CaU(PO₄)₂: 2H₂O), even not selected, were pointed out in NEA-OECD reviews (Grenthe et al., 1992; Guillaumont et al., 2003). The thermodynamic functions from Muto (1965) were adapted in PRODATA.

Concerning the hydrolysis of U(IV), the original selection in Grenthe et al. (1992) only selected $U(OH)^{3+}$ and $U(OH)_4(aq)$. The selection was modified in Guillaumont et al. (2003), but not other $U(OH)_n^{4-n}$ complexes were selected. In PRODATA, $U(OH)_2^{2+}$ and $U(OH)_3^+$ from Neck and Kim (2001), were added.

364 One of the major lack in the available data is the formation constants for $^{II}M_{n}UO_{2}(CO_{3})_{3}^{(4-2n)-}$ complexes — with $^{II}M^{2+}$ being the alkaline earth cations. The first 365 evidence of these complexes was in a seepage water from a uranium mine where 366 367 Bernhard et al. (1996) — after the first data selection in Grenthe et al. (1992) — proposed the formation of $Ca_2UO_2(CO_3)_3(aq)$. Other authors confirmed the formation of 368 $CaUO_2(CO_3)_3^{2-}$, $Ca_2UO_2(CO_3)_3(aq)$, and $MgUO_2(CO_3)_3^{2-}$ complexes (Kalmykov and 369 370 Choppin, 2000; Bernhard et al., 2001; Dong and Brooks, 2006, 2008; Lee and Yun, 2013; 371 Endrizzi and Rao, 2014; Lee et al., 2017), and their importance in theoretical speciation 372 calculation was clearly shown (Kohler et al., 2004; Reiller et al., 2012; Vercouter et al., 373 2015; Neiva et al., 2019; Wang et al., 2019). The evidence of these species is particularly 374 easy in time-resolved laser-induced luminescence as the triscarbonatouranyl(VI) complexes are the only ones to shown a hypsochromic shift relative to $\mathrm{UO}_2^{2^+}$. Endrizzi and 375

Rao (2014) has proposed $\Delta_f H_m^o$ values for ${}^{II}M_n UO_2(CO_3)_3^{(4-2n)-}$ complexes (Mg and Ca), which was included in PRODATA. Jo et al. (2019) proposed an analytical expression of the dependence of $\log_{10}\beta(Ca_n UO_2(CO_3)_3^{(4-2n)-})$, which is not accounted in PRODATA due to its publication after the dead line fixed for the exercise (vide ante). These values are needed further confirmation.

381 Up to now, the NEA-OECD compilation of data does not recommend the use of these data 382 because of a possible bias in extrapolation to zero ionic strength of the original data — see 383 the discussion in Guillaumont et al. (2003) about Kalmykov and Choppin (2000). The use 384 of the corresponding solids proposed by Alwan and Williams (1980) are not 385 recommended either — see the discussion in Grenthe et al. (1992). Nevertheless, these 386 complexes have been added to the PRODATA database in view of their importance in a 387 wide range of carbonated waters conditions (Maher et al., 2013; Grivé et al., 2015). The 388 results from the experiments from Dong and Brooks (2006) were chosen for $SrUO_2(CO_3)_3^{2-}$, $BaUO_2(CO_3)_3^{2-}$, 389 $CaUO_2(CO_3)_3^{2-}$, $Ca_2UO_2(CO_3)_3(aq),$ and $Ba_2UO_2(CO_3)_3(aq)$. Concerning $MgUO_2(CO_3)_3^{2-}$ the extrapolation to infinite dilution 390 391 proposed by Dong and Brooks (2008) was chosen, even if the SIT parameters can be 392 viewed as too important compared to other divalent anions (Guillaumont et al., 2003). A 393 discussion of this selection — in particular with the first proposition in Dong and Brooks 394 (2006) —, in view of the speciation results, will be presented later (vide post).

For the solid phases, the problems in the data from Alwan and Williams (1980) identified in Grenthe et al. (1992), was later corrected by O'Brien and Williams (1983), and are included in PRODATA for scoping calculation. Endrizzi et al. (2016) proposed a re398 estimation of these solubility products in consistence with the formation of 399 ${}^{II}M_{n}UO_{2}(CO_{3})_{3}^{(4-2n)-}$ complexes in Endrizzi and Rao (2014). Even if they are known as 400 alteration phases or uraninite (UO₂), in view of the high solubility of these phases, they 401 should only be sparingly observed in monitoring of mining activities.

402 2.1.9. Radium

403 The thermodynamic functions and constants were taken from literature: Ra^{2+} and $RaNO_{3}^{+}$ 404 were taken from NBS (Wagman et al., 1982). $RaOH^{2+}$, $RaCl^{+}$, $RaSO_{4}(aq)$, and $RaCO_{3}(aq)$ 405 were taken from Langmuir and Riese (1985); $Ra(HCO_{3})_{n}^{(2-n)+}$ were taken from Beneš et 406 al. (1982).

407 For the solids, Ra(cr) and $Ra(NO_3)_2(s)$ are taken from NBS (Wagman et al., 1982), while 408 $RaSO_4(s)$ and $RaCO_3(s)$ are taken from Langmuir and Riese (1985).

409 2.1.10. Auxiliary data

In order to perform the calculation needed for mining and environmental monitoring, a
wide range of auxiliary data is needed, as uranium and radium are submitted to side
complexation reactions.

413 2.1.10.1. Column VIIIA

Even if they are not necessary for the purpose of the database, noble gases — He, Ne, and
Ar —, added as gases and dissolved species, are included in the PRODATA database. They
could be used to fix a total pressure of inert gas over a solution.

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417 2.1.10.2. Column VIIA

The halogens were mostly taken from CODATA, NBS, and NEA-OECD compilations (Wagman et al., 1982; Cox et al., 1989; Guillaumont et al., 2003; Olin et al., 2005) and complemented for I_3^- (Ramette and Sandford, 1965).

421 2.1.10.3. Column VIA

As already seen earlier, sulphur is an important auxiliary element for the monitoring of
 mining operation, through sulphuric acid, particularly for ISR operations. Data for S²⁻,

424 $S_2O_3^{2-}$, SO_3^{2-} , and SO_4^{2-} were selected in Guillaumont et al. (2003), but they have been

425 complemented by the selected data from Chivot (2004) for S_n^{2-} , $SO_2(aq)$, and other $S_nO_m^{2-}$.

Selenium, which isotope ⁷⁹Se is a fission product, is associated to uranium ores. It has been
the subject of an NEA-OECD volume (Olin et al., 2005) including uranium complexes,
which data are accounted for in PRODATA.

429 2.1.10.4. Column V5

430 Nitrogen and phosphorus species are taken from NBS (Wagman et al., 1982), CODATA
431 (Cox et al., 1989) and NEA-OECD (Guillaumont et al., 2003).

Arsenic can be an important contaminant that is accompanying uranium-mining activities
(Katsoyiannis et al., 2007; Neiva et al., 2019). The thermodynamic data selected during
the NEA-OECD compilation (Grenthe et al., 1992; Olin et al., 2005) are included in
PRODATA.

437 Due to its concentration in atmosphere, dissolution in water, and primordial importance 438 in the life cycle on Earth, carbon is an important auxiliary element to consider. Only 439 species from $CO_2(g)$ dissolution in water ($CO_2(aq)$, HCO_3^- , and CO_3^{2-}) and reduction to 440 methane ($CH_4(g)$ and $CH_4(aq)$) are considered in PRODATA. Data from NBS (Wagman et 441 al., 1982), CODATA (Cox et al., 1989), and NEA-OECD (Guillaumont et al., 2003) are used. 442 The other organic compound or complexes from NBS (Wagman et al., 1982) or Hummel 443 et al. (2005) are not accounted for the time being.

Silicon is an important element in minerals, rock and sediment formation. The dissolved
silicate and polysilicate selected in NEA-OECD review are considered in PRODATA
(Guillaumont et al., 2003). Aluminum, iron (Hummel et al., 2002), and uranium
(Guillaumont et al., 2003) aqueous complexes are taken into account.

Only Si(cr) and quartz (SiO₂(cr)) are selected in the NEA-OECD data base (Guillaumont et
al., 2003). The SiO₂ solids are complemented by amorphous silica and chalcedony
(Nordstrom et al., 1990), coesite, cristobalite, quartz-alpha, quartz-beta, stishovite, and
tridymite (Fabrichnaya et al., 2004), and silicalite (Robie and Hemingway, 1995).

Lead is an important element as the end-result of the uranium decomposition chain. The data were mainly selected from NBS (Wagman et al., 1982), CODATA (Cox et al., 1989), Brown and Ekberg (2016), Sverjensky et al. (1997), Blanc et al. (2006) and Lothenbach et al. (1999). For solids the compounds from NBS (Wagman et al., 1982) and CODATA (Cox et al., 1989) are complemented by selenium compounds from NEA-OECD (Olin et al., 457 2005), phosphate compounds (Nriagu, 1974), and hydroxocarbonate compounds (Taylor458 and Lopata, 1984)

459 2.1.10.6. Column IIIA

Aluminum is an important element as the counterpart of silicon in aluminosilicate
minerals. The properties of aluminum have been proposed in NBS (Wagman et al., 1982)
and CODATA (Cox et al., 1989), but more recent data were chosen for hydrolysis (Castet
et al., 1993), fluoride (Nordstrom et al., 1990), and sulfate complexation (Tagirov and
Schott, 2001).

