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Characterization of Heat-treated Clay Minerals in the Context of Nuclear Waste Disposal

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1) Overview

Clay minerals are likely candidates to aid in ***nuclear waste isolation*** due to their *low permeability*, *favorable swelling properties*, and *high cation sorption capacities*.

Establishing the thermal limit for clay minerals in a nuclear waste repository is a potentially important component of repository design, as flexibility of the heat load within the repository can have a major impact on the selection of repository design. For example, the thermal limit plays a critical role in the time that waste packages would need to cool before being transferred to the repository.

Understanding the *chemical* and *physical changes* that occur in clay minerals at various temperatures above the current thermal limit (of 100 °C) can enable decision-makers with information critical to evaluating the potential trade-offs of increasing the thermal limit within the repository.

Most critical is gaining understanding of how varying thermal conditions in the repository will impact *radionuclide sorption* and *transport* in clay materials either as engineered barriers or as disposal media.

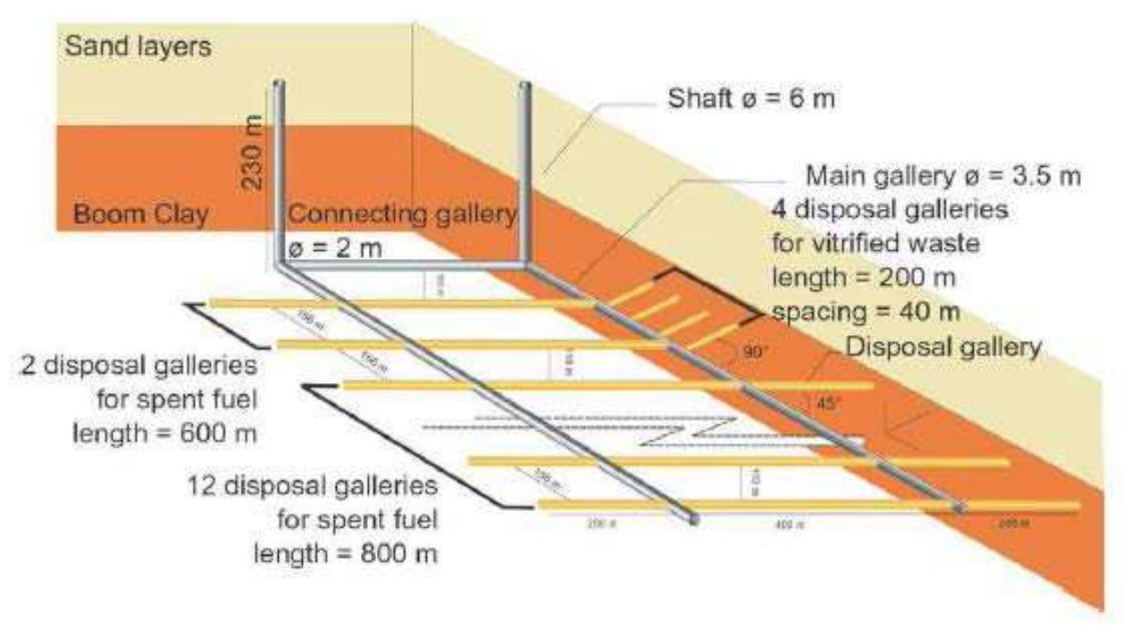


***Figure 1**. Nuclear Waste Repository design concept – Boom Clay*

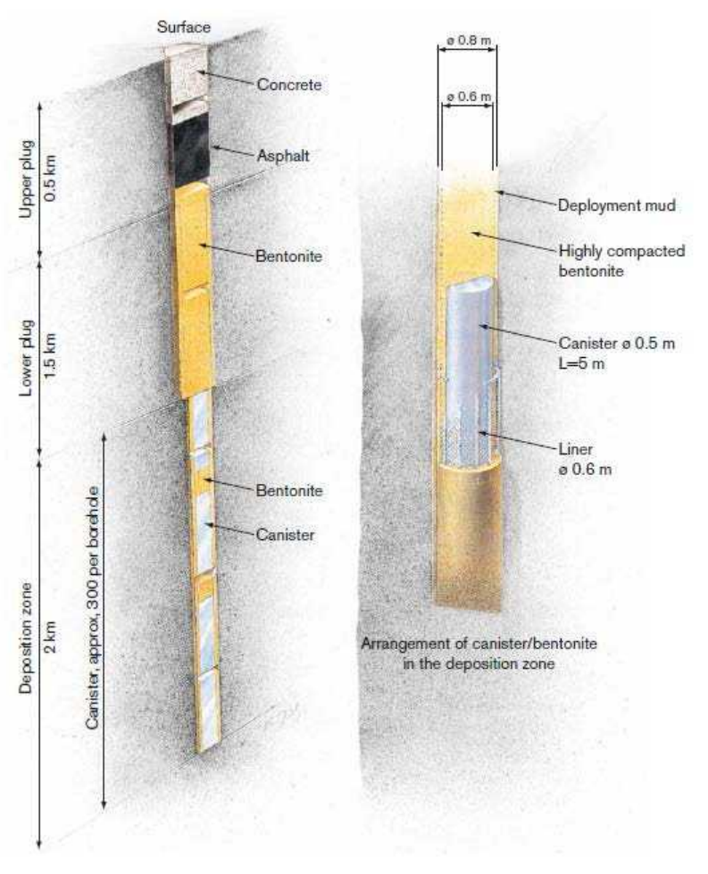


***Figure 2**. Nuclear Waste Repository design concept – Deep Borehole*

2) Sample Preparation

<u>Clay minerals and purification</u>

