Scientific Report on Research Stay at the ICIQ

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Introduction

Polyoxometalates (POMs) constitute a well-established family of molecular nanoclusters composed of transition metals in high oxidation states (Mo, W, V, Nb, Ta) and oxygen atoms. Since the discovery of the first POM more than two centuries ago, their chemistry has demonstrated remarkable versatility, with applications in catalysis, materials science, biomedicine and electronic devices.

Unlike other fields, such as organic synthesis where reactivity patterns are well-defined, the formation of POMs remains a challenge due to the complex influence of parameters such as pH, ionic strength, metal concentration and temperature. To address this complexity, computational approaches and automated methodologies have been developed in recent years, enabling the prediction of reaction mechanisms and speciation processes in solution.

At the ICIQ, the POMSimulator software has been developed as a tool capable of modelling and predicting aqueous speciation and reaction mechanisms of different families of polyoxometalates.

During my summer research stay at the ICIQ, I worked on a project focused on applying this methodology to the study of uranyl speciation in carbonate media, inspired by the article ***"Uranyl Speciation in Carbonate-Rich Hydrothermal Solutions: A Molecular Dynamics Study".*** The objective was to verify and extend the results presented in that paper, treating the uranyl-carbonate system as a heteropolyoxometalate using POMSimulator.

Objectives

To reproduce and validate speciation results for uranyl in carbonate solutions under different temperature conditions.

To adapt and apply the POMSimulator workflow to the specific case of the uranyl-carbonate system.

To identify limitations and technical issues in the modelling and scaling of formation constants.

Methodology

The work was developed in several stages:

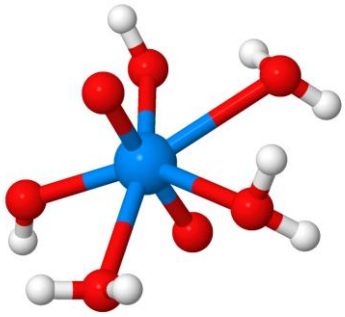
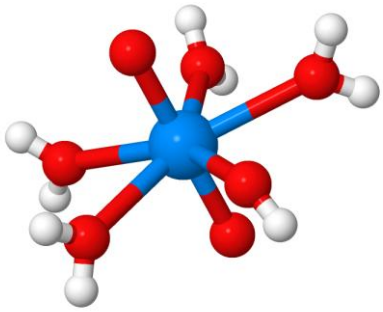
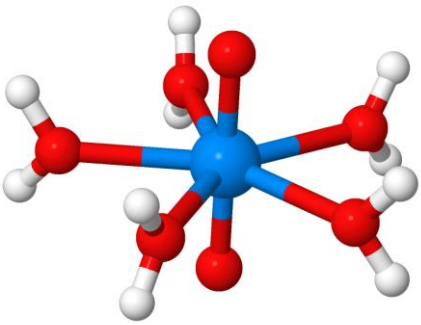
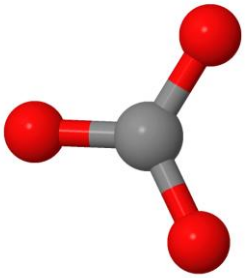
1. Preparation of initial species