Oxides (Robie and Hemingway, 1995), and sulfates (Helgeson et al., 1978; Wagman et al., 1982) were included. Several aluminosilicate are included (Helgeson et al., 1978; Robie and Hemingway, 1995; Gailhanou et al., 2012; Gailhanou et al., 2017). Some aluminosilicate selected in the GWB database were included in PRODATA even if it was not possible for the time being to identify the origin of the data. They are clearly marked as non-identified.

471 *2.1.10.7. Column IIB*

472Zinc may be found in environmental mining context. Only Zn^{2+} , Zn(cr), ZnO, and some473selenium compounds are available in NEA-OECD (Guillaumont et al., 2003; Olin et al.,4742005). The hydrolysis is taken from Brown and Ekberg (2016) and Zhang and Muhammed475(2001), the chloride complexes and $Zn(SO_4)(aq)$ and $Zn(SO_4)_2^{2-}$ from Powell et al. (2013),476and the carbonate complexes from Smith et al. (2004).

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The hydroxide is taken from Zhang and Muhammed (2001), sulphide phases are taken from Pankratz et al. (1987), sulphate and carbonate phases are from Robie and Hemingway (1995) — with the addition of $ZnSO_4$: H₂O from Wateq4f (Ball and Nordstrom, 1991) —, and phosphate from Nriagu (1984).

481 2.1.10.8. Column IB

Copper can form very insoluble compounds with uranium (Cretaz et al., 2013). Even if
data are available from NBS (Wagman et al., 1982), the hydrolysis data from Plyasunova
et al. (1997), chloride from Wang et al. (1997), carbonate data from Smith et al. (2004)
were chosen. The sulfate complex from NBS (Wagman et al., 1982) is included.

Silver Ag⁺ ion, and the selenocyanate complex, is included in the NEA-OECD auxiliary data
(Guillaumont et al., 2003; Olin et al., 2005). The selection is complemented by hydroxide
(Bard et al., 1985), halogenide (Wagman et al., 1982; Bard et al., 1985), nitrate (Wagman et al., 1982), and carbonate (Sverjensky et al., 1997) complexes and solids.

490 *2.1.10.9. Column VIIIB*

Two nickel isotopes (⁵⁹Ni and ⁶³Ni) are activation products, and it is associated to uranium
ores. Nickel has been the subject of a volume from NEA-OECD (Gamsjäger et al., 2005).
Selenium compound were also selected (Olin et al., 2005).

Fe is ubiquitous on Earth. A first volume has been the subject of an NEA-OECD review
(Lemire et al., 2013), and a selenium complex was selected (Olin et al., 2005). As this first
NEA-OECD volume does not cover the entirety of the iron chemistry, other data were
chosen to complement the selection for hydrolysis and chloride (Chivot, 2004), and
25 -

phosphate complexes (Nriagu, 1972b; Nriagu, 1972a). In addition to the solids selected in
the NEA-OECD review (Lemire et al., 2013), hydroxide (Chivot, 2004), sulphur (Pankratz
et al., 1987; Robie and Hemingway, 1995), and phosphorus (Nriagu, 1972b) are chosen.
The Na-jarosite phase from LLNL database is included even if the origin were not
identified up to now, but is identified as such.

503 2.1.10.10. Column VIIB

504 Manganese is often controlling the redox properties (Duro et al., 2000a). The 505 thermodynamic data for redox and hydrolysis are chosen from Shock et al. (1997). 506 Chloride and carbonate complexation are from Nordstrom et al. (1990), and fluoride are 507 from Chandratillake et al. (1988) — these latter data are only added as $log_{10}K^{\circ}$ and not as 508 $\Delta_f G_m^{o}$.

509 Solids from NBS (Wagman et al., 1982) and Robie and Hemingway (1995) are 510 complemented by (oxo)hydroxides and carbonate (Nordstrom et al., 1990) and sulphur 511 compounds (Pankratz et al., 1987; Dyrssen and Kremling, 1990).

512 2.1.10.11. Column VIB

Molybdenum has a rich chemistry, is often associated with uranium ores, and can be a
secondary contaminant. The redox properties are mainly taken from Bard et al. (1985),
and solids from Bard et al. (1985) and NBS (Wagman et al., 1982).

516 2.1.10.12. Column VB

Vanadium forms insoluble compounds with uranium. The redox chemistry is taken from
Shock et al. (1997) and complemented by, NBS (Wagman et al., 1982), and Brown and
Ekberg (2016). The solids are taken from Langmuir (1978), and NBS (Wagman et al.,
1982).

521 2.1.10.13. Column IVB

Titanium and zirconium in the form of oxide minerals are often found in the environment.
The data for titanium are taken from Brown and Ekberg (2016) for the aqueous species
completed by solids from Bard et al. (1985), Robie and Hemingway (1995), and Pankratz
et al. (1987). Zirconium has been the subject of a NEA-OECD review volume (Brown et al.,
2005) due to its use as cladding for the nuclear fuel rods. The thermodynamic data and
uncertainties recommended are included in PRODATA.

528 2.1.10.14. f-Transition Elements – Thorium

Apart uranium, thorium is the only *f*-transition element included up to now in PRODATA
— other lanthanides or actinides are not of primary concern for the monitoring of mining
activities. Thorium is part of the uranium radioactive decay chain. It has been the subject
of one volume of the NEA-OECD (Rand et al., 2009). The thermodynamic data
recommended, and uncertainties, are included in PRODATA.

534 2.1.10.15. Column IIA

Alkaline earth metals are important major cations to consider for environmental monitoring of mining activities. They are implied in competition reactions for the main environmental ligands, e.g. CO_3^{2-} through the formation of ${}^{II}M_nUO_2(CO_3)_3^{(4-2n)-}$ complexes (c.f. § 2.1.8), and SO_4^{2-} for the (co-)precipitation reaction of Ra in sulfate media (Curti et al., 2010; Lestini et al., 2019).

The thermodynamic function for the free ions ^{II}M²⁺ are available in NEA-OECD 540 compilations (Guillaumont et al., 2003), but some important auxiliary data are not yet 541 542 available. Hydrolysis is taken from Palmer and Wesolowski (1997), Shock et al. (1997), 543 and Wagman et al. (1982). Fluoride and chloride complexes formation are taken from 544 Sverjensky et al. (1997). Sulfate complexes are taken from NBS (Wagman et al., 1982), Yeatts and Marshall (1969), Reardon (1983), and Martell and Smith (1976). Nitrate 545 546 complexes are taken from NBS (Wagman et al., 1982). Carbonate complexes are taken 547 from Plummer and Busenberg (1982), Busenberg et al. (1984), and Busenberg and 548 Plummer (1986).

Some phases are selected in NEA-OECD compilations (Guillaumont et al., 2003), but they
do not allow calculating speciation in the conditions of mining activities monitoring.
Particularly, the hydroxide (Wagman et al., 1982; Chase, 1998; Felmy et al., 1998; Altmaier
et al., 2003), sulphur (Pankratz et al., 1987; Reardon and Armstrong, 1987; Robie and
Hemingway, 1995), and carbonate phases were added (Plummer and Busenberg, 1982;
Busenberg et al., 1984; Busenberg and Plummer, 1986; Nordstrom et al., 1990; Robie and

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Hemingway, 1995). Other data from the LLNL or GWB databases were added even if notidentified, and marked as such.

557 2.1.10.16. Alkaline metals in Column IA

558 Thermodynamic function of the alkaline ^IM⁺ free ions are available in CODATA (Cox et

al., 1989) and NEA-OECD (Guillaumont et al., 2003) selections. As the interaction between

the ^IM⁺ free ions and ligands are supposed to occur *via* specific ion interaction in SIT, no

other complex are taken into account, e.g. AkHCO₃(aq).

562 Concerning solids, data from NEA-OECD (Guillaumont et al., 2003) were complemented
563 by data on oxides (Robie and Hemingway, 1995), sulphur (Harvie et al., 1984; Pankratz et
564 al., 1987; Robie and Hemingway, 1995), carbonates (Wagman et al., 1982; Robie and
565 Hemingway, 1995).

566 2.2. Modelling

This exercise can be viewed as a benchmark of the PRODATA database itself, having in mind the limitations that are coming from the modeller's choices (Emrén et al., 1999). After the selection of the different water compositions, the obtained results were compared with the different calculations obtained using other available databases, either included in the PhreeqC package or not.

572 2.2.1. PRODATA database file and software version used

573 The PhreeqC version of PRODATA 1.1.0.4 database, extracted on October 26th 2018, was 574 used. It means that later works have not been taken into account in the building of the 575 database (e.g., Jo et al., 2019).

The PHREEQC version 3.4.0.12927 (Parkhurst and Appelo, 1999, 2013) was used for the speciation calculation, and Phreeplot 1.0 (Kinniburgh and Cooper, 2004, 2011), which includes a version of PHREEQC 3.4.0.12927, for the calculation of the predominance diagrams. The PHREEQC 3.4.0.12927 was chosen as the stable version at the beginning of the project, i.e. 2015. No difference has been noted in the output results using the more recent version 3.5 in preliminary tests.

