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***In-Situ* Angstrom-to-Micrometer Characterization of the Structural and Microstructural Changes in Kaolinite on Heating using Ultra-Small-Angle, Small-Angle, and Wide-Angle X-ray Scattering (USAXS/SAXS/WAXS)**

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Abstract

Synchrotron-based *in-operando* multi-scale X-ray scattering analyses are used to connect microstructural changes to phase changes in kaolinite on heating from 30 °C to 1150 °C. Combined ultra-small-angle and small-angle X-ray scattering (USAXS and SAXS) data are modeled to determine the hierarchical morphology of kaolinite comprising nano-scale interlayer pores, meso-scale pores, and larger interparticle voids, while wide-angle X-ray scattering (WAXS) data reveal the simultaneous evolution of molecular phases in kaolinite. We found that the transformation of kaolinite to metakaolin corresponds to the disappearance of nano-scale porosity, and the onset of sintered phases such as mullite consistent with the overall reduction in porosity. The emergence of nanoscale particulate features on heating above 900 °C corresponds to the onset of sintered phases such as spinel and mullite. This study illustrates the application of multi-scale X-ray scattering measurements to connect the thermally induced phase changes with changes in pore structure and fine morphology evolution.

TOC Graphic

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Supporting Information

- Figure S1. Changes in the characteristic mullite peak
- S2. Description of the scattering model for pore populations
- S3. Description of the interparticle interference effects for high-temperature nanoscale features

1. Introduction

Understanding the microstructural and structural changes in clays on heating enables us to develop efficient technologies for energy recovery from clay-rich subsurface environments,^{1–3} design effective barrier materials for long-term nuclear waste storage,⁴ engineer the sorption of radioactive⁵ and rare earth metals,⁶ and synthesize additives for construction materials.^{7,8} In particular, kaolinite, which has a 1:1 layered structure composed of alternating sheets of tetrahedral silicate and octahedral alumina groups, is a raw material for ceramics, porcelain, paper, coatings, rubber, plastics, fire-proof materials, chemicals, pesticides, medicines, textiles, petroleum, building materials, catalysts and catalyst supports.^{9,10}

While various studies have investigated the effect of heat treatment on the chemical composition and the morphology of kaolinite,^{11–22} to date there have been no *in-operando* investigations simultaneously linking the changes in the molecular structure with the microstructure of clays with the exception of Na- and Ca-montmorillonite.²³ In this study, we use multi-scale X-ray scattering measurements which encompass Ultra-Small-Angle, Small-Angle, and Wide-Angle X-ray Scattering (USAXS / SAXS/ WAXS)^{23,24} to connect the thermally induced phase changes in kaolinite with the microstructure. The information obtained from these measurements, which ranges from the micrometer scale down to the angstrom scale, is complementary to results from other microstructural measurements such as Brunauer–Emmett–Teller (BET) determinations of pore size and surface area, mercury intrusion porosimetry, particle size analysis, and electron microscopy measurements, while providing quantitative and statistically significant insights into the hierarchical morphologies of this technologically important material.

From a structural point of view, heating kaolinite from ambient temperature up to $150\text{ }^{\circ}\text{C}$ is accompanied by the removal of loosely bound water and nanoscale-confined interlayer water,²⁵ which does not significantly alter the interlayer basal distance or the structure, unlike in swelling clays such as Na-montmorillonite and Ca-montmorillonite.^{23,26} The transformation of kaolinite to metakaolin on heating in the range of $400\text{ }^{\circ}\text{C}$ to $700\text{ }^{\circ}\text{C}$ has

been extensively investigated.^{11,15–18,20,27–30} These studies suggest that metakaolin retains the pseudo-hexagonal morphology of kaolinite without the crystallinity. Pask and Tomsia (1991)³¹ showed that the formation of metastable spinel-type phases such as γ -alumina, and more stable phases such as mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) and cristobalite (SiO_2) on heating in excess of 900 °C is sensitive to the heating rate, presence of water vapor, and the purity of the kaolinite precursor.