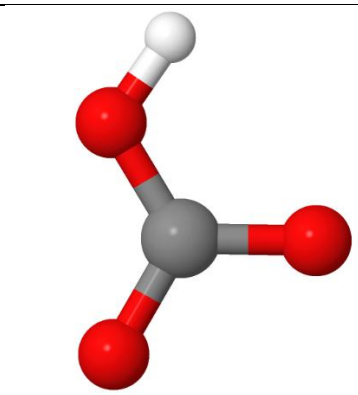
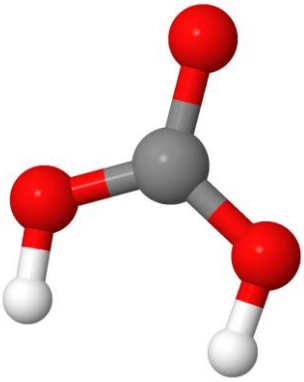
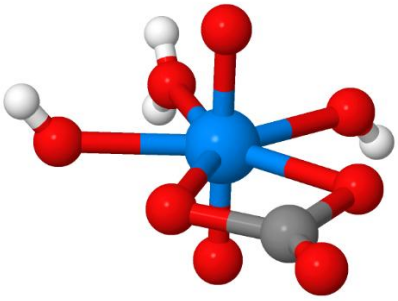
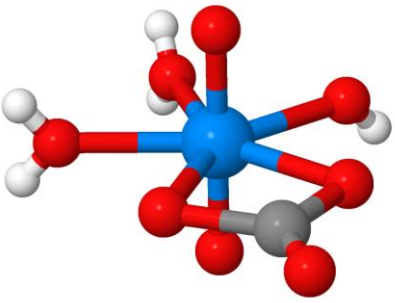
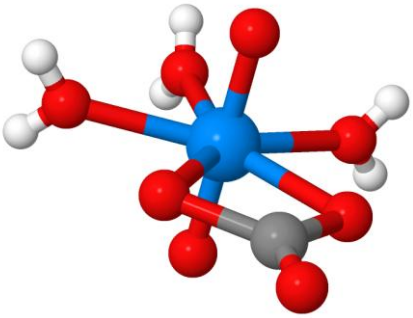
- Bibliographic review to identify the relevant chemical species of the uranyl-carbonate system, including potential intermediates.

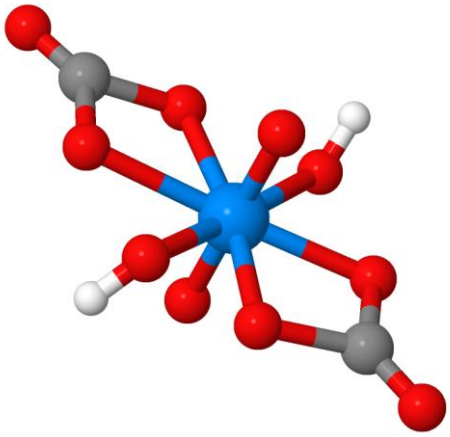
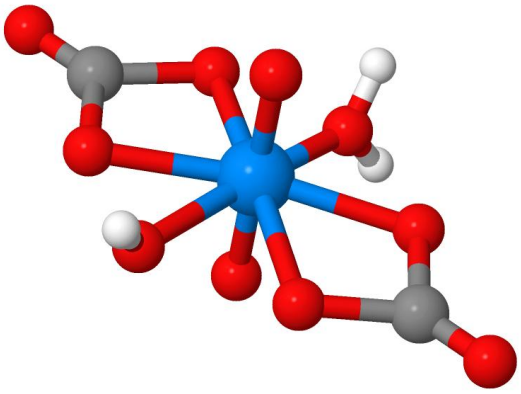
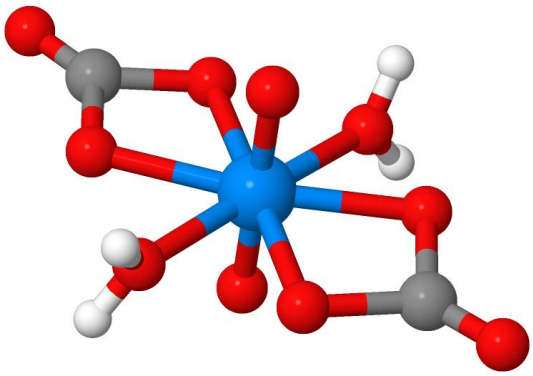
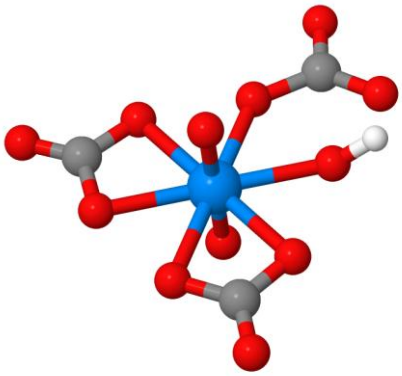
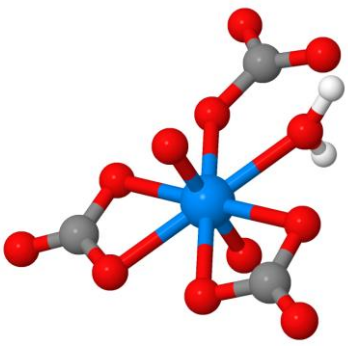
- Modelling of these species using *Amsterdam Density Functional (ADF)* to obtain initial geometries and energies.