The clays used all originate from the Clay Mineral Society source clays project at Purdue University. Two clays were used:, illite, montmorillonite, palygorskite, sepiolite, and a 70/30 illite/smectite mixed layer (ID numbers: IMt-1, and SWy-2, respectively). The clays used were relatively pure. The main purification step used for all of the clays was mechanical separation at 75 microns. The <75 microns size fraction was used in all the experiments presented here.

<u>Heat Treatments</u>

For each clay, samples of the <75 micron size fraction were individually heated for 2 hours at 100 °C, 200 °C, 300 °C, 400 °C, and 500 °C. Samples were weighed before and after heat treatments to measure weight loss. Immediately after heat treatment, samples were treated one of two ways – 1) allowed to cool in the open environment of the furnace and 2) in closed environment of a dessicator.

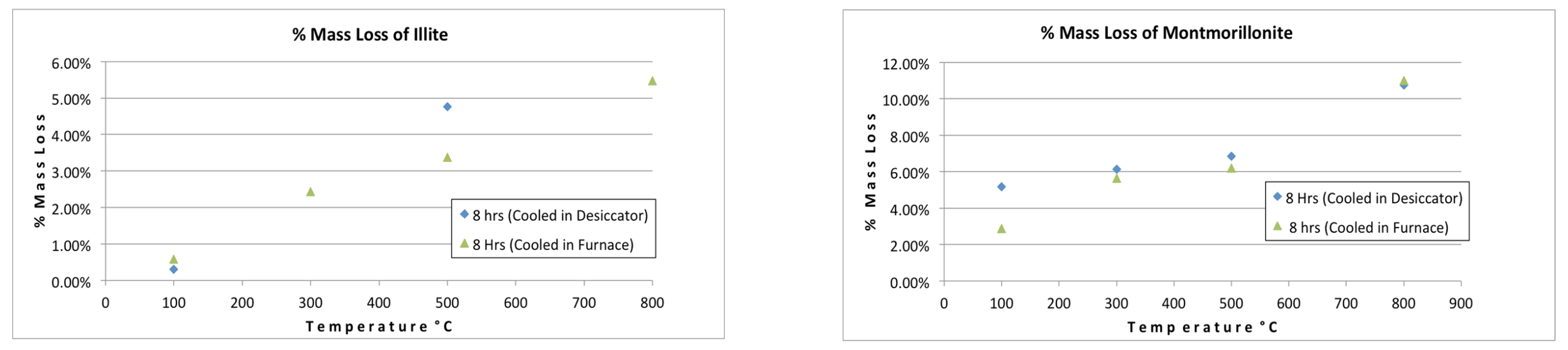


***Figure 3. Summary of Percent Mass Loss as a function of heat treatment temperature for Illite (left) and Montmorillonite (right).** Two cooling methods were tested and showed that the different cooling modes only produced a % mass loss difference on the order of a few percent.*

3) Results I – Surface Area Measurements

<u>Method</u> Nitrogen adsorption was performed on all heat treated clay minerals, as well as on untreated samples of each clay type to form a basis of comparison. Due to the heating involved in standard sample preparation protocols for NAD, none of these samples were heated and pumped under vacuum prior to NAD analysis. The Brunauer, Emmett, and Teller (BET) isotherm was used to determine surface area (herein referred to as "BET surface area").

