



Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal:
<https://www.esrf.fr/misapps/SMISWebClient/protected/welcome.do>

Deadlines for submission of Experimental Reports

Experimental reports must be submitted within the period of 3 months after the end of the experiment.

Experiment Report supporting a new proposal (“relevant report”)

If you are submitting a proposal for a new project, or to continue a project for which you have previously been allocated beam time, you must submit a report on each of your previous measurement(s):

- even on those carried out close to the proposal submission deadline (it can be a “*preliminary report*”),
- even for experiments whose scientific area is different from the scientific area of the new proposal,
- carried out on CRG beamlines.

You must then register the report(s) as “relevant report(s)” in the new application form for beam time.

Deadlines for submitting a report supporting a new proposal

- 1st March Proposal Round - **5th March**
- 10th September Proposal Round - **13th September**

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report in English.
- include the experiment number to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

**Experiment title:**

Evolution of Insoluble Organic Matter during the differentiation of Titan and Ganymede

Experiment**number:**

HC-5066

Beamline:

ID15B

Date of experiment:

from: 26th October 2022 to: 30th October 2022

Date of report:1st March 2023**Shifts:**

12

Local contact(s):

Michael Hanfland (ID15B)

*Received at ESRF:***Names and affiliations of applicants (* indicates experimentalists):**

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Recent models and observations suggest that “primordial” organic matter (OM) could be a major compound of the refractory cores of the icy moons of the solar system, and by extension of water-rich exoplanets. Before the formation of the refractory cores of these worlds (i.e. during their accretion and differentiation), the OM would have been exposed to large amounts of liquid water at relatively high pressures and temperatures. Inside large icy moons like Ganymede and Titan, water-rich environments may have reached pressures of several GPa and temperatures of 500 K. Inside larger (warmer) water-rich exoplanets, temperatures may even have exceeded the critical point of water (647 K). The evolution of the OM at these PTX conditions remains largely unknown.

Consequently, we proposed to use *in situ* powder and single-crystal XRD, on anvil cell samples of OM and water at high pressure and temperature, to establish a comprehensive picture of the fate of OM during the formation of water-rich worlds. To conduct these experiments, we had gained access to analogues of primordial OM synthesized at the CRPG in Nancy. Our aim for these experiments was to determine 1) what chemical species are released during the thermal destabilization of the OM in presence of water, and 2) if (and at what temperature) the graphitization of the OM in the presence of water occurs. Our motivation to use XRD at the ESRF was 1) to circumvent the limitation of Raman spectroscopy (our standard diagnostic tool) due to the fluorescence of the OM in our samples, and 2) to determine the precise nature (formula and structure) of the precipitates formed after the reaction of the OM with water. Our experimental plan was as follow:

- load half-and-half mixtures of water and OM in DACs to reach GPa pressures (between 1 and 5 GPa);
- heat four DACs at the ESRF, on the beamline, step-by-step from 300 to 800 K, to monitor the progressive evolution of the water-OM samples through continuous XRD analyses;
- conduct XRD analyses on additional DACs we would bring to the ESRF, but with samples already reacted at 800 K in our lab in Nantes;
- explore the effects on the water-OM interactions, with our multiple DACs, of two OM compositions (N-rich or N-poor) and two gasket materials (steel or rhenium)

As noted in the *User Evaluation Form*, due to technical issues during our beamtime, we lacked the time to perform the intended step-by-step heating runs at the ESRF. However, we successfully heated one cell at the ESRF to the maximum target temperature (800 K), and were able to bring to the ESRF the intended additional cells with pre-reacted samples (also at 800 K). Consequently, while we were not able to explore the water-OM interactions below 800 K, we have otherwise fulfilled our initial goals by 1) exploring the intended water-OM

mixtures, 2) exploring the intended pressure range, 3) exploring the higher target temperature, 4) reacting each of the two OM (N-rich and N-poor) within both types of gaskets, and 5) using XRD to characterize the products of the water-OM interactions. The analysis of the XRD data has revealed the following:

- carbonates appear as the major species formed during our experiments; the cations associating with the CO₃ groups depend on the chemistry of the environment: steel gasket samples led to the formation of iron carbonate (FeCO₃) regardless of OM chemistry, while the N-rich sample with the rhenium gasket led to the formation of two new high-pressure polymorphs of ammonium bicarbonate (NH₄HCO₃) (these new structures are presented in Figure 1 below);
- iron oxydes (Fe₃O₄) appear from the reaction between the steel gasket and supercritical water;
- despite the temperatures reached, no crystalline carbon phase (e.g. graphite or diamond) was found;
- two additional (still unresolved) structures have been spotted in our samples (analysis is ongoing)