582 2.2.2. Software database files for radium

There a two database files provided with PhreeqC that allow calculating the speciation of radium, i.e. Thermochimie 9b and LLNL. The database file for the Swiss radioactive waste management program (PSI/NAGRA 12/07) is also containing thermodynamic constants for radium (Thoenen et al., 2014).

587 2.2.3. Software database files for uranium

There are four database files provided in the PhreeqC package that allow calculating the uranium speciation, i.e. Thermochimie 9b (Giffaut et al., 2014), LLNL, Wateq4f (Ball and Nordstrom, 1991), and Minteq (EPA, 1998). The PSI/NAGRA 12/07 database file is also containing uranium thermodynamic constants (Thoenen et al., 2014). This latter database file has been built with the specific application field in radioactive waste management and 593 misses some important data in the field of environmental and mining activities594 monitoring. Nevertheless, it will give interesting viewpoints on several issues.

After the beginning of this program, NEA-OECD made public a PhreeqC version database file of the selected thermodynamic constants (Martinez et al., 2019). For the reasons explained earlier, this database have not been considered.

598 2.2.4. Comments on auxiliary and ancillary data

The choice of the auxiliary — directly linked to the uranium or radium chemistry —, or ancillary — linked to species or elements that are linked to uranium and radium — can be important. As an example, the formation of $CaSO_4(aq)$ complexes can be discussed. Within Thermochimie 9b the value comes from Bell and George (1953), when the choice of Sverjensky et al. (1997) is done in PRODATA 1.1.0.4. It is noteworthy that Yeatts and Marshall (1969) proposed even lower $log_{10}K^\circ$ values based on a wider range of ionic strength.

606 Knowing the particularly important concentration of total sulphate, or rather SO_4^{2-} 607 activity, implied in an ISR process, this can have an impact on the monitoring of an 608 industrial process. In different cases in the following the consequences of these choices 609 will be shown to have noticeable, but often limited, impact on the theoretical speciation 610 obtained using the different databases.

611 2.3. Selection of studied water compositions

612 There is a large body of data on water composition in literature. The main objective of this
613 exercise is to verify the applicability of PRODATA for water that linked to uranium mining

activities, and mostly waters that are under the monitoring of ORANO Mining. In order to
have a large body of data, we have chosen to select other water composition, either linked
to nuclear energy cycle, or of more general interest.

All solution compositions are given as their PhreeqC input script in the SupplementaryInformation (SI).

619 2.3.1. Waters linked to a uranium mine activity

620 2.3.1.1. Groundwaters in ISR context

621 In Situ Recovery (ISR) is one of the main mining techniques for Uranium (IAEA, 2001, 622 2016). Dedicated generally to extract uranium from low-grade deposits in highly 623 permeable geological formations, ISR implies water/rock reactions to enhance the 624 solubility of uranium through oxidative attack and solubilisation in acid or alkaline 625 conditions. We will consider several water compositions taken in an ISR context from 626 ORANO mining sites: from non-acidified waters — TNU_N_18, PZOV_0013_1, 627 PZOV_0001_1, PZOV_0033_1, MOZO_0007_1, MOZO_0009_1, PTZO_0001_1, 628 PZOV_0021_1, PZOV_0022_1, PZOV_0024_1, and ISRW_0001 in Figures S1-1 to S1-11 of 629 the SI — to moderately — TNU N 39 Figures S1-12 and S1-13 of the SI — and highly 630 acidified waters — TNU N 37 and ISRW 0098 in Figure S1-14 and Figure S1-15 of the SI. 631 These cases will be complemented by water compositions directly at the input — Entrée 632 Usine in Figure S1-16 of the SI — and the outlet — Sortie Usine in Figure S1-17 of the SI — 633 of a mill. The pH values, sulphate concentrations, and redox conditions are the main 634 chemical parameters for which variations are observed concurrently with aqueous 635 uranium concentrations.

636 2.3.1.2. Waters sampled in the vicinity of uranium mining sites

637 Concurrently to waters taken in ISR context, we considered several waters sampled in the 638 vicinity of mining sites: either upstream — i.e. without any mining activity influence 639 — ARLI_3082, RVA1, and Henriette in Figures S2-1 to S2-3 of the SI — or within the 640 mining sites — i.e., under anthropic influence, COMI_79, ES-85, CHD3, V105, BD200, PT4 641 Rejet in Figures S2-4 to S2-9 of the SI. The pH values, sulphate, and carbonate 642 concentrations are the main chemical parameters for which variations are observed 643 concurrently with aqueous uranium concentrations.

These waters compositions are complemented by the uranium mining pile where the $Ca_nUO_2(CO_3)_3^{(4-2n)-}$ complexes were first evidenced (Bernhard et al., 1996) — results are presented in Figure S2-10 of the SI.

647 2.3.1.3. Waters sampled downstream former uranium mine

648 In a recent publication, Stetten et al. (2018) studied the speciation of uranium in a 649 lacustrine sediment (Lac Saint-Clément) impacted by the former uranium mine of Bois 650 Noirs Limouzat in France. The authors proposed the composition of waters from 4 cores 651 at different depths. We selected core C4, which is the more complete dataset, containing 652 U and Fe(II) concentration, which allows calculating speciation and redox conditions. The 653 concentration of dissolved organic carbon are available but will not be used within the 654 framework of this exercise. This example will only be treated using PRODATA 1.1.0.4 655 database file.

656 *2.3.1.4. Cluff Lake former uranium mine*

At the former Cluff Lake uranium mine, von Gunten et al. (2018) studied the uranium
content in two meromictic lakes. The authors calculated the theoretical speciation from
the water compositions using PhreeqC and the Minteq database — output file were kindly
provided by the corresponding author. Results are presented in Figure S4-1 to S4-8 of the
SI.

662 2.3.2. Radioactive waste management

663 Water compositions in underground research laboratories (URL) for radioactive waste 664 management have been proposed. In France, the water compositions from clayey 665 environments were proposed: the Callovo-Oxfordian was proposed by Gaucher et al. 666 (2009) — results in Figures S5-1 of the SI —, and the water from Tournemire by 667 Beaucaire et al. (2008) — results in Figure S5-2 and S5-3 of the SI. In Belgium, the Boom 668 clay water composition is proposed in de Craen et al. (2004) — result in Figure S5-4 of 669 the SI. In Switzerland, the Mont-Terri tunnel has been thoroughly studied, and water 670 compositions from the clay environment can be found in Courdouan Merz (2008) and 671 Thury and Bossart (1999), and results are presented in Figure S5-5 to S5-7 of the SI. In Sweden, a reference granite water composition for the site of Äspö can be found in Emrén 672 673 et al. (1999), and the results are shown in Figure S5-8 of the SI. As no uranium 674 concentrations are reported in these water compositions, the calculations were 675 performed at equilibrium with crystalline UO₂ — except for PSI/NAGRA 12/07 database 676 which excludes the crystalline phase — considering no perturbation of the water

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677 compositions given the buffering capacity of the host rock, even if this latter hypothesis678 can eventually be discussed (Emrén et al., 1999).

679 2.3.3. FOREGS

These waters are issued from the general dataset generated through the European project FOREGS (Forum of European Geological Surveys), and can be considered in a first approach as non-impacted waters. Details are given in Lartigue et al. (submitted). Results are presented in Figure S6-1 to S6-8 of the SI. The general water compositions can be downloaded at http://weppi.gtk.fi/publ/foregsatlas/ForegsData.php.

685 2.3.4. Other sources

The migration of uranium has been monitored in a uranium impacted podzol in the French Landes of Gascony (Crançon, 2001; Crançon and Van der Lee, 2003; Crançon et al., 2010). The composition of the water is mildly acidic and carbonated. Results are presented in Figure S7-1 of the SI.

Investigating the uranium contain in groundwaters of Al-Batin Alluvial Fan (southern
Iraq), Alkinani et al. (2016) provide the composition of the sample W43, which will be
included in the pool of water composition. Results are presented in Figure S7-2 of the SI.

693 Prat et al. (2009) provided the composition of Finnish well waters that are rather 694 concentrated in uranium. The $Ca_nUO_2(CO_3)_3^{(4-2n)-}$ complexes were calculated to be 695 predominant, and were observed in time-resolved luminescence spectroscopy. Results 696 from this exercise are presented in Figure S7-3 to S7-15 of the SI.

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697 2.3.5. Canadian aquitard

698 Ranville et al. (2007) studied the weak association of natural organic matter (NOM) with 699 uranium in an aquitard highly concentrated in Mg, Ca, sulphate, and carbonate (Hendry 700 and Wassenaar, 2000). The formation of ${}^{II}M_{n}UO_{2}(CO_{3})_{3}^{(4-2n)-}$ complexes has been shown 701 to prevent the formation of U-NOM complexes (Reiller et al., 2012). Nevertheless, the 702 resulting ionic strengths within the majority of these waters were outside the validity of 703 the used activity correction (Davies, 1962). These waters were included in the exercise, 704 and results are presented in Figure S8-1 to S8-8 of the SI.

705 2.3.6. Oklo

The natural nuclear reactors in Oklo have been the subject of a rich literature. The Okélobondo uraninite body has been the subject of a blind prediction modelling exercise using several water compositions (Duro et al., 2000a; Duro et al., 2000b). Water compositions from these exercises can be retrieved in Gurban et al. (2000) for Bagombé, and Salas and Ayora (2004) for Okélobondo. Results are presented in Figure S9-1 to S9-15 of the SI for Okélobondo and in Figure S9-16 to S9-18 of the SI for Bagombé.

