

PRELIMINARY RESULTS OF EXPLORING THE BEHAVIOUR OF PHYLLOSILICATES WHEN SUBJECT TO THERMAL CONDITIONS RELEVANT TO ASTEROID RYUGU. D. Hallatt^{1,2}, H. Leroux¹, and P. Roussel³, ¹Univ. Lille. CNRS, INRAE, Centrale Lille, UMR 8207 - UMET - Unité Matériaux et Transformations, F-59000 Lille, France, ²School of Physical Sciences, University of Kent, Canterbury, Kent, CT2 7NH, UK, ³Univ. Lille. CNRS, Centrale Lille, Univ. Artois, UMR 8181 - UCCS - Unité Catalyse et Chimie du Solide, F-59000 Lille, France (email: daniel.hallatt@univ-lille.fr).

Introduction: As the targets of JAXA's recently returned Hayabusa2 and NASA's ongoing OSIRIS-REx sample return missions respectively, the near-Earth, C-group asteroids Ryugu and Bennu present an extraordinary opportunity to materially expose the history of our Solar System and the evolution of the bodies that it has comprised. It is from these missions' consistent detections of a recognizable near-infrared (NIR) spectral signature (the $\sim 2.7 \mu\text{m}$ absorption band), that both asteroids' surfaces are predicted to consist of at least one phyllosilicate component, despite both being extremely dark and otherwise generally featureless [1, 2]. Across global and local scales, this phyllosilicate-like NIR absorption on Ryugu and Bennu has been reportedly widespread on the surface of both asteroids, and thus it is plausible that these familiar minerals could be present in the samples collected from either body.

Although such observations of phyllosilicates have not been unexpected (similar minerals have already been found on/from extraterrestrial bodies) their occurrence on small, near-Earth, carbonaceous asteroids may face particular attention. This is because such bodies are believed to have likely experienced a dynamical history, and are also, as their classification suggests, expected to contain carbonaceous materials in addition to the silicate minerals. It is from the balance of having been subject to a myriad of potentially material altering events while also being relative geologically inactive (being small and undifferentiated for example), that the use of hydrated silicates as messengers of past alteration may be particularly attractive for understanding the history of small asteroids such as Ryugu and Bennu.

This work, in particular, aims to report the preliminary efforts of a broad investigation (a doctoral thesis) that is based on questions concerning the effect that asteroidal impact has on the composition, structure, thermal behaviour, and detection of phyllosilicate structures related to Ryugu. Here focused on serpentine, this work will later be extended to similarly study saponite and *organic-infused* phyllosilicates, starting from a bulk investigation of their behaviour under relevant conditions, continuing with the use of a light-impact gun and pulsed laser shock experiments, and concluding with an attempt to formulate a functional

story of phyllosilicate behaviour from a multi-disciplinary suite of experimental techniques including electron microscopy, x-ray diffraction, spectroscopy, thermal analysis, and evolved gas analysis.

Conveniently, a presently developing story from Ryugu is concerned with the interpretation of phyllosilicate(s) role in explaining an apparent trend in both the strength and position of the asteroid's only reported absorption band [3, 4]. Consistent with a visible-wavelength spectral trend found between Ryugu's natural craters [3], it has been suggested from a trend in the asteroid's NIR signature near the artificial crater (where subsurface material was likely recently exposed/ejected) that there is/has been a surface-related phenomena that affects phyllosilicates in a way that changes their spectral absorption around $2.7 \mu\text{m}$. One of the suggested mechanisms for these spectral trends is the thermal decomposition of previously aqueously altered phyllosilicates, in particular from solar radiative heating [3, 4]. It is here where an early extension of our *impact-centric* thermal annealing work may be applied.

Methods: A reference, magnesium-rich serpentine, known as UB-N SARM, was used in its as-received powder state. UB-N is from Col des Bagenelles, France, and is reported to be structurally dominated by the lizardite polymorph [5]. For bulk analysis of its high-temperature behaviour, High-Temperature Powder X-ray Diffraction (HT-PXRD) was first performed. These XRD experiments employed a Bruker D8 Advance instrument operating with a Cu anode ($\lambda = 1.5418 \text{ \AA}$) in Bragg-Brentano geometry equipped with a Lynxeye XE 1D detector and an Anton Parr XRD 900 reactivity chamber. Using XRD allowed insights to be made into not only the serpentine phase-field with subsequent scans at points along a temperature ramp, but also the kinetics of specific phase transitions and the accuracy of ramped HT-PXRD by taking repeated scans at isothermal temperatures of interest. Each of the HT-PXRD temperature-ramp scans were performed between 9 to $64^\circ (2\theta)$ every 25°C from ambient to 850°C . Simultaneous ThermoGravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) (also known as STA) was also performed at conditions complementary of the HT-PXRD experiments. In this way, STA was also performed both isothermally and in

ramps between two temperatures informed by the HT-PXRD results. STA was performed using a Mettler-Toledo TGA/DSC 3+ instrument. In both the HT-PXRD and STA, a redox-controlling H_2/N_2 (3 vol.%) environment was usually used (along with an ambient control and a weak vacuum was also explored). Scanning electron microscopy and electron dispersive spectroscopy were also employed, to characterize the sample's morphology and composition respectively.