The thermal treatment of kaolinite also produces significant morphological changes. Previous studies by Wang and co-workers (2011)¹¹ showed 25 % and 40 % increases in the cumulative BET pore volume on heating kaolinite to 700 °C and 1050 °C, respectively, relative to untreated kaolinite at ambient temperature. Using combined USAXS/SAXS analysis, the cumulative changes in the porosity can be quantitatively related to specific microscale or mesoscale pores. Another aspect to consider is the change in the hierarchical structure of the kaolinite on heating. While previous studies have suggested that the layered structure collapses on heating to 1050 °C,³² the precise changes in the mean interlayer basal distance can now be related to the structural and the microstructural changes using these multi-scale X-ray scattering measurements.

In this study, we relate the structural changes as kaolinite transforms to metakaolin, and higher temperature phases such as mullite, determined from the WAXS measurements to the changes in the porosity, and the nanoscale structure using combined USAXS/SAXS measurements. While previous studies have quantified porosities in shales^{33–37} and sandstones^{38–40} using Ultra-Small-Angle and Small-Angle Neutron or X-ray Scattering measurements, simultaneous *in-operando* measurements of the microstructural and structural changes in kaolinite have not been reported to date. Nevertheless, the methodology described in this study could be applied more generally to characterize a broad class of materials exhibiting hierarchical structures and microstructures.

2. Materials and Methods

Kaolinite (KGa-1b) procured from The Source Clays Repositories* (Purdue University, West Lafayette, IN) is ground to a particle size smaller than 75 μm , and compacted into pellets with a thickness of ≈ 0.5 mm using a manual press. The pelletized clay sample is heat-treated in a Linkam TS1500 heating stage (Linkam Scientific Instruments Ltd., Tadworth, UK). The starting and final temperatures are set to 30 °C and 1150 °C, respectively. The ramp rate is set to 2 °C/min where significant structural transitions are evident, and up to 4 °C/min where no obvious transitions are evident. The Linkam TS1500 stage is set up with the sample mounted vertically for the synchrotron beamline experiments. The heating stage allows the horizontal X-ray beam to enter through a small aperture before the sample and to exit through a range of scattering angles up to $\approx 25^\circ$ from the incident beam direction after the sample. While this arrangement is very suitable for the USAXS/SAXS/WAXS measurements, recent calibration measurements by some of the present authors suggest that, depending on the emissivity of the sample, thermal radiation losses may cause the actual

*Certain commercial materials, equipment and references are identified in this paper only to specify adequately experimental procedures. In no case does such identification imply recommendation by NIST nor does it imply that the material or equipment identified is necessarily the best available for this purpose.

sample temperature to be less than the nominal temperature when the stage is at the highest nominal temperatures of interest (1150 °C). The expected sequence of transformations was observed as the nominal temperature was raised to 1150 °C, but the possibility that the maximum temperatures reached may be lower than the nominal temperature set must be considered in interpreting some of the high-temperature results.

The multi-scale X-ray scattering experiments were performed at sector 9-ID at the Advanced Photon Source (APS), Argonne National Laboratory, Argonne, IL.^{41,42} Data collection was achieved in a repeated sequence of USAXS, SAXS, and WAXS. The data acquisition times for USAXS, SAXS and WAXS measurements were 90 s, 30 s, and 30 s, respectively. Since all three measurements were made over a relatively short time interval while maintaining the sample configuration in the beam path, uncertainties due to changes in sampling geometry between the measurements were eliminated. The beam size was defined by high-resolution X-ray slits, which were set to (0.8 × 0.8) mm for USAXS and (0.2 × 0.2) mm for SAXS and WAXS. This latter setting allows the detector pixel size, (172 × 172) μm for both the SAXS and WAXS detectors, to provide outgoing scattered or diffracted beam resolution comparable with those for the incident beam collimation and flux. The sample-to-detector distances for SAXS and WAXS are set to 547 mm and 181 mm, respectively. The total X-ray flux at the sample was 10¹³ photon mm⁻² s⁻¹. The q values (where $q = (4\pi/\lambda)\sin\theta$, λ , is the X-ray wavelength, and θ is half the scattering angle) and sample-to-detector distances (and geometry) were calibrated using silver behenate for SAXS and the NIST standard reference material, SRM 640d (Si)⁴³ for WAXS. The X-ray energy was 21.0 keV, corresponding to an X-ray wavelength of 0.589 Å.