712 2.3.7. Standard seawater

Seawater represents an important source of uranium (OECD, 2014) of over 4 billion tU, but at a very dilute concentration (3-4 ppb). The speciation of uranium is a major problem for the uranium recovery from seawater, as well as the one from potential competitor, to develop a method of extraction. From recent theoretical speciation exercise, and from synthetic water experimental observations, the speciation of uranium in seawater is

- 36 -

expected to be controlled by carbonate species (Maloubier et al., 2015). Millero et al.
(2008) proposed a standard composition for seawater — nearly charge balanced —,
which will be used in this work. Results are presented in Figure S10-1 of the SI.

721 3. Results and Discussions

722 3.1. General comments on results

723 The output files from the different calculations as well as the detailed repartitions of 724 species for uranium and radium for all the cases studied are provided as SI. In the case of 725 uranium, estimations of the uncertainty of the speciation results were attempted. The 726 uncertainties of the calculation using Prodata was done using the simplistic 727 approximation of the propagation of errors varying the $\log_{10}\beta^{\circ}$, and eventual $\varepsilon(M^+, X^-)$ or $\Delta_r H_m^o$, values for the main species. More sophisticated approaches could be applied — see 728 e.g. Ekberg and Ödegaard-Jensen (2011) —, but are currently out of the framework of the 729 730 project.

731 *3.2.* Radium

Radium is only present in the waters analysed in the framework of the monitoring of
mining activities from Orano Mining. PRODATA 1.1.0.4, Thermochimie 9b, LLNL, and
PSI/NAGRA 12/07 databases include Ra data, and only PRODATA 1.1.0.4, Thermochimie
9b, and PSI/NAGRA 12/07 are including RaSO₄(aq), the presence of which is crucial for
monitoring data from mining activities — LLNL only includes Ra²⁺ in solution, see SI.

From calculations using the PRODATA 1.1.0.4 database file, evolution of radium speciation as a function of calculated $a(SO_4^{2-})$ is shown in Figure 1; comparable results

are obtained using Thermochimie 9b and PSI/NAGRA 12/07 databases, and only differ from slightly different choices of auxiliary data and from activity corrections, see SI. The free ion Ra²⁺ is major at low calculated $a(SO_4^{2-})$ values in non-anthropized waters. Conversely, RaSO₄(aq) is major in the strongly anthropized waters, i.e. for water that are strongly impacted by mining activities at $log_{10}(a(SO_4^{2-})) > -2.4$.

744 It must be noted that radium total concentrations in natural waters in natural waters and 745 in mining environments are controlled in many cases by coprecipitation with other 746 alkaline earth sulphate phases — i.e., celestite and barite (Curti et al., 2010; Lestini et al., 747 2019) —, and also adsorption onto clay minerals (Reinoso-Maset and Ly, 2016; Robin et 748 al., 2017), ferric (oxi-)hydroxide (Sajih et al., 2014), and organic matter (Bordelet et al., 749 2018). Nevertheless, this would not drastically change the general speciation results.



Figure 1. Evolution of the repartition of radium species in selected waters containing sulphate using the PRODATA 1.1.0.4 database and SIT ionic strength correction: (a) as a function of calculated $\log_{10} (a(SO_4^{2-}))$; and (b) identification of waters in the order of calculated $a(SO_4^{2-})$.

754 3.3. Uranium

755 3.3.1. General results

756 From a general point of view, it can be seen in the SI that uranium speciation results are 757 mostly the same for PRODATA 1.1.0.4 and Thermochimie 9b databases. This is mainly due 758 to the same body of data (Guillaumont et al., 2003; Dong and Brooks, 2006) and the same 759 activity correction. Some slight differences are occurring at temperature different from 25°C for ${}^{II}M_nUO_2(CO_3)_3^{(4-2n)-}$ complexes, as the enthalpy determinations from Endrizzi 760 and Rao (2014) are included in PRODATA 1.1.0.4. One can also remind that other species 761 than $Ca_n UO_2(CO_3)_3^{(4-2n)-}$ are not considered in Thermochimie 9b. In the following, except 762 763 explicitly noted, the results can be considered the same for uranium between these two

databases, and the results from the calculations using PRODATA 1.1.0.4 will mainly bediscussed.

766 3.3.1.1. Uncertainties

The uncertainties of the speciation results also confirm that PRODATA 1.1.0.4 and Thermochimie 9b are providing comparable results. One of the the largest uncertainty is coming from the formation of $(UO_2)_2CO_3(OH)_3^-$, which is given in Guillaumont et al. (2003) as

771
$$2UO_2^{2+} + 4H_2O + CO_2(g) \rightleftharpoons (UO_2)_2CO_3(OH)_3^- + 5H^+ \log_{10}\beta^\circ = -19.01 \pm 0.50$$

and is expressed as follows in PRODATA.

773
$$2UO_2^{2+} + 3H_2O + CO_3^{2-} \rightleftharpoons (UO_2)_2CO_3(OH)_3^- + 3H^+ \quad \log_{10}\beta^\circ = -0.86 \pm 0.50$$

This large uncertainty value is responsible of the large error bars on Figure S2-3a and S7-1 of the SI.

The other large uncertainty is coming from cumulative uncertainty of the solubility of $UO_2(hyd, am)$ and fourth hydrolysis of U⁴⁺.

778 $UO_2(hyd, am) + 4H^+ \rightleftharpoons U^{4+} + 2H_2O = \log_{10}K^\circ = 1.5 \pm 0.03$

779 $U^{4+} + 4H_20 \rightleftharpoons U(0H)_4(aq) + 4H^+$ $\log_{10}\beta^\circ = -10.01 \pm 1.40$

780
$$UO_2(hyd, am) + 2H_2O \rightleftharpoons U(OH)_4(aq) \quad \log_{10}K^\circ = -8.51 \pm 1.40$$

This explains the large uncertainties in Figure S5-5 and S5-6, and to a lesser extend inFigure S4-5.

783 3.3.1.2. Main differences between database files

In LLNL database file, it seems that the uranium data are taken from the original uranium NEA review (Grenthe et al., 1992). It can be seen for some cases that the $UO_2(OH)_2(aq)$ complex can be major in the LLNL cases — e.g. Figures S2-3, S4-6, S4-7, S4-8, S6-1, S7-1, S9-3, S9-4, S9-5, S9-8, and S9-14 of the SI — or at least show some importance — e.g. Figures S1-11, S1-12a, S2-9, S4-1, S4-2, S4-3, S6-6, S6-7, S6-8, S7-14, S9-12, S9-16, S9-17, and S9-18 of the SI.

- 790 It is noteworthy that the $UO_2H_2PO_4^+$ complex contributes as a minor species in acidic
- media (Figures S1-14, S1-16, and S1-17 of the SI) in LLNL output data. This is due to a difference in the $\log_{10}\beta^{\circ}$ value.
- 793 For the equilibrium

794 $UO_2^{2+} + HPO_4^{2+} + H^+ \rightleftharpoons UO_2H_2PO_4^+$ $\log_{10}\beta^\circ = 11.54$

in LLNL, when for NEA-OECD the equilibria

796 $UO_2^{2+} + H_3PO_4(aq) \rightleftharpoons UO_2H_2PO_4^+ + H^+ \log_{10}\beta^\circ = 1.12 \pm 0.06$

is expressed as

798 $UO_2^{2+} + HPO_4^{2+} + H^+ \rightleftharpoons UO_2H_2PO_4^+$ $\log_{10}\beta^\circ = 10.47 \pm 0.07$

calculated in PRODATA 1.1.0.4 from Guillaumont et al. (2003) from the selected $\Delta_f G_m^o$.

800 In Wateq4f and Minteq databases, the data from the more recent review are used (Guillaumont et al., 2003), but the ${}^{II}M_nUO_2(CO_3)_3^{(4-2n)-}$ complexes are not present. In the 801 802 light of the common use of Minteq database in the geochemical community, we will 803 principally compare the results from PRODATA 1.1.0.4 database to the Minteq one. A marked difference is the occurrence of $UO_2(HPO_4)_2^{2-}$ complex in Wateq4f (Ball and 804 805 Nordstrom, 1991) and Minteq (EPA, 1998) results, which is not selected in the NEA-OECD review — after reinterpretation of original data in Grenthe et al. (1992) — and thus not 806 807 present either in PRODATA 1.1.0.4, Thermochimie 9b, or PSI/NAGRA 12/07. It is 808 noteworthy that the $\log_{10}\beta^{\circ}(UO_2(HPO_4)_2^{2-})$ values are different in Wateq4f and Minteq 809 $-\log_{10}\beta^\circ$ = 43.44 and 42.99 for Wateq4f and Minteq, respectively, which explains the 810 slight difference in speciation results. This complex is occurring for Wateq4f and Minteq 811 output results (Figures S7-2, S7-3, S7-4, S7-7 of the SI), but can be a major species (Figures S1-14, S2-1, S7-11, S7-12, S7-13, S7-14 of the SI) outcompeting $UO_2(CO_3)_n^{(2-2n)+}$ 812 813 complexes. This is inducing a major difference in the theoretical speciation results, which 814 has also been emphasized in Wang et al. (2019). Because of the non-selection of this 815 complex in NEA-OECD (Grenthe et al., 1992) (vide supra), the implication of this complex 816 will not be discussed further.