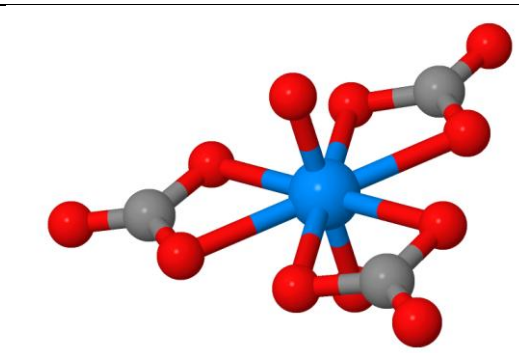
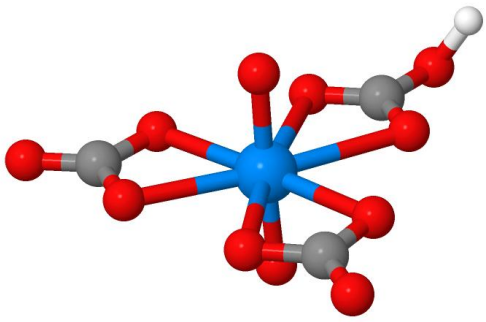
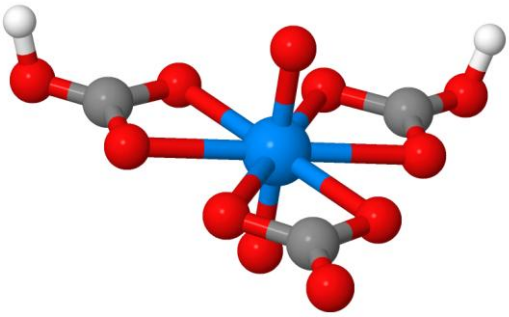
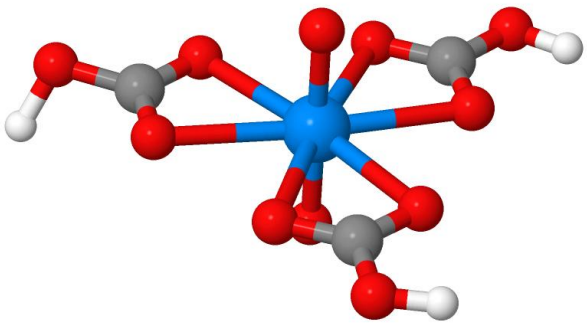
- Conversion of the results into .mol files using the script *generate_mol_file.py* from POMSimulator. These files were visually inspected to correct possible erroneous bonds generated automatically.