The USAXS, SAXS and WAXS data collected were reduced and analyzed using the *Irena*⁴⁴ and *Nika*⁴⁵ software packages written in *Igor Pro* (Wavemetrics, Lake Oswego, OR). The USAXS measurement configuration is slit-smeared.⁴¹ In principle, these data can be desmeared and then merged with the appropriately sector-averaged pinhole SAXS data (where a 2D X-ray detector is used). In practice, numerical instability in the desmearing routine introduces unwanted noise into the USAXS data. It is better for model fitting purposes to slit-smear the sector-averaged pinhole SAXS data, merge these with the slit-smeared USAXS data, and fit to the combined slit-smeared USAXS/SAXS data. Standard deviation uncertainties in the reduced data are represented by vertical bars in the figures (where visible). Estimated or computed standard deviation uncertainties in our fit results are typically ± 5% of the value, unless indicated otherwise. The morphological features are imaged using a Tecnai T-12 Transmission Electron Microscope (FEI, OR).

3. Results and Discussion

3.1 Structural changes on heating kaolinite from ambient temperature to 1150 °C

Heating clays to temperatures up to 150 °C is associated with the removal of loosely bound or nanoscale-confined interlayer water.²⁵ In swelling clays such as Na-montmorillonite and Ca-montmorillonite, the removal of one layer of interlayer water causes the interlayer basal distance to be reduced by ≈ 3 Å on heating to temperatures in excess of 125 °C.^{23,46,47} However in kaolinite, the interlayer basal distance remains stable at 7.2 Å on heating to 650 °C (Figure 1 (a)). The reduction in the intensity of the peak that corresponds to the

interlayer basal spacing on heating in excess of 500 °C suggests a reduction in the number of interlayer nanopores (Figure 1 (b)). In this connection, we point out that kaolinite is not a swelling clay like montmorillonite. At room temperature and under ambient conditions, some water may initially exist in some of the nanoscale interlayer pore space, but this is insufficient to change the overall mean repeat distance of the interlayer basal spacing. Nevertheless, the presence of even a small amount of water makes the regularly-spaced interlayer pores reasonably well-defined with respect to the overall clay morphology. As the clay is heated significantly above 100 °C, this water is removed. While this does not significantly reduce the interlayer basal spacing (since this was not swollen in the first place), and the repeat distance remain unchanged, it is reasonable to assume that the loss of water causes some local collapse in the interlayer pores and a general loss of definition in the regular interlayer spacing. Thus, we see a reduction in the interlayer diffraction peak intensity associated with dehydration, even though the average basal spacing remains the same. Once water has been removed, the morphology remains remarkably unchanged up to 500 °C. Above 500 °C, as the dehydroxylation process progresses, the regular basal interlayer morphology is further disrupted, and the intensity of the basal interlayer diffraction peak disappears above 600 °C, even though the average basal repeat distance of the surviving layered structure does not change until the clay morphology is finally gone.

On the structural front, the dehydroxylation of kaolinite on heating in excess of 480 °C is evident from the reduced intensity of the characteristic kaolinite peak that corresponds to $q = 3.47 \text{ \AA}^{-1}$, $d = 1.81 \text{ \AA}$, or $\text{CuK}\alpha \ 2\theta = 50.2^\circ$ (h k l: $(-2 \ 2 \ 3)$)^{48–50} (Figure 2). Overall, the dehydroxylation of kaolinite in the range of 400 °C to 700 °C is consistent with the results of thermal gravimetric analysis (TGA) reported for the calcination of kaolinite.¹⁸ The reduced crystallinity of kaolinite on heating in excess of 500 °C (Figure 2) is also consistent with the formation of metakaolin.^{11,18,20,51,52} In this connection, the chemical transformation of kaolinite to metakaolin is represented by the following reaction:

WAXS (or XRD) analyses of kaolinite at ambient temperature showed that the kaolinite sample contains impurities of quartz (SiO_2) and anatase (TiO_2) (Figure 3) which is consistent with the XRD results reported for the kaolinite sample type, kGa-1B.⁵³ The formation of mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) on heating to a nominal 1150 °C is also noted. The use of *in operando* high-resolution synchrotron-based XRD to detect the onset and growth of such new phases as the temperature is increased complements the more common *ex situ* investigations of high-temperature structural transformations in kaolinite.^{14–16,18,20–22,28,31,52,54,55}