817 Concerning the ${}^{II}M_{n}UO_{2}(CO_{3})_{3}^{(4-2n)-}$ complexes, Thoenen et al. (2014) proposed slightly 818 different data from PRODATA 1.1.0.4 and Thermochimie 9b, as the value for 819 $\log_{10}\beta^{\circ}(MgUO_{2}(CO_{3})_{3}^{2-})$ is chosen from Dong and Brooks (2006), and 820 $\log_{10}\beta^{\circ}(Ca_{2}UO_{2}(CO_{3})_{3}(aq))$ is chosen from Kalmykov and Choppin (2000). The activity 821 coefficient of $Ca_{2}UO_{2}(CO_{3})_{3}(aq)$ is fixed to 1 in Thoenen et al. (2014) for this neutral 822 species, even if one can remark that Kalmykov and Choppin (2000) evidenced a marked ionic strength dependence on $\log_{10}\beta(Ca_2UO_2(CO_3)_3(aq))$. One can remind that this evolution is strongly discussed in Guillaumont et al. (2003), and is at the centre of the nonselection of the thermodynamic data. This latter value is lower than the one proposed by Dong and Brooks (2006), which was extrapolated using Davies (1962) equation.

827 3.3.1.3. Repartition of the main species

828 The repartition of the major species obtained after calculation using PRODATA 1.1.0.4 is 829 shown in an Eh-pH plot in Figure 2 — the same repartition is awaited for Thermochimie 830 9b following the companion study (Lartigue et al., submitted). It can be seen that only nine 831 complexes are controlling the speciation of uranium for the selected waters. The free uranyl, UO_2^{2+} , dominates in low pH and low carbonated non-anthropized waters. The 832 833 $UO_2(SO_4)(aq)$ complex, dominates in all the anthropized waters where uranium 834 extraction are (or were) occurring. The $UO_2(CO_3)(aq)$ complex, dominated for mildly acidic and carbonated waters, as also calculated in others instances (Neiva et al., 2019). 835 836 The $U(OH)_4(aq)$ complex, dominates in highly reductive conditions. The $(UO_2)_2CO_3(OH)_3^-$ complex dominates in only one context of a podzol (Crançon, 2001), 837 838 because of the relatively mildly acidic pH, high uranium and carbonate concentrations. Finally, the $UO_2(CO_3)_2^{2-}$ and $Ca_nUO_2(CO_3)_3^{(4-2n)-}$ complexes — with $n = \{0; 1; 2\}$ — are 839 840 dominating in a wide region from mildly acidic to mildly basic carbonated waters, with no 841 apparent systematic repartition — this results is slightly more complicated than the 842 predominance Pourbaix diagram provided by Maher et al. (2013), which was considering 843 only one calcium concentration. It can nevertheless be noted already that in the case of reducing waters - like the ones from envisaged underground radioactive waste 844



Figure 2. Major uranium species obtained in the speciation calculations of the

different waters considered using the PRODATA 1.1.0.4 database and SIT ionic

Figure 3 is showing the repartition of the same major species in a Piper plot. The strongly

anthropized waters containing high concentration of sulphate — i.e. more than 80% —,

and showing the $UO_2(SO_4)(aq)$ complex as major species, are containing more Ca and Mg

- 44 -

strength correction in the Eh-pH domain.

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846 $Ca_2UO_2(CO_3)_3(aq)$ are calculated to be major species — see e.g. Grivé et al. (2015).

management sites (de Craen et al., 2004; Gaucher et al., 2009) — that $CaUO_2(CO_3)_3^{2-}$ or 845

compared to Na⁺ and K⁺. The waters that are showing $UO_2(CO_3)(aq)$ complex as major species do not seem to have a particular localization in the Piper plot. Concerning the $Ca_nUO_2(CO_3)_3^{(4-2n)-}$ complexes, it can be seen that they seem to be more likely regrouped along the bisectrix Ca(0%)-Mg(50%), and in the lower part of the bisectrix Ca(100%)-Na+K (50%).

The repartition of the major species in a $\log_{10}[U]_{total} - \log_{10}([C(IV)] + [S(VI)])$ diagram (Figure S11-1 of the SI) shows the wide distribution of total uranium concentration. It seems that the higher the S(VI) concentration, the higher the total uranium concentration, but there is no particular trend.



Figure 3. Piper plot for the major species obtained in the speciation calculations of
the different waters considered using the PRODATA 1.1.0.4 database and SIT ionic
strength correction.

865 3.3.2. Mining activities monitoring: effect of sulphate

The first interesting domain that can be identified in Figure 2 is due to the dominance of $UO_2(SO_4)(aq)$ complex. These waters are mainly corresponding to anthropized waters implied in the monitoring of mining activities. In the following section, we will focus on these waters emphasizing on the influence of the activity of SO_4^{2-} .

870 3.3.2.1. Calculation in the framework of PRODATA 1.1.0.4 database

871 The obtained speciation results are shown as percentages for the mining activity waters 872 in Figure 4 — similar results are obtained using the Thermochimie 9b database, see SI. In Figure 4a only the $UO_2(SO_4)_n^{(2-2n)+}$ complexes are shown as a function of the calculated 873 $\log_{10}(a(SO_4^{2-}))$. More complete speciation results including more than 5% complexes are 874 shown on Figure 4b with the water origin in increasing order of $a(SO_4^{2-})$. Using SIT, 875 $UO_2(SO)_4(aq)$ is the major complex when $-3 < log_{10}(a(SO_4^{2-})) < -1.5$. With increasing 876 $a(SO_4^{2-})$, the percentage of $UO_2(SO_4)_2^{2-}$ becomes increasingly important, and $UO_2(SO_4)_3^{4-}$ 877 is noticeable at the highest $a(SO_4^{2-})$ value. This can have an impact on the efficiency of the 878 879 ion exchange resins used in an ISR process. The output results are mostly the same for 880 Thermochimie 9b, LLNL, Wateq4f and PSI/NAGRA 12/07 databases with slight 881 differences that are due to different choices of auxiliary data and activity corrections. The 882 Minteg database outputs are showing significant differences, which will be discussed in 883 the next section (vide infra).



Figure 4. Evolution of the repartition of uranium species in selected sulphated waters calculated using the PRODATA 1.1.0.4 database and SIT ionic strength correction as a function of (a) calculated $a(SO_4^{2-})$, and (b) the origin of the waters.

888 In addition to the earlier comment (cf. § 3.3.1), the particular effect of the choices of the 889 database and activity correction for speciation calculations is shown through the analysis 890 of the differences between the calculation using PRODATA 1.1.0.4 (Figure 4) and the 891 results obtained using the Minteq database (Figure 5). For these water compositions, main differences come from the choice of $\log_{10}\beta^{\circ}(UO_2(SO_4)(aq))$. In PRODATA 1.1.0.4 892 — and also in Thermochimie 9b and PSI/NAGRA 12/07 — the value from Guillaumont et 893 894 al. (2003) $(\log_{10}\beta^{\circ}(UO_2(SO_4)(aq)) = 3.15 \pm 0.02)$ is chosen, whereas a lower value is chosen in the Minteq database $(\log_{10}\beta^{\circ}(UO_2(SO_4)) = 2.709)$. Hence, UO_2^{2+} is major at low 895 $a(SO_4^{2-})$ value, and $UO_2(SO_4)_2^{2-}$ is major at $log_{10}(a(SO_4^{2-})) > -2$. It is noteworthy that the 896 $\log_{10}\beta^{\circ}(UO_2(SO_4)_2^{2-})$ values only differ by 0.04 between the two databases — this 897 difference is less than the uncertainty of $\log_{10}\beta^{\circ}(UO_2(SO_4)_2^{2-}) = 4.14 \pm 0.07$ in 898 899 Guillaumont et al. (2003) —, and that $\log_{10}\beta^{\circ}(UO_2(SO_4)_3^{4-})$ is absent from the Minteq 900 database — and also from the LLNL and Wateq4f databases. This can have an impact on 901 the theoretical speciation concerning the monitoring of an ISR process.



902 Figure 5. Evolution of the repartition of uranium species in selected sulphated 903 waters calculated using the Minteq database as a function of (a) calculated $a(SO_4^{2-})$, 904 and (b) the origin of the waters sorted in the order of calculated $a(SO_4^{2-})$.

905 3.3.3. Environmental monitoring: effect of Ca²⁺

906 The second most striking region in Figure 2 is the occurrence of the $Ca_nUO_2(CO_3)_3^{(4-2n)-}$ 907 complexes. In the following section, we will discuss the repartition of these complexes.

From the plot in Figure 2, it can be seen that the $Ca_nUO_2(CO_3)_3^{(4-2n)-}$ complexes are occurring from oxic mildly acidic and alkaline carbonated waters to slightly reducing waters. No real trend could be evidenced. Kohler et al. (2004) proposed a repartition in the narrow pH range of their study, showing the predominance of the $Ca_2UO_2(CO_3)_3(aq)$ complex, but the wider range of conditions explored here is showing a more intricate repartition.