- Molecular set:

Name of the species	Name in POMsimulator	Image
$[H_8UO_7]$	C00U01O07-08H	
$[H_9UO_7]^+$	C00U01O07-09H	
$[H_{10}UO_7]^{2+}$	C00U01O07-10H	
$[CO_3]^{2-}$	C01U00O03-0H	

$[HCO_3]^-$	C01U00O03-1H	
$[H_2CO_3]$	C01U00O03-2H	
$[H_4CUO_8]^{2-}$	C01U01O08-4H	
$[H_5CUO_8]^-$	C01U01O08-5H	
$[H_6CUO_8]$	C01U01O08-6H	

$[H_2C_2UO_{10}]^{4-}$	C02U01O10-2H	
$[H_3C_2UO_{10}]^{3-}$	C02U01O10-3H	
$[H_4C_2UO_{10}]^{2-}$	C02U01O10-4H	
$[HC_3UO_{12}]^{5-}$	C03U01O12-1H	
$[H_2C_3UO_{12}]^{4-}$	C03U01O12-2H	

$[C_3UO_{11}]^{4-}$	**C03U01O11-0H**	
$[HC_3UO_{11}]^{3-}$	**C03U01O11-1H**	
$[H_2C_3UO_{11}]^{2-}$	**C03U01O11-2H**	
$[H_3C_3UO_{11}]^{-}$	**C03U01O11-3H**	

In order to enhance the present investigation, we propose considering a new compound, identified in POMsimulator with the label $[H_2C_2UO_9]$ OR C02U01O09-2H. This compound is hypothesized to act as an intermediate which, upon hydration, could be transformed into $[H_4C_2UO_{10}]^{2-}$.

2. Speciation simulation

- The script *simulation_hpa.py* was used to calculate the formation constants of each species.

- Main parameters:
    - *energy_threshold* > 33 (to include all possible reactions).
    - Maximum proton difference: 3.
    - Ionic strength: 0.6 M.
    - Initial temperature: 298.15 K.
    - Reference species: $[CO_3]^{2-}$ y $[H_8UO_7]$.

- The system generated approximately 1200 speciation models, a manageable number that allowed all configurations to be resolved.

- The results were stored in:
    - *logkf_C_U.csv* (formation constants).
    - *.txt files* with species labels and the reaction map (CRN).

3. Scaling of constants

The constants obtained were scaled using *scale_constants.py* through three approaches:

- **Universal scaling**: did not produce satisfactory results. (m= 0.29 and b=17.994)

- Scaling based on experimental databases (***Uranyl_thermochimie_v11a_2022***) and the **"average"** method produced acceptable but not perfect results. (m = 0.2559 and b = - 2.2876)

- **Best_rmse**: individual adjustment for each species, yielding the highest accuracy. (m=0.2850 and b= -3.6082)

4. Generation of speciation diagrams

- The script *hpa_speciation.py* was used to build the speciation system as a function of pH, producing files: *Array_C_U.npz* and *features_C_U.csv*.

- Subsequently, *SM_clusterization.py* was applied to obtain clustered diagrams of species, selecting those that best matched the experimental observations reported in the literature.

Results and discussion

The application of different scaling methods revealed notable differences in the quality of the results. Although *universal scaling* initially appeared to be the most promising approach, it ultimately failed to adequately reproduce the expected values. In contrast, scaling based on experimental databases provided more consistent and acceptable results *("average")*, though these outcomes still left room for improvement when compared against bibliographic references. The most robust method proved to be the species-specific adjustment based on the *best_rmse scale system*, as it yielded values much closer to the experimental data for each case studied.

Nevertheless, the process was not free of challenges. A critical limitation emerged when the carbonate-to-uranium ratio approached values close to 10:1. Under these conditions, the number of successfully generated models decreased significantly, and the chemical speciation became less stable, leading to inconsistencies that hindered further analysis.