It is recognized that the BET surface area provides a measurement of the the external surface area (particle-partcile) owing to the fact that the nitrogen does not penetrate the clay interlayer. The methylene blue method of measuring surface area, under circumneutral pH, provides a measure of the total surface area -- edge sites plus basal surfaces (Kahr and Madsen 1995). Internal surface area, then, can be calculated as the difference between the BET surface area and the methylene blue surface area.

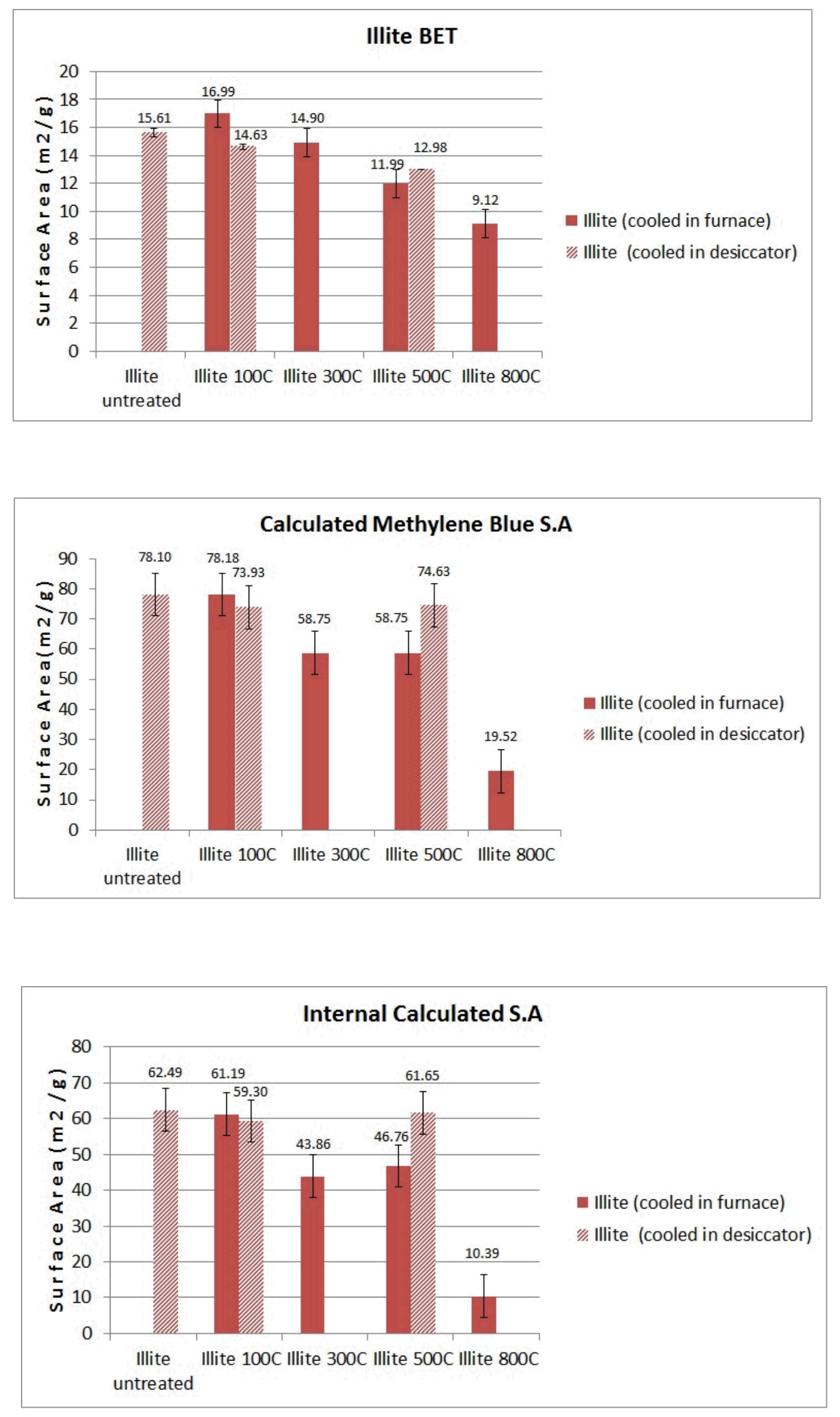


***Figure 4.** Surface area measurements for Illite.*

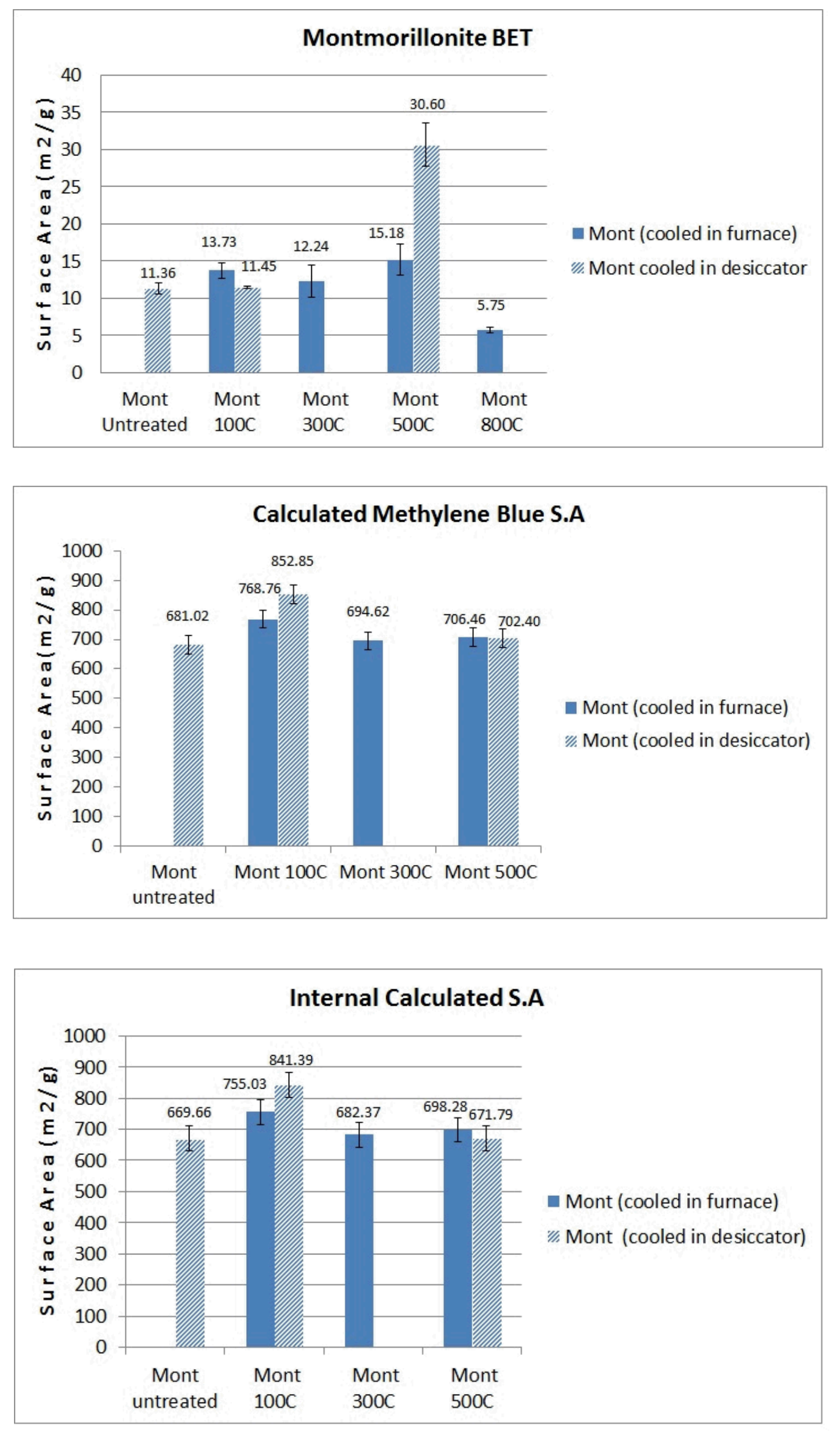
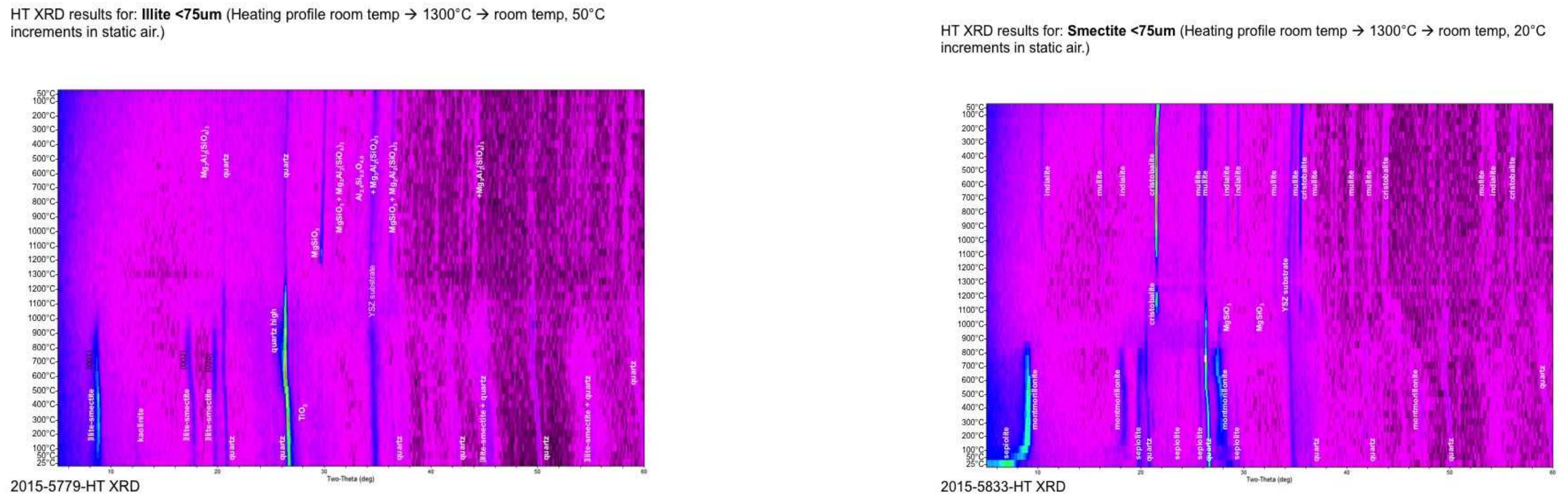