914 The representation as a function of $a(CO_3^{2-})$ for the selected waters from the 915 environmental monitoring given in Figure 6a permits only partly understanding the 916 pattern. It seems that the proportion of the $Ca_2UO_2(CO_3)_3(aq)$ complex decreases with 917 $a(CO_3^{2-})$ except for three water compositions, i.e. PZOV_0021_1 (Figure S1-8 of the SI), 918 PZOV_0022_1 (Figure S1-9 of the SI), PZOV_0024_1 (Figure S1-10 of the SI). The proportion of $UO_2(CO_3)_2^{2-}$ in ARLI 3082 — $log_{10}(a(CO_3^{2-})) = -5.45$, Figure S2-1 of the 919 920 SI — does not fit with the general pattern too. In Figure 6c it can be seen that the $a(Ca^{2+})$ 921 of these waters are the lowest.

922 However, plotting the obtained speciation of selected waters from environmental 923 monitoring *vs.* calculated $\log_{10}(a(Ca^{2+}))$ in Figure 6b, allows clearly distinguishing the 924 evolution of $CaUO_2(CO_3)_3^{2-}$ from $Ca_2UO_2(CO_3)_3(aq)$ with a crossing point at

- 50 -

925 $\log_{10}(a(Ca^{2+}))$ ca. – 3.2 — the origin of the waters are given in Figure 6c in the order of 926 the calculated $a(Ca^{2+})$.

Extending the representation from Figure 6b to all the waters that are showing significant proportions of the $Ca_nUO_2(CO_3)_3^{(4-2n)-}$ complexes yields to the representation given in Figure S12-1a of the SI, which is showing the same pattern even with a slightly higher dispersion — the origin of the waters is given in Figure S12-1b of the SI in the order of the calculated $a(Ca^{2+})$. It is also noteworthy that a large part of these waters are oversaturated relative to calcite (CaCO₃) and dolomite (CaMg(CO₃)₂) — see in Figure S12-2 of the SI.

As for the previous case of sulphate complexes, differences in obtained speciation of carbonate complexes is shown in Figure S12-3 of the SI when using the Minteq database. The evolution of $UO_2(CO_3)_n^{(2-2n)+}$ percentage is typically evolving with calculated $a(CO_3^{2-}) - {}^{II}M_nUO_2(CO_3)_3^{(4-2n)-}$ complexes are not implemented in the database.



Figure 6. Evolution of repartitions of uranium species in selected carbonated waters linked to the monitoring of mining activities using the PRODATA 1.1.0.4 database and SIT ionic strength correction as a function of calculated (a) $a(CO_3^{2-})$, (b) $a(Ca^{2+})$, and (c) origin of the waters in the order of calculated $a(Ca^{2+})$.

942 3.3.4. Effect of Eh

943 Uranium is a redox sensitive element. The oxidation/reduction reactions are very
944 important in the formation of ores (Langmuir, 1978), and are at the center of the
945 radioactive waste management in deep geological formation. Under its +IV redox state,
946 uranium is highly insoluble either as oxide, phosphate, or silicate. In the next section, we
947 will focus on the results from waters representative of nuclear waste management sites
948 — to test the wider applicability of PRODATA 1.1.0.4 —, and some other waters linked to
949 environmental monitoring.

950 3.3.4.1. Radioactive waste management

Depending on national contexts, the disposal of nuclear wastes is envisaged in deep geological formations, where reducing conditions assure low solubility of actinides, and particularly of uranium. The repartition of the different species obtained in the calculations using PRODATA 1.1.0.4 database are given in Figure 7 as a function of different parameters: (i) the influence of redox potential (Figure 7a), represented *via* the *pe* values;

$$pe = \frac{FE_{h}}{RT\ln(10)}$$
(10)

957 (ii) the influence of the calculated $a(Ca^{2+})$ (Figure 7b); and (iii) the Ca^{2+} and CO_3^{2-} 958 activities *vs. pe* (Figure 7c). From a general point of view, the results obtained with 959 PRODATA are comparable to the one with the dedicated waste management databases, 960 i.e. Thermochimie 9b and PSI/NAGRA 12/07. In the case of PSI/NAGRA 12/07 database - 53 -

the choice of the MgUO₂(CO_3)²⁻₃ complex from Dong and Brooks (2006) and using Davies 961 962 (1962) equation for activity correction is slightly favouring the complex compared to the 963 PRODATA 1.1.0.4 results. It can be seen that redox potential has an important influence 964 on the uranium speciation, but does not allow fully understanding the general pattern. 965 For instance, the waters that are showing the three lowest *p*e values, are showing different 966 speciation — $U(OH)_4(aq)$ for BWS-A1 (pH = 7.3, pe = -4.82, Figure S5-5 of the SI) and BWS-A2 (pH = 7.1, pe = -4.51, Figure S5-6 of the SI), and CaUO₂(CO₃)₃²⁻ for Mol reference 967 968 water (pH = 8.5, *p*e = -4.78, Figure S5-4 of the SI),. The combination with Figure 7c shows that $\log_{10}(a(Ca^{2+}))$ and $\log_{10}(a(CO_3^{2-}))$ have opposite — and mostly mirrored — trends, 969 970 which allows understanding that even if BWS-A1 — and to a lesser extent BWS-A2 — is showing the mostly same *p*e value as Mol reference water — and higher $\log_{10}(a(Ca^{2+}))$ 971 value —, the more important pH and carbonate contents — or overall the more important 972 $\log_{10}(a(CO_3^{2-}))$ value — is leading to the stabilisation of U(VI) as CaUO₂(CO₃)₃²⁻ complex 973 974 for Mol reference water.

One can also notice that in the PSI/NAGRA 12/07 database, the $UCO_3(OH)_3^-$ is added as a 975 976 "maximum feasible value for ternary hydroxide-carbonate complexes of U(IV)..." to 977 account for the influence of carbonate on the actinides(IV) oxides solubility (Thoenen et 978 al., 2014), based on a study of Hummel and Berner (2002). This species is usually minor 979 except for the most reductive potentials — i.e., BWS-A1 (Figure S5-5) and BWS-A2 (Figure 980 S5-6), where it is clearly the major species, and Äspö (Figure S5-8) to a lesser extent. 981 Further works are clearly needed to ascertain the influence of this species on the solubility 982 product of UO₂ phases.

Equivalent to Figure 7a, Figure S13-1 of the SI is showing the repartition of species vs. *p*e for the calculation using Minteq database. Uranium(IV) controls the speciation under the form of $U(OH)_5^-$ whatever the conditions, as ${}^{II}M_nUO_2(CO_3)_3^{(4-2n)-}$ are not implemented in the database. It is noteworthy that $U(OH)_5^-$ is not selected in NEA-OECD selection (Guillaumont et al., 2003).

988 The choice of the database can have here again a strong influence on the calculated
989 equilibrium concentration of uranium under the conditions of an underground storage,
990 or disposal, site of radioactive waste.



Figure 7. Evolution of the uranium species for the radioactive waste management waters using PRODATA 1.1.0.4 database and SIT ionic strength correction as a function of *p*e (a), and $\log_{10} \left(a(Ca^{2+}) \right)$ (b); and plot of the $\log_{10} \left(a(Ca^{2+}) \right)$ and $\log_{10} \left(a(CO_3^{2-}) \right)$ vs. *p*e (c).

995 3.3.4.2. Lac Saint-Clément, Bois Noirs U mine

In their recent publication, Stetten et al. (2018) estimated the speciation of uranium insolution of a lacustrine sediment near the former mine of Bois Noirs Limouzat (France).

998 The authors calculated the uranium speciation using JCHESS geochemical speciation code, 999 but without specifying the database used — the default chess database is guessed. No 1000 speciation result was given. The uranium speciation was driven by the Fe(II) amount in 1001 the water and no redox potential was reported. The authors estimated the U(IV) 1002 repartition assuming that either ningyoite $(CaU(PO_4)_2: 2H_2O)$ or amorphous UO_2 could 1003 precipitate. In the default CHESS database, the complexation constant of $U(OH)_4(aq)$ 1004 seems based on the Grenthe et al. (1992) analysis, and solubility of $UO_2(am)$ is different 1005 from Guillaumont et al. (2003).

For this exercise we performed the calculation using only PRODATA 1.1.0.4 database file. The obtained equilibrium redox potentials, as *p*e values, are those that can be calculated from the Fe³⁺/Fe²⁺ couple. As in section 3.3.3 (vide ante), the Ca_nUO₂(CO₃)⁽⁴⁻²ⁿ⁾⁻₃ complexes are dominant and are increasing with depth in Figure 8a, but more clearly with $a(Ca^{2+})$ in Figure 8b — Figure 8c is showing the different waters in the order of $a(Ca^{2+})$.

1011 The crossing point in Figure 6b and Figure S12-1a of the SI occurs here at slightly lower 1012 $a(Ca^{2+})$ because of the lower *p*e value — and the initial importance of $U(OH)_4(aq)$ —, 1013 which can be understood through the combination of $log_{10}(a(Ca^{2+}))$ and $log_{10}(a(CO_3^{2-}))$ 1014 vs. *p*e in Figure S13-2 of the SI, as in Figure 7c (cf. § 3.3.4.1).

1015 The saturation indices in Figure S13-3 of the SI are showing that the water compositions 1016 are close to saturation with either ningyoite or $UO_2(am)$ depending on depth. This is in 1017 agreement with the dominant U(IV) speciation revealed in the sediment analyses in 1018 Stetten et al. (2018).