To illustrate this issue, a series of progressive ratio adjustments were tested. Starting from a 1:1 ratio (carbonate: uranyl), the carbonate proportion was gradually increased to approximate a 10:1 relationship. The ratios analysed included 1:0.9, 1:0.8, 1:0.7, and so forth, down to 1:0.1. Representative results for selected ratios are presented below:

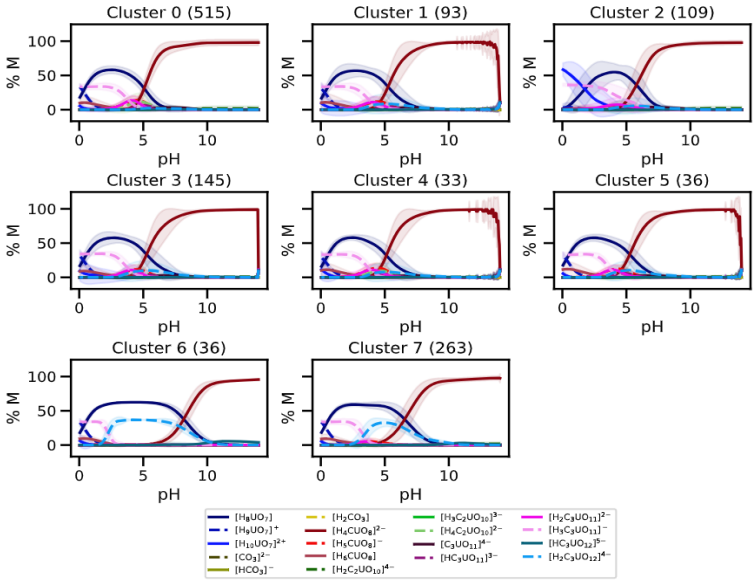


Figure 1: Speciation at 1:0.9 ratio – 1230 models generated.

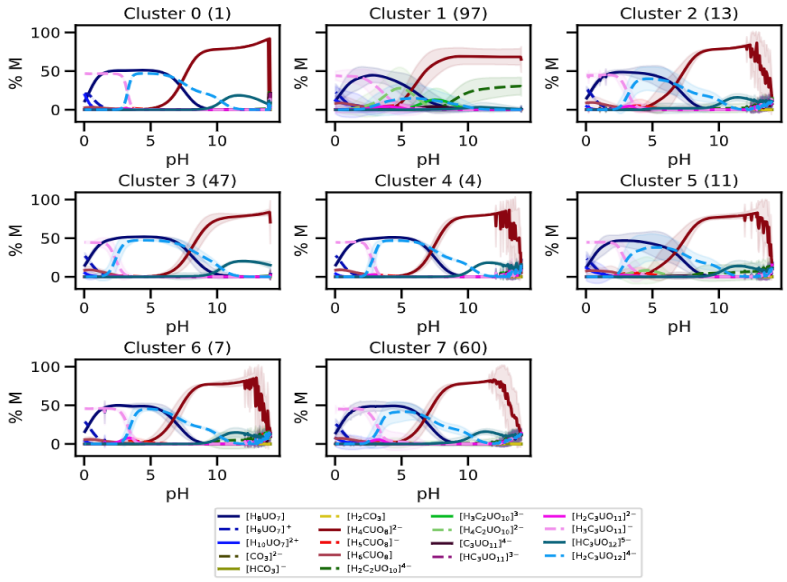


Figure 2: Speciation at 1:0.7 ratio – 240 correct models.