***Figure 5**. Surface area measurements for Montmorillonite.*

4) Results II – X-ray Diffraction (XRD) Measurements

<u>Method</u> X-ray diffraction (XRD) was performed on samples od ilite and montmorillonite. Samples were heated *in-situ*ˆ, such that XRD patterns could be acquired continuously as the samples was heated. The figures below present the XRD data as a function of temperature.


HT XRD results for: **Illite <75um** (Heating profile room temp → 1300°C → room temp, 50°C increments in static air.)

HT XRD results for: **Smectite <75um** (Heating profile room temp → 1300°C → room temp, 20°C increments in static air.)

Figure 5. XRD patterns for Illite (left) and Montmorillonite (right) as a function of temperature.. Transitions of clay minerals into quartzitic phases can be seen in the data.

5) Results III -- Cation Exchange Capacity Measurements

<u>Method</u> Cation Exchange Capacity was measured using the barium chloride method, as described by Gillman. Heat treated samples were weighed and 0.1M $BaCl_2$ solution was added at a solid to solution mass ratio of ~1:20. The suspension of clay and $BaCl_2$ solution was then shaken for 24 hours, centrifuged, and sampled (from the supernatant). After removing all of the supernatant for sampling, fresh $BaCl_2$ was added to the clay, which was again shaken, centrifuged, and sampled. This was repeated a third time – all 3 supernatant samples were collected cumulatively (i.e. sequentially added to a single sample collection vial) and analyzed on a Perkin Elmer 8000 series ICP-OES. Each clay sample was prepared and analyzed in triplicate.