Various studies have provided conflicting observations of the formation of spinel-type phases such as γ -alumina, prior to or concurrent with the formation of more stable phases such as mullite.^{13,21,56–68} Pask and Tomsia (1991)³¹ have suggested that only the heating of kaolinite slowly over the course of days results in the consumption of the Al-O-Al linkages to form spinel. The free silica and spinel then react to form mullite (indirect mullite formation). Metakaolin subjected to relatively rapid heating rates, also accompanied by the

loss of water, as is the case here, results in the direct formation of mullite from the Al-O-Si linkages – bypassing the formation of spinel-type phases, altogether. In contrast, Lee, Kim & Moon (1999) suggest the formation of a discretely sized nanoscale spinel morphology as a result of heating rates to the order of 10 °C/min.⁴⁹

The possible formation of a distinct spinel-type phase with our experimental conditions where the heating rates are either 2 °C min⁻¹ (at temperatures where major transformations are expected) or 4 °C min⁻¹ (at temperatures where only incremental changes are expected) is discussed in relation to high-temperature changes in the USAXS/SAXS data below. The emergence of a characteristic mullite (orthorhombic) peak at $q = 1.87 \text{ \AA}^{-1}$, $d = 3.36 \text{ \AA}$, or $\text{CuK}\alpha \ 2\theta = 26.5^\circ$ (h k l: (2 1 0)) is evident as the nominal temperature is raised from 1000 °C to 1050 °C (Figure 4). Figure S1 provides further supportive evidence of the formation of mullite. This is consistent with other reported results.^{12,21,69,70} TEM analyses have suggested the growth of crystalline mullite features up to sizes in the range of 100 Å to 300 Å in scale.^{69,70} The formation of the crystalline silica phase known as cristobalite (SiO₂) is not observed in this study. This is consistent with previous studies that report the onset of this phase only on heating in excess of 1200 °C.¹² Thus, after the disappearance of the low-temperature crystalline silica phase (Figure 3), any silica phase present persists as an amorphous phase at least on heating up to a nominal 1150 °C. As we discuss below, these structural changes in kaolinite, measured by XRD peaks in the WAXS data, can be related to the microstructural changes on heating, as characterized in the USAXS and SAXS data.

3.2 Development of a representative microstructural model of kaolinite on heating from ambient temperature to 1150 °C

Determination and application of the appropriate scattering contrast factor, between the void and solid phases within the sample is essential for quantifying the microstructural changes in kaolinite on heating. It is a function of both the chemical composition and the density of the scattering features, and for X-rays is proportional to the squared difference in the electron density between the solid matrices and the void spaces. The thermo-chemical events that influence the scattering contrast factor are the dehydration of kaolinite on heating to 150 °C, the dehydroxylation of kaolinite on heating to 700 °C, and the formation of high temperature phases such as mullite. The composition of kaolinite on heating which is used to determine the appropriate contrast factors is based on the compositional phase diagram of kaolinite proposed by Pask and Tomsia (1991).³¹ The phase diagram that best represents our experiments is the specific case in which the water vapor is allowed to escape.³¹ The X-ray contrast factor between any two scattering phases is the squared difference between the X-ray scattering-length or form-factor densities within the two phases. The X-ray form-factor density is that for a single electron multiplied by the atomic electron density within a given phase. Obviously, if one phase is an empty pore the form-factor density is zero within that phase. The X-ray contrast factor associated with a given phase was determined here using the scattering contrast calculator in the *Irena* analysis package written in *Igor Pro*.⁴⁴ This algorithm conveniently calculates the form-factor density for a given phase using just the elemental composition and the skeletal mass density. The package also calculates the scattering contrast factors between any two phases as simply the squared difference in the

form-factor densities. Further explanation is provided in the Supporting Information, while the scattering contrast factors and the associated chemical changes are presented in Figure 5.

This contrast curve applies to the nanoscale pore populations where water can be assumed to fill the voids at ambient temperature, and is gradually lost as the temperature is increased to 150 °C. For coarse features, the voids are assumed to be empty and the scattering contrast for heating up to 150 °C is already assumed to be the higher value shown for 150 °C. For the discrete fine features that emerge at the highest temperatures studied, other contrast factors may apply as discussed below. The scattering contrast factors are incorporated into model fits to the absolutely calibrated combined USAXS/SAXS intensity data to provide absolute volume fraction and surface area information for the various scattering features modeled. This volume fraction and surface area information, together with the mean size and shape of the scattering features (and where relevant their size distribution) extracted from the model fitting provide the means to quantitatively follow the changes in the hierarchical morphology of kaolinite on heating.