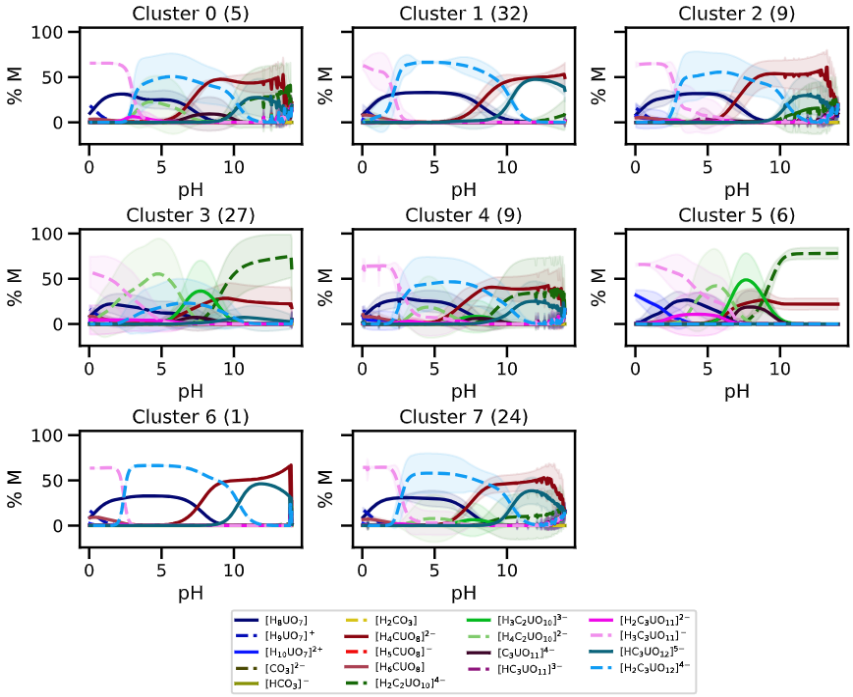


Figure 3: Speciation at 1:0.5 ratio – 113 correct models.

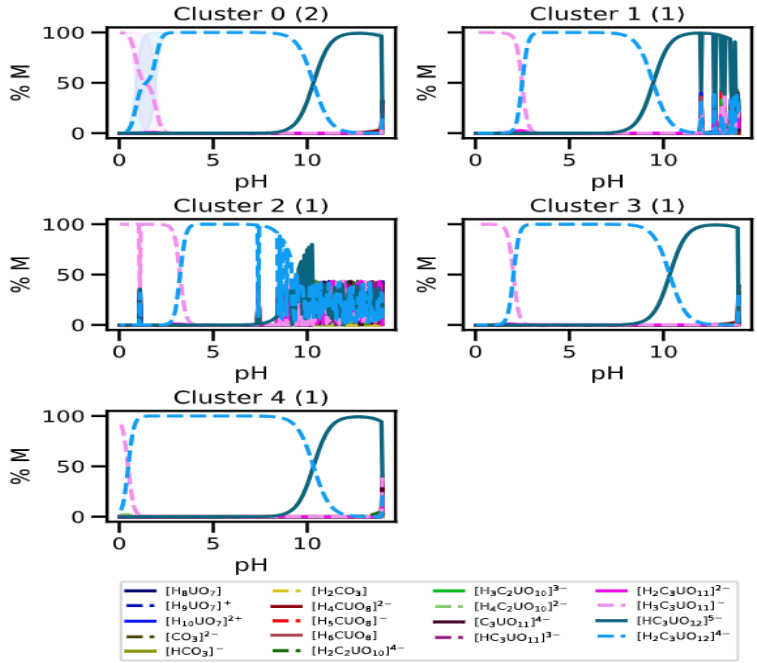
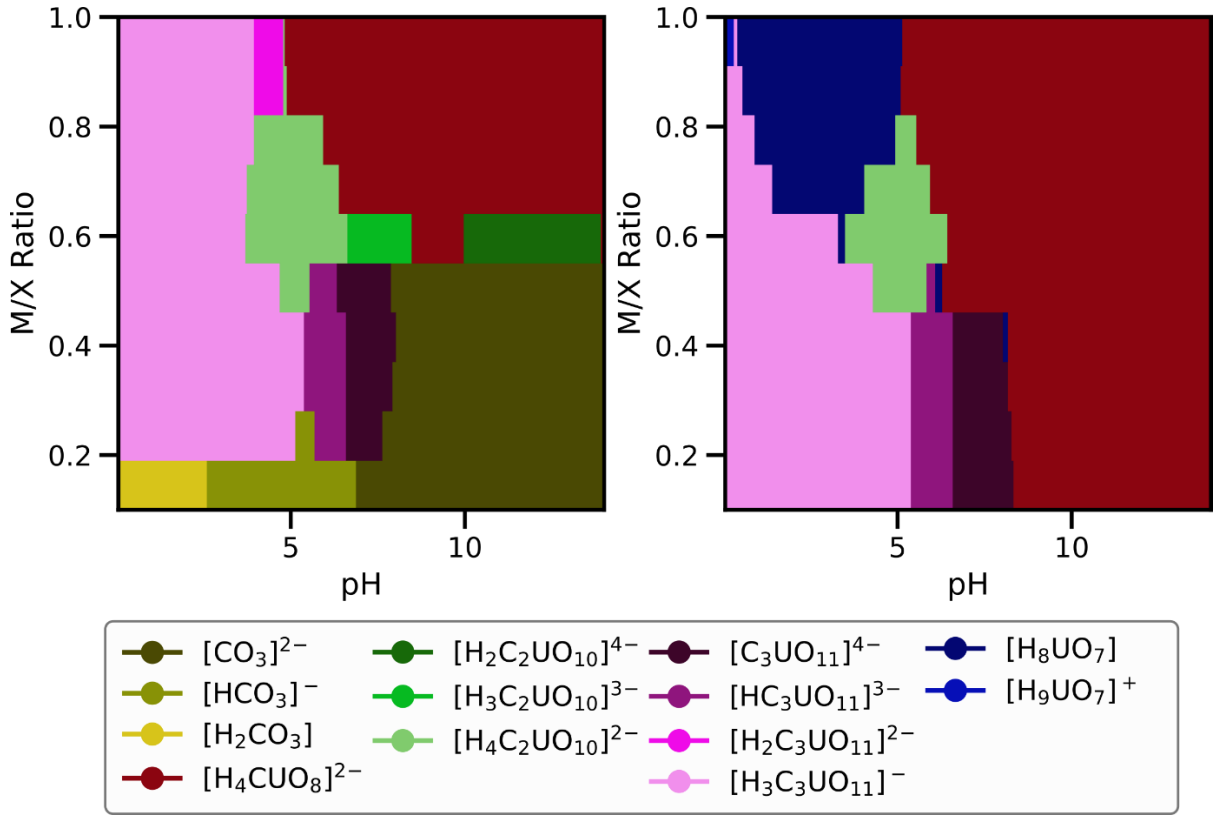