1019Figure 8. Evolutions of the uranium speciation vs. depth (a), $log_{10}(a(Ca^{2+}))$ (b), and1020origin of the waters using the PRODATA 1.1.0.4 database file and SIT ionic strength1021correction in the order of calculated $a(Ca^{2+})$ (c) in the water compositions from1022the core C4 of a lacustrine sediment near the Bois Noirs U mine (in SI of Stetten et1023al., 2018).

1025 A recent work from von Gunten et al. (2018) reported speciation calculation in samples 1026 from meromictic lakes at the former Cluff Lake uranium mines (Saskatchewan, Canada). 1027 The authors performed their calculations using the Minteq database provided with 1028 PhreeqC proposing that in the D-pit lake, uranium was controlled by oxic chemistry, under 1029 the form of U(VI) from the lake surface down to 10 m depth, and was reduced to U(IV) at 1030 depth lower than 13 m. Using the output files form the calculation provided by the 1031 authors, the same calculations were performed with all databases. The representations in 1032 Figure 9 illustrate the results using PRODATA 1.1.0.4 (Figure 9a) and Minteq (Figure 9b) 1033 databases. The results obtained with Minteg database confirm the calculated reduction of 1034 uranium. Nevertheless, the results obtained using PRODATA 1.1.0.4 are showing a slightly different pattern. The $Ca_nUO_2(CO_3)_3^{(4-2n)-}$ complexes are calculated to be dominant from 1035 1036 the surface down to 13 m; only at 20 m depth do U(IV) is major in the form of the $U(OH)_4(aq)$ complex — and $U(OH)_3^+$ complex to a lesser extent. 1037

The evolution of calculated speciation results vs. $a(CO_3^{2-})$ on Figure S13-4 of the SI, shows 1038 1039 the influence of U(VI)/U(IV) ratio in these waters. It is also interesting to note that 1040 dissolved $CH_4(aq)$ is not implemented in the Minteq database, which implies a higher $a(CO_3^{2-})$ value compared to the calculation with other databases that do contain CH₄(aq). 1041 1042 The evolution of the SI for U(IV) containing phases (Figure S13-5 of the SI) is showing that 1043 even if the U(VI)/U(IV) limit in solution can be slightly moved down from 10 to 13 m 1044 considering Minteq or PRODATA 1.1.0.4, $UO_2(am)$ seems to be the controlling phase 1045 lower than 10 m in both cases.



b



- 1047 **Cluff Lake uranium mine (von Gunten et al., 2018) using PRODATA 1.1.0.4 database**
- 1048 file and SIT ionic strength correction (a) and Minteq (b) database file.
- 1049 3.3.4.4. Aquitard, South Saskatchewan
- 1050 The last example is the uranium speciation in a highly sulphated aquitard in south
- 1051 Saskatchewan (Canada) see Hendry and Wassenaar (2000) —, where the eventual

1052 association with natural organic matter was tested by Ranville et al. (2007). Theoretical 1053 calculation already confirmed that uranium was not associated significantly to natural 1054 organic matter (Reiller et al., 2012) under these conditions, but the ionic strength was not 1055 correctly accounted as high concentrations of Ca, Mg and sulphate were reported in these 1056 waters (Hendry and Wassenaar, 2000). Concentrations of carbonate and pH values also imply that the ${}^{II}M_nUO_2(CO_3)_3^{(4-2n)-}$ complexes — with ${}^{II}M^{2+}$ being either Mg²⁺ or Ca²⁺, 1057 and $n = \{0; 1; 2\}$ — control the uranium speciation instead of natural organic matter 1058 1059 (Reiller et al., 2012). Using the water composition from Hendry and Wassenaar (2000) 1060 and the uranium concentrations from Ranville et al. (2007), the repartition of uranium species as a function of depth is shown in Figure 10a for PRODATA 1.1.0.4 and Figure 10b 1061 for Minteq databases. Here again the particular importance of the ${}^{II}M_nUO_2(CO_3)_3^{(4-2n)-}$ 1062 complexes is clearly shown. A total reduction of U(VI), mainly as $UO_2(CO_3)_3^{4-}$, to U(IV) as 1063 $U(OH)_{5}$, is calculated at depth higher between 6 and 9 m using Minteq database 1064 1065 (Figure 10b), whereas uranium is calculated under U(VI) form at whatever depth (Figure 10a) using PRODATA 1.1.0.4. The speciation of the ${}^{II}M_nUO_2(CO_3)_3^{(4-2n)-}$ 1066 1067 complexes can be explained in two ways: (i) there is a variation in the ratio Mg/Ca vs. 1068 depth that can help understanding the decrease in $Ca_2UO_2(CO_3)_3(aq)$ proportion and increase of $CaUO_2(CO_3)_3^{2-}$ and $MgUO_2(CO_3)_3^{2-}$ (Figure 11a); (ii) there is a high variation 1069 1070 of calculated ionic strength from 1.41 mol kgw⁻¹ at 2.3 m, down to 0.07 mol kgw⁻¹ at 30.4 m 1071 (Figure 11b).



Figure 10. Comparisons of uranium species repartitions as a function of depth using
(a) PRODATA 1.1.0.4 database file and SIT ionic strength correction, and (b) Minteq
database file, in the case of a Canadian Aquitard (Hendry and Wassenaar, 2000;
Ranville et al., 2007).



Figure 11. Uranium species repartition vs. Mg/Ca ratio (a) and calculated ionic
strength (b) using PRODATA 1.1.0.4 database file and SIT ionic strength correction,
in the case of a Canadian Aquitard (Hendry and Wassenaar, 2000; Ranville et al.,
2007). Lines are guides to the eye.

1080 3.3.5. Effect of activity correction

1081 3.3.5.1. Impact of the choice of $log_{10}\beta^{\circ}(MgUO_2(CO_3)_3^{2-})$ and activity correction

1082 As seen in this exercise (vide supra), the impact of the choice for the complexation 1083 constant of MgUO₂(CO₃) $_3^{2-}$ can be somewhat important. As an illustration, the evolution of $\log_{10}\beta$ (MgUO₂(CO₃)²⁻) as a function of ionic strength (Figure S14-1 of the SI) implies 1084 1085 a relatively lower importance of the complex when using Dong and Brooks (2008) and the specific ion interaction parameter with Na⁺, i.e. ϵ (MgUO₂(CO₃)²⁻₃, Na⁺), than using the 1086 1087 value determined by Dong and Brooks (2006) and the Davies (1962) equation at $I_m < 0.4$ mol kg_w⁻¹; but the situation is inversed at $I_m > 0.4$ mol kg_w⁻¹. This explain partly both the 1088 evolution of MgUO₂(CO₃) $_3^{2-}$ proportion in radioactive waste management waters using 1089 1090 the PSI/NAGRA 12/07 database (c.f. § 3.3.4.1), and in the Canadian aquitard (c.f. § 3.3.4.4). It can also be evidenced that the ionic strength dependence of $\log_{10}\beta$ (MgUO₂(CO₃)²⁻) has 1091 1092 not received sufficient attention up to now.

1093 One can also remind that using the SIT defined in PhreeqC is implying that if the ε value 1094 of a complex relative to a counter ion is not given, then its value is considered nil. The 1095 calculation is not strictly equivalent to the calculation using the Davies (1962) equation 1096 — see Grenthe et al. (1997) for detailed analysis.

The implication of the alkali metals, which was suggested by the review from Guillaumont
et al. (2003), is also suspected from molecular dynamics study (Li et al., 2017). A
particular effort seems to be needed to tackle this particular point.

1101 In addition to the preceding examples, one can have a closer look to the results in Figure 1102 S10-1 of the SI. The already discussed differences induced by the account of the $^{II}M_{n}UO_{2}(CO_{3})_{3}^{(4-2n)-}$ complexes in the different database files is apparent here again. One 1103 can have a closer look at the differences between e.g., PRODATA 1.1.0.4 —formatted for 1104 1105 SIT formalisms — and Thermochimie 9b results, obtained using SIT, and the theoretical 1106 speciation proposed by Maloubier et al. (2015), where the choice of the activity correction 1107 is not clearly stated, and is guessed to be a simplified Debye-Hückel relation. Notwithstanding the fact that $MgUO_2(CO_3)_3^{2-}$ complex was not considered, the 1108 predominance of $Ca_2UO_2(CO_3)_3(aq)$ (ca. 70%) over $CaUO_2(CO_3)_3^{2-}$ (ca. 30%), and nearly 1109 inexistence of $UO_2(CO_3)_3^{4-}$, is not observed in our results using SIT, where 1110 $Ca_2UO_2(CO_3)_3(aq)$ and $CaUO_2(CO_3)_3^{2-}$ are mostly equal and $UO_2(CO_3)_3^{4-}$ is much more 1111 important — 19% if MgUO₂(CO₃)₃²⁻ is not considered (data not shown). One has to 1112 remind that using eq. 9, as no ε (CaUO₂(CO₃)²⁻₃, Na⁺) is given in the database, then it is 1113 1114 considered nil. Nevertheless, the results from Maloubier et al. (2015) are directly comparable with the proportions obtained using the database file dedicated to the Davies 1115 (1962) equation calculation — Prodata Davies in Figure S10-1 of the SI —, which 1116 1117 enlightens the need of an accurate determination of both the thermodynamic constants 1118 and SIT parameters. As no direct determination of these specific ion interaction parameters are existing for $Ca_n UO_2(CO_3)_3^{(4-2n)-}$ complexes, it is currently not possible to 1119 1120 propose a definitive answer on which case is closer to the reality. Further determinations and assessments of the constants and ε values are required. 1121

1122 This also clearly shows the importance of the choice of the activity correction model to1123 provide reliable speciation calculations for monitoring activities.