Figure 6 presents combined slit-smeared USAXS/SAXS data as a function of temperature from ambient temperature up to a nominal 1150 °C. The data show that heating to 1150 °C does not produce significant microstructural changes in kaolinite for spatial scales, $2R$, associated with $q < 0.04 \text{ \AA}^{-1}$ (Figure 6 (a–d)), or $2R > \approx 50 \text{ \AA}$ ($qR \approx 1$ for small-angle scattering). This is not the case for finer spatial scales associated with $q > 0.05 \text{ \AA}^{-1}$. On heating from 300 °C to 700 °C, the disappearance of the peak that corresponds to the interlayer basal distance is already noted. In this connection, it is important to note that this is not a diffraction peak in the usual sense of lattice planes that are crystallographically aligned. Instead, it is a small-angle diffraction peak associated with a regular repeat distance of very fine planar interlayer voids.

The disappearance of the small-angle diffraction peak is attributed to the closing up or loss by sintering of these interlayer void spaces, resulting in a loss of the regular interlayer pore basal spacing throughout an increasing amount of the sample volume; it is this that provides the peak intensity. Further heating from 700 °C to 1000 °C yields subtle changes in the high- q SAXS regime. Heating in excess of 1000 °C is accompanied by the onset of a discrete population of nanoscale features of well-defined size (Figure 6(d)). As heating continues, the increase in volume fraction (number density) initially without significant change in size is noted before the onset of a growth regime at the highest nominal temperatures (Figure 6 (d)). While the average contrast factor for the scattering features at high temperature is given in Figure 5, the discrete features formed, almost certainly comprise one phase – either mullite or possibly spinel. This is discussed further below.

In a previous study we modeled the hierarchical morphologies of Na-montmorillonite and Ca-montmorillonite²³ in terms of four distinct feature size populations. These corresponded to the fine interlayer pores, nanoscale porosity, mesoscale porosity, and coarser void spaces in the pressed powder pellets that mimic the clay particle size distribution. For ambient and lower nominal heating temperatures, we were able to extend this basic approach to the present heating study of kaolinite.

For kaolinite at ambient temperature, the first population is attributed to the nano-scale porosity. The removal of any confined pore water is assumed to occur linearly on heating to 150 °C which results in a variable contrast factor in this heating range. The starting scattering contrast (the square of the difference in the X-ray scattering-length density, or form-factor density, of the solid with respect to water) of kaolinite assuming a solid–water interface is determined to be $164.0 \times 10^{28} \text{ m}^{-4}$. The fraction of the pore interface filled with interlayer or loosely bound water is assumed to linearly decrease from 100 % at an ambient temperature down to 0 % at 150 °C. Therefore, the scattering contrast for the nanoscale pores in kaolinite is assumed to increase over this temperature range to become that for kaolinite with an air interface at 150 °C. This contrast factor, determined from the contrast calculator in the *Irena* analysis package discussed above is $494.0 \times 10^{28} \text{ m}^{-4}$. As indicated above, coarse pores should be assumed to be air-filled even at ambient temperature, and the contrast factor is assumed to be $494.0 \times 10^{28} \text{ m}^{-4}$ from the start of heating to 150 °C.

For all pores, at temperatures above 150 °C, the onset of dehydroxylation of kaolinite to form metakaolin is gradual before becoming more rapid on heating in excess of 500 °C. The compositional variation of metakaolin mixed with kaolinite has been deduced, based on our observations from published TGA data and our results reported in Figure 2(b). Kaolinite had completely transformed to metakaolin on reaching 680 °C. The scattering contrast factor for pure metakaolin is $441 \times 10^{28} \text{ m}^{-4}$. The scattering contrast factor for metakaolin then remained unchanged in the heating range from 700 °C to 970 °C. The phase diagram proposed by Pask and Tomsia (1991)³¹ was used in conjunction with our observations of mullite formation on heating above 1000 °C to derive average contrast factors on heating from 1000 °C to 1150 °C (Figure 5). The detailed microstructural features deduced by incorporating these contrast factors into our models fitted to the combined USAXS/SAXS data are discussed in the following section.