Figure 4: Speciation at 1:0.3 ratio – only 6 correct models.

At ratios below 1:0.3, no relevant information could be obtained, and therefore speciation plots for 1:0.2 or 1:0.1 were excluded. These results clearly show that as the carbonate-to-uranium ratio increases, the number of stable and valid models decreases drastically, compromising the reliability of the simulations.

And we can also plot a phase diagram to see the effect more generally:



Future research should focus on resolving this ratio-dependent instability. Once addressed, it will be possible to extend the analysis by generating speciation diagrams across the full range of temperatures considered in the study, thereby enabling a more comprehensive comparison and validation of the models.

Conclusions

The stay at ICIQ allowed me to go through the entire POMSimulator workflow, from the initial preparation of the species to the generation of speciation diagrams. The results show that the software is a powerful tool for studying complex systems such as uranyl-carbonate, while also highlighting the importance of proper scaling of formation constants. The best_rmse method was confirmed as the most effective strategy to achieve precise agreement with experimental data, whereas other approaches, such as universal or average, although useful as an initial approximation, did not reach the same level of accuracy.

In short, although a fully stable speciation diagram matching the reference article was not obtained, the work carried out provides a solid foundation for future research. This exercise not only allowed a partial reproduction of the speciation described in the literature, but also helped identify the limits and challenges of the method, particularly under high carbonate ratio conditions. The learning acquired during this process represents a valuable step toward improving the modelling of complex systems using POMSimulator.

And although this report is written as an almost last version of the work completed this summer, the research can still continue along the same line to achieve the expected results, by resolving the ratio issue and carrying out comparisons across different temperatures.

Acknowledgements

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References

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