1124 3.3.6. Rationale on uranium results

1125 To cover the widest possible space of conditions relevant to mining and environmental monitoring activities, some water compositions are plotted in a $\log_{10}(a(SO_4^{2-}))$ vs. pH 1126 predominance plots at fixed total uranium, $-\log_{10}(P_{CO_2})$, i.e. pCO₂, $-\log_{10}([Ca]_{tot})$, i.e. 1127 1128 pCa, and $-\log_{10}([Mg]_{tot})$, i.e. pMg, constructed using PhreePlot (Figure 12). The choice of the values of pCO₂, pCa, and pMg are based on the analysis of the frequency of these 1129 parameters in waters that are showing $Ca_n UO_2(CO_3)_3^{(4-2n)-}$ as major complex (Figure 1130 S15-1 of the SI). In these plots, the $a(SO_4^{2-})$ value is fixed adding Na₂SO₄ to the solution. 1131 As some waters are oversaturated respective to calcite and dolomite, the precipitation of 1132 1133 these phases was not requested during calculation in agreement with the saturation 1134 indices (Figure S12-2 of the SI).

The waters that are showing predominantly the free ion UO_2^{2+} or $(UO_2)_2CO_3(OH)_3^-$ at low 1135 1136 total Ca and Mg, as major species are correctly represented. Concerning highly 1137 anthropized waters, as seen in Figure 3, the cations in these waters are more controlled by Ca^{2+} , Mg^{2+} , and H^+ , than by Na^+ and K^+ . Hence, the transition between $UO_2(SO_4)(aq)$ 1138 and $UO_2(SO_4)_2^{2-}$ is slightly overestimated, but the solutions are correctly represented in 1139 1140 every situation at the exception of DJX-pit 50 m at the higher calculated pCO₂. The water 1141 from the podzol (Crancon, 2001) is well represented in the two higher pCO_2 cases; the formation of $(UO_2)_2CO_3(OH)_3^-$ is impeded at the higher total Ca value. 1142

1143 Concerning the ${}^{II}M_{n}UO_{2}(CO_{3})_{3}^{(4-2n)-}$ complexes, CaUO₂(CO₃)₃²⁻ can only be represented 1144 in the second case (Figure 12b), with the exception of the Mol Reference Water, which is 1145 also well represented in the highest total Ca value. The Ca₂UO₂(CO₃)₃(aq) complex is well 1146 represented under the conditions of the highest total Ca value. The MgUO₂(CO₃)₃²⁻ 1147 complex only occurs at high calculated $a(SO_{4}^{2-})$ — at thus high ionic strength, see 1148 Figure 12c. This could be considered as a bias from the choice that has been made on the 1149 original data from Dong and Brooks (2008).

1150 The predominance domains of the ${}^{II}M_{n}UO_{2}(CO_{3})_{3}^{(4-2n)-}$ complexes can be modified when 1151 accounting for the oversaturation for calcite and dolomite. Figure S16-1 of the SI is clearly 1152 showing a narrowing of the $Ca_{n}UO_{2}(CO_{3})_{3}^{(4-2n)-}$ domains — the one of $MgUO_{2}(CO_{3})_{3}^{2-}$ 1153 complex is totally suppressed in the case of dolomite precipitation — calculation not 1154 shown.



Figure 12. Predominance plot of the uranium species in the $\log_{10} (a(SO_4^{2-}))$ vs. pH at fixed P_{CO_2} and total Ca and Mg: $[U]_{tot} = 1\mu mol \ kg_{w-1}$ using PRODATA 1.1.0.4 database file and SIT ionic strength correction. No precipitation of calcite or dolomite is requested during calculation.

1159 The representation is complemented by Figure 13 at fixed pH values and varying *pe*. 1160 Under low redox conditions, the plot of waters composition relevant of radioactive waste management are plotted in a $\log_{10}(a(Ca^{2+}))$ vs. *pe* predominance plot at fixed uranium 1161 concentration constructed using Phreeplot. The $a(Ca^{2+})$ are fixed adding CaCl₂. As shown 1162 1163 previously (Figure 7c and Figure S13-2 of the SI), at pH values ca. 7, $pCO_2 = 2.2$, high $a(Ca^{2+})$, and low pe values, the waters from Mont-Terri that are showing the 1164 predominance of $U(OH)_4(aq)$, and the waters where $Ca_2UO_2(CO_3)_3(aq)$ predominates, 1165 1166 are correctly represented. The water composition from Äspö, which is showing the highest $a(Ca^{2+})$ value and one of the four lowest E_h value, is also well represented. The 1167 water from the Mol site, which is showing a predominance of $CaUO_2(CO_3)_3^{2-}$, due to its 1168 relatively low $a(Ca^{2+})$ value and relatively high pCO₂ value, is correctly represented at pH 1169 = 8.5 and pCO_2 = 2.6 — the water from Tournemire TN2, which has a pH =7.7 is 1170 necessarily not represented correctly and is not shown. 1171



1172Figure 13. Predominance plots of the uranium species in the $\log_{10} (a(Ca^{2+}))$ vs. pe,1173at fixed pH — pH 7.1 plain line, and pH 8.5 dotted line — and P_{CO_2} and major species1174obtained in the calculation of selected waters for radioactive waste management1175using PRODATA 1.1.0.4 database file and SIT ionic strength correction: $[U]_{tot} = 1$ 1176nmol kgw⁻¹. No precipitation of calcite is requested during calculation.

1177 **4.** Conclusions and Perspectives

The use of the PhreeqC database output file from PRODATA 1.1.0.4 database has been shown to provide valuable information for the speciation of both radium and uranium in all the aspects of the monitoring of mining activities: from exploration to remediation. It has also been shown that PRODATA 1.1.0.4 can be applied largely outside of its development domain, from groundwaters — including aquifer and aquitard —, to stream waters, and finally to seawaters.

1184 The radium speciation is mainly controlled either by Ra^{2+} or $RaSO_4(aq)$ depending on the

1185 activity of dissolved sulphate, generated particularly by an ISR operation.

The $UO_2(SO_4)_n^{(2-2n)+}$ complexes have been shown to control the speciation in ISR-1186 impacted waters; the use of the ${}^{II}M_nUO_2(CO_3)_3^{(4-2n)-}$ complexes has been shown to be of 1187 particular importance in mildly acidic or alkaline carbonated waters. The thermodynamic 1188 1189 constants of these latter complexes are still under discussion as well as their evolution 1190 with ionic strength. It is of particular importance that these data will be determined with 1191 correct level of confidence as one can remind that these complexes are susceptible to 1192 control uranium speciation in seawater (Maloubier et al., 2015; Endrizzi et al., 2016; 1193 Beccia et al., 2017).

As the PRODATA database was though as a solution of the use of different database files to estimate a speciation or transport of uranium and radium in the particular contexts of mining and environmental monitoring. This necessarily induces the account for: (i) the major elements contained in the water of the particular site (e.g., Na, K, Ca, Mg, S, C, P...); (ii) the other elements that can be in direct competition with uranium or radium, or directly impact the chemistry of the site (e.g., Fe, Mn, V...); and (iii) the potential secondary contaminants eventually released (e.g., As, Pb, Zn, Cu, Ni...) as part of the ore treatment.

Out of these elements the particular examples of As, Zn, Cu, and Ni are particularly interesting. Significant differences exist between all the different databases for As(III) hydrolysis, As(V)-F(-I), As(V)-U(VI), and As(V)-Ca(II) species. Only Zn^{2+} , Cu⁺, and Cu²⁺ are implemented in the Thermochimie 9b database file. The Ni(CO₃)_n⁽²⁻²ⁿ⁾⁺ complexes are either not present in LLNL, or thermodynamic constants are very different in Minteq and Wateq4f database files compared to the others. It would then be likely to provide a similar exercise with a particular focus on the potential secondary contaminants
encountered in mining or environmental activities monitoring, as proposed otherwise(Katsoyiannis et al., 2007; Neiva et al., 2019).

1210 The PRODATA database is now a tool to perform speciation calculations with different 1211 speciation codes using the same body of thermodynamic data for the different elements 1212 that are relevant for the monitoring of exploration, exploitation, and finally remediation 1213 and environmental monitoring for the mining activities. It will evolve in the future as a 1214 function of new determination of constants in the literature, and new (or revised) data 1215 selection, e.g., as those currently under review in the TDB project of NEA-OECD. The next 1216 step is the use into reactive transport modelling, which requires the implementation of 1217 adsorption reactions for U and Ra — e.g. Waite et al. (1994), Murphy et al. (1999), 1218 Reinoso-Maset and Ly (2016), Robin et al. (2017), Sajih et al. (2014) —, and also for the 1219 other different elements and aqueous species — e.g. Dzombak and Morel (1990), Siroux 1220 et al. (2017), Siroux et al. (2018), Wissocq et al. (2018) — that can be in competition, 1221 based on the same constraint of traceability.

1222 **Declaration of conflict of interest**

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