3.3 Microstructural changes in kaolinite on heating from ambient temperature to 1150 °C

The hierarchical morphology of kaolinite at ambient and intermediate annealing temperatures is explicitly modeled based on four model pore populations and is fitted to the experimental data directly. This modeling approach differs from the entropy maximization approach⁷¹ which was used to model the hierarchical pore morphology in Na- and Ca-montmorillonite.²³ The entropy maximization approach is not applied to kaolinite because the discrete fine features that manifest themselves in the scattering at high q in the upper temperature regime are not mathematically well-conditioned for entropy-based characterization. Furthermore, the fine features, themselves, do not appear to be voids, yet their scattering masks that from the finest void population.

Following on from the basic pore morphologies found in Na- and Ca-montmorillonite²³, the four populations used to describe the morphology of kaolinite are as follows. Population 1 is a nanoscale population of oblate pores (mean oblate diameter $\approx 30 \text{ \AA}$) having a Gaussian size distribution. This population represents the interlayer pores in the kaolinite. Population 2 is assumed to be a population of slightly larger nanoscale pores (also oblate in character) with a lognormal size distribution and mean oblate diameters typically in the $500 \text{ \AA}$ to $600 \text{ \AA}$ range. These are assumed to comprise the gaps between individual clay stacks. Population 3

represents coarser oblate mesoscale voids between larger stacks of clay particles. These are also assumed to have a lognormal size distribution and have a mean oblate diameter close to $\approx 3000 \text{ \AA}$. Population 4 comprises the coarsest population of oblate voids, and the oblate diameter distribution is assumed to approximate the clay powder grain size distribution. These are the residual void spaces that persist after pressing the crushed kaolinite powder into a pellet. These voids have a broad size distribution with a mean oblate diameter in the $2 \text{ }\mu\text{m}$ to $3 \text{ }\mu\text{m}$ regime, somewhat coarser than for montmorillonite. While it should be noted that the small-angle scattering profile can be reproduced for spheroidal features of almost any aspect ratio with an appropriately adjusted size distribution⁴³, there is ample independent evidence that the pore and void populations in clay systems are planar or lamellar in nature, especially within pressed powder pellets as studied here.²³ Furthermore, for the reasonably discrete (and sometimes narrow) size distributions identified in either montmorillonite or kaolinite, somewhat better fits to the data are obtained on assuming oblate shapes than when assuming either spherical or prolate shapes (also see the supporting information). Figure 7(a) shows that the oblate microstructure is an approximation of the platelet morphology in kaolinite. Another microstructural feature that is observed in TEM and modeled in this study is the growth of crystalline mullite features in an amorphous alumino-silicate matrix on heating kaolinite above $1000 \text{ }^\circ\text{C}$ as shown in Figure 7(b). The observed crystalline features are smaller than 100 nm which is consistent with previously reported studies of mullite growth.^{70,71} These microstructures of kaolinite observed in real space are quantified from the combined USAXS/SAXS measurements.

Figure 8 (a) presents combined USAXS/SAXS data for kaolinite at ambient temperature ($30 \text{ }^\circ\text{C}$), together with a fit using the 4-population model. (Although the small-angle diffraction peak associated with the interlayer basal spacing is included in these data, the microstructural model fit, itself, does not extend to a maximum q sufficient to include it.) Figure 8 (b) presents the actual void size distributions modeled and fitted to the USAXS/WAXS data, with the 4 void populations identified. Figure 9 presents the temperature variations of the various void parameters of interest. Referring to Figure 9, parameters for population 1 are only given for temperatures up to $443 \text{ }^\circ\text{C}$, because the associated scattering is masked at higher temperatures by the emergence of the discrete fine features. With a working assumption, aspect ratio = 0.2, the oblate diameter found of $30 \text{ \AA}$ or less corresponds to a mean opening dimension of $4 \text{ \AA}$ or less.