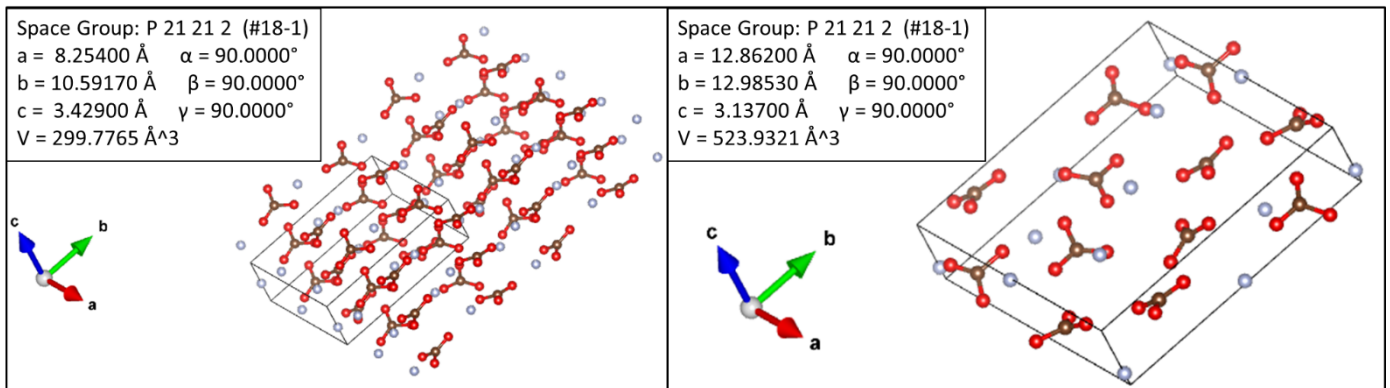


Figure 1 : New high-pressure polymorphs of ammonium bicarbonate identified in our samples.
(atom colors: carbon in brown, oxygen in red, and nitrogen in grey)

From a technical standpoint, these results illustrate the excellent adequacy of XRD to analyze our samples. Before coming to the ESRF, Raman analyses on our samples had revealed the occurrence of the CO₃ group, but the specific nature of these carbonates had remained elusive; furthermore, the opacity and strong fluorescence of the OM had prevented any other Raman determination. Thanks to the XRD analyses performed at the ESRF, we have now established 1) the nature of the forming carbonates, 2) the release of nitrogen by the OM (to form ammonium bicarbonate), 3) the critical importance of the choice of gasket for our experiments, and 4) the apparent absence of graphitization of the OM in presence of water despite the high temperatures reached.

From a scientific standpoint, these results bring precious constraints, and open interesting questions, in relation to our project dedicated to the evolution of OM in water-rich worlds:

- our results appear to preclude the formation of graphite from the OM in the refractory cores of the icy moons of the solar system, even at higher temperatures more relevant to their post-differentiation; this would support the recent planetary evolution models relying on the lower density of the OM (rather than the higher density of graphite) to explain the density and moment of inertia of these bodies;
- the thermal release of C and O from the OM leading to the seemingly systematic formation of carbonates offers an interesting pathway to explain the presence of carbonates on organics-rich primitive bodies showing signs of aqueous alteration, such as Ryugu (Yabuta *et al.*, 2023, doi:10.1126/science.abn9057), as well as on water-rich worlds, such as Enceladus (Postberg *et al.*, 2009, doi:10.1038/nature08046) and Ceres (De Sanctis *et al.*, 2016, doi:10.1038/nature18290);
- iron carbonates could be a major species resulting from the decomposition of the OM in the refractory cores where iron should be abundant

In view of the importance of these results for the thermo-chemical evolution of water-rich planetary bodies, we intend to publish this work in a high impact factor planetary science journal. We also think that the results from these experiments at 800 K, while conclusive for larger (warmer) water-rich worlds, raise the major question of the consequences of water-OM interactions at lower temperatures, particularly below the critical point of water (647 K), a temperature domain more relevant to the icy moons of the solar system. Consequently, we intend to propose a continuation of the current proposal to clarify 1) what the OM dissolution capabilities of subcritical water is, and 2) what precipitates may form from this interaction.