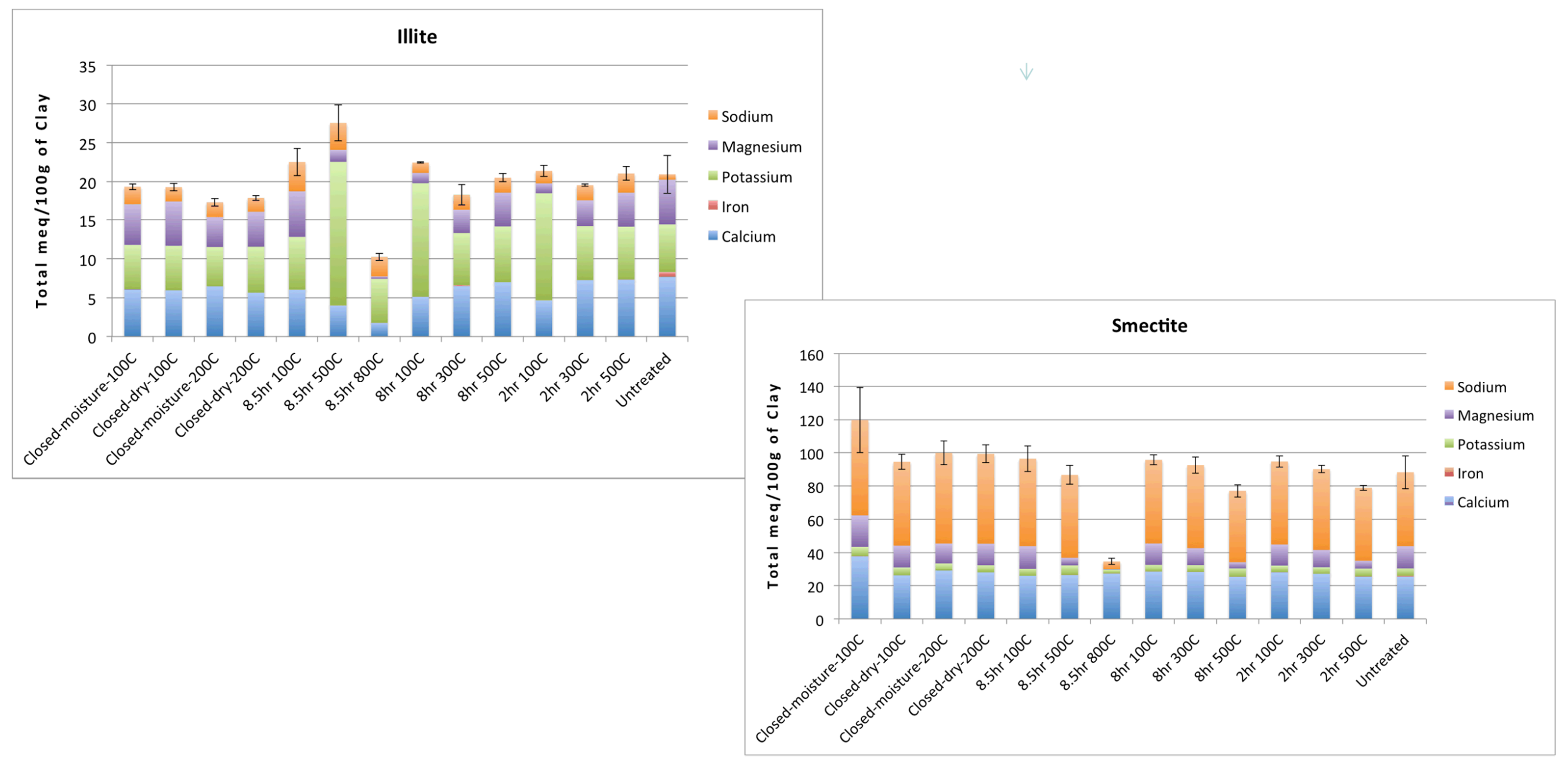


***Figure 5. Summary of CEC for Illite (left) and Montmorillonite (right) under various modes of heat treatment**.* These results show that CEC is not altered so long as the clay mineral assemblage remains intact. For example, the dramatic decreases in CEC for both clays correspond to a case where the all of the clay has been converted into quartz phases.

6) Conclusions and Future Work

Taken together, the surface area, CEC, and XRD results suggest that mineralogic alteration as a function of heat treatment will exert the greatest control on chemical and physical properties of both Illite and Smectite clays.

The most significant changes to both surface area and CEC coincided with significant changes in the mineralogic phase assemblage, i.e., CEC change is directly related to the amount of clay mineral converted to other silicate and aluminosilicate mineralogic phases (e.g., Quartz, mullite, etc.).

These conclusion suggests a future need to understand smectite to illite transition mechanisms under the relevant and/or likely repository conditions. In addition to temperature, availability of illitizing cations (such as potassium), pressure, and duration of heating are variables that must be better understood to predict how the permeability, swelling capacity, and sorption capacity of clay buffers may evolve under thermal loads in excess of 100 °C.

Future work should focus on understanding of illitization and cementation, as the two most likely and predominant mineralogic alteration pathways for buffer material. Diffusion, permeability, sorption capacity, and swelling measurements of clays altered as such will be important to accurately predicting evolution of buffer behavior under increased thermal load.

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