Even at the lowest temperatures, the volume fraction (porosity) associated with population 1 remains below 0.003, significantly less than found in montmorillonite,²³ and the surface area is also correspondingly low, never dominating the overall total surface area (Figure 9(c)). We assume that population 1 pores persist to higher temperatures, even though the associated scattering is masked by other fine features (discussed below). However, the intensity of the small-angle diffraction peak at $q \approx 0.88 \text{ \AA}^{-1}$, associated with the regular inter-lamellar pore basal spacing, vanishes for temperatures above $680 \text{ }^\circ\text{C}$. Since the diffraction contrast for this peak comes exclusively from the approximately parallel and regularly-spaced inter-lamellar pores, we conclude that the population 1 porosity must diminish to a negligible level once the temperature is above $680 \text{ }^\circ\text{C}$.

The characteristics of the remaining 3 pore populations (2, 3, 4) can be followed to the highest annealing temperatures studied, as presented in Figure 9. The population 2 pores are also assumed to have an oblate aspect ratio of 0.2 for modeling purposes. Over much of the temperature range, they have an oblate pore diameter between 500 Å and 600 Å, although there is a more complex variation, shown in Figure 9 (a), for temperatures above 900 °C – almost certainly due to the phase transformations encountered in kaolinite. The population 2 volume fraction decreases from ≈ 0.03 at ambient temperature to 0.003 at 1000 °C. These transformations correspond to the onset of mullite phase (Figure 4). The surface area of population 2 follows a similar trend but is more erratic. Above 900 °C, and more so above 1000 °C, a more complex behavior is observed, and the population 2 pores becomes less oblate, necessitating an aspect ratio = 0.333 as a working assumption, rather than 0.2. The structural changes in kaolinite have a more significant impact on void fractions corresponding to populations 1 and 2 than on populations 3 and 4.

Population 3 comprises a remarkably constant void population having a mean oblate diameter ≈ 3000 Å (aspect ratio = 0.2) from ambient temperatures up to the highest annealing temperatures studied. The volume fraction actually increases slightly from under 0.09 at ambient temperature to nearly 0.1 at 900 °C, thereafter decreasing to less than 0.06 at a nominal 1150 °C, probably associated with sintering effects at high temperature. This trend is also supported by a marked decrease in the population 3 surface area above 1000 °C (Figure 9 (c)). Population 4 comprises a broad distribution of oblate coarse features (aspect ratio = 0.2 up to 850 °C, then 0.1 at higher temperatures) with oblate diameters in the several micrometers regime, and even coarser at the highest temperatures studied. The porosity is ≈ 0.05 over much of the range but then increases to match the porosity of population 3 above 900 °C, decreasing as for population 3 at higher temperatures. The population 4 surface area increases significantly at ≈ 1000 °C, then decreases for higher annealing temperatures. More importantly, the total specific surface area of kaolinite (kGa-1b) on heating to 130 °C is 13.2 m²/g (which is obtained when the specific surface area of 35 m²/cm³ is normalized to the density of kaolinite, 2.65 g / cm³) which is in close agreement with the mean specific area of 13.1 m²/g determined by BET⁷² (after outgassing at 130 °C). Since our microstructural model correctly determines the specific surface area which is in close agreement with BET surface area, this is further validation of the appropriateness of the four population model as it relates to the determination of the morphology of kaolinite.

We attribute the more complex variations in the pore populations at the higher annealing temperatures to the complex microstructural changes and general densification associated with striking topotactic transformations, unique among clay systems to kaolinite. In other clay systems, there is a change in the overall shape of the USAXS/SAXS data curve on annealing. For example, in montmorillonite it was found convenient to transition from a 4-population pore model to a fractal model for the porosity at the highest annealing temperatures.²³ In kaolinite, the overall scattering curves do not change shape over much of the q range, and the 4-population pore model can be used across the whole temperature range (except for population 1 as discussed above). Instead, the scattering from kaolinite exhibits new features at high q (fine size) that can be considered hallmarks of transformations characteristic of the kaolinite clay system.

3.4 Quantification of the crystalline phases at high temperatures

Figure 10 shows the evolution of the USAXS/SAXS curves at high q . For temperatures above 500 °C fine features appear in the scattering at high q ($q > 0.1 \text{ \AA}^{-1}$), as shown in Figure 10 (b). These can be associated with a new nanoscale population of scattering objects with a narrow size distribution and discrete size. After reviewing the literature, we assume these fine nanoscale features to result from the topotactic transformation of metakaolinite to form γ -alumina spinel – following the arguments of Lee, Kim & Moon (1999)⁴⁹, the scattering contrast factor is initially assumed to be that between the spinel and a changing mix of metakaolin and silica/mullite. At higher temperatures, the spinel phase also transforms but the distinctive morphology persists,⁴⁹ as appears also to be the case here. For analysis purposes, we assume a nominal scattering contrast factor of $100 \times 10^{28} \text{ m}^{-4}$. This value has been used to derive the volume fraction and surface area results presented in Figure 11.