Results: The ramp HT-PXRD spectra summarized in the colour-clusters of Figure 1 identifies a potential thermal progression of UB-N serpentine while under H_2/N_2 . The most dominant change is observed around 600 °C (turquoise) where a few of the remaining lizardite peaks (e.g. $\sim 12^\circ$) are in brief coexistence with high-temperature peaks believed to be representative of forsterite (e.g. $\sim 25.3^\circ$ and 33°) before they mature (beige). Prior to this however, a presently unattributed peak at $\sim 44.5^\circ$ forms in accompaniment with the significant decay of most of the lizardite-interpreted peaks (e.g. $\sim 24.4^\circ$ and 60°) at $\sim 425^\circ\text{C}$ (green). From the level of calculated XRD background, Figure 1.c depicts evidence that a period of amorphization may start at the approximate onset of lizardite peak decomposition around 425 °C. At higher temperatures, the XRD background returns to a lower level, where recrystallization may be interpreted to be consistent with the maturation of high-temperature peaks from $\sim 775^\circ\text{C}$. Lastly, somewhere between 750 and 775 °C a distinct peak forms on the right shoulder of the forsterite-like $\sim 29.6^\circ$ peak, defining the (red) domain between 750 and 850 °C where this peak is only found before it disappears again before or at 850 °C.

The ramp STA performed under H_2/N_2 shows a progressive behaviour of lizardite as expected from previously reports, with three distinct stages of mass change up to 1000 °C [6]. The temperature of the first and third differential mass change (less than 600 °C and around 800 °C, respectively) is similar to literature, but the intermediate transition seems to occur at lower temperatures than reported under just N_2 [6]. At the end of these three processes, UB-N serpentine has lost $\sim 12\%$ of its mass, similar to that also recently reported [6].

Discussion: No STA signature is clearly associated with the unidentified $\sim 425^\circ\text{C}$ XRD precursor to lizardite decomposition. The temperature domain of such changes and the amorphization found in these preliminary results is noticeably similar to those previously proposed to be experienced from radiative heating on Ryugu [4]. Here may be an area to explore the possibility that the phyllosilicate trends seen on Ryugu may reside in the domain of amorphous complexity, inspiring further work to study the details of this realm under conditions relevant to Ryugu.

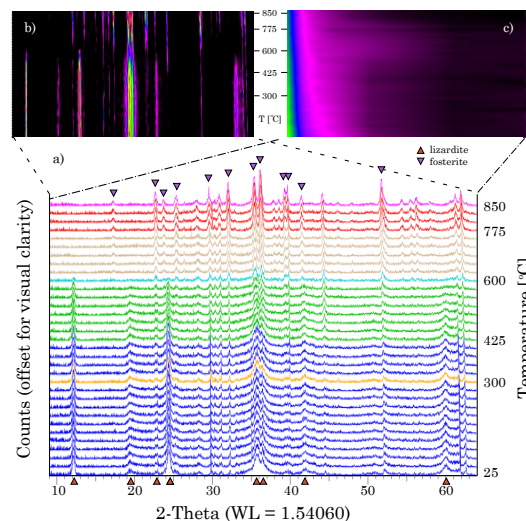


Figure 1. HT-PXRD patterns collected from UB-N serpentine heated under H_2/N_2 (3 vol.%) from 25 to 850 °C at 5°C min^{-1} . Individual plots are: a) the entire series of ($k\alpha_2$ subtracted) measured patterns, b) a peak intensity map in λ -T space of those patterns minus a calculated background, and c) a heatmap of the associated background.

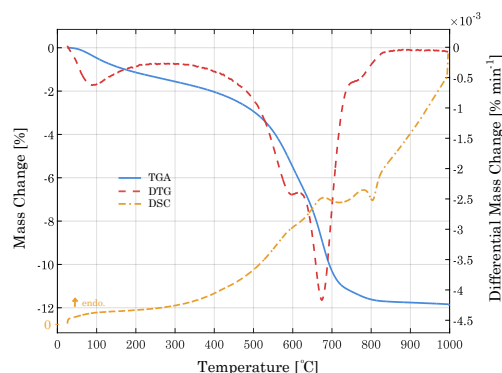


Figure 2. Simultaneous TGA/DSC thermal analysis of ~ 39 mg of UB-N serpentine heated under H_2/N_2 (3 vol.%) from 25 to 1000 °C at $10^\circ\text{C min}^{-1}$.

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