These objects start to form at a temperature $\approx 500 \text{ }^\circ\text{C}$, and there appears to be continuous nucleation without significant increase in size up to $\approx 600 \text{ }^\circ\text{C}$, after which the new population of scattering features shows little change until the temperature is 800 °C. Between 800 °C and 900 °C, the features remain constant in mean size (mean diameter $\approx 13 \text{ \AA}$), but the surface area decreases, and so does the volume fraction. Above 900 °C, these features start to coarsen, and the coarsening becomes very significant as the nominal temperature is increased above 1000 °C (Figure 11 (a)), surpassing 50 Å at the highest annealing temperature reached. Two other important characteristics of this emerging nanoscale morphology are that (i) the aspect ratio becomes more globular with increasing temperatures: 0.5 up to 1052 °C, and 1.0 at higher temperatures; and (ii) the nanoscale population is locally concentrated with strong inter-particle interference effects present in the small-angle scattering profile. More information is provided on this in the supporting information.

The nearest-neighbor distance, determined from interparticle interference effects in the scattering data, is close to the mean diameter of the features (Figure 11(a)), and this remains the case as the features coarsen above 1000 °C, while the local particle concentration is typically $\approx 30 \%$, rising to $\approx 50 \%$ at the highest temperatures reached. All of this evidence suggests a “correlation hole” effect between neighboring solid objects of globular shape – consistent with TEM images of the emerging and evolving spinel morphology in kaolinite.⁴⁹ To clarify, the volume fractions and surface areas reported in this section correspond to solid crystal phases formed at high temperature. More detailed are provided in Section S3 in the Supporting Information file.

It is not clear why both the volume fraction and surface area of the new population decreases (halves) between 800 °C and 900 °C, although careful examination of the scattering curves in Figure 10 (a) reveal this effect to be true, regardless of any other assumptions made. This effect is probably associated with the complex set of transformations (with associated changes in contrast factor) occurring throughout the kaolinite system starting in this temperature regime, already seen in the various pore populations previously discussed (Figure 9). However, above 900 °C, these nanoscale features exhibit a simpler coarsening process, with volume fraction remaining approximately constant, mean diameter increasing,

and surface area decreasing as expected for a decreasing number of coarsening features (see Figure 11). Particularly above 1000 °C, it is this coarsening of a locally concentrated particle morphology that produces the striking changes in the USAXS/SAXS data curves (Figure 10(b)). Interpreting these scattering objects as “precipitates” of spinel within the bulk solid matrix, as described above, then a 5 % volume fraction of the sample volume with a 30 % local packing of individual precipitates suggests an overall morphology accounting for $\approx$ 15 % of the sample volume, but this could be significantly more if a smaller scattering contrast factor were applied. While the spinel phase, itself, does not show up significantly in the WAXS data measured here, the progressive increase in the diameter of the features points to mullite transformation (Figure 4).

Possible uncertainties in the actual highest temperatures reached in this study (nominal 1150 °C), previously indicated as due to thermal radiation losses from the sample, do not have a significant impact on our results. Even if the highest temperature is less by 100 °C or so, other studies have shown that each transformation in the kaolinite system takes place on heating over a significant temperature range.^{11–22}

3.5 Conclusions

In this study, the changes in the phase composition and the morphology of kaolinite are related using *in-operando* X-ray scattering measurements that span spatial scales of Angstroms to micrometers. The hierarchical morphology of kaolinite comprising nano-scale interlayer pores, meso-scale pores, and larger interparticle void fractions are represented in this study. The disappearance of nano-scale porosity on heating corresponds to the transformation of kaolinite to metakaolin. The reduction in the overall porosity of kaolinite on heating in excess of 950 °C is consistent with sintering and onset of mullite. The emergence of nano-scale particulate features in the q-range of 0.04 to 0.4 Å⁻¹ corresponds to the onset of the sintered phases such as spinel and mullite. The microstructural model was validated by complementary TEM and BET measurements. The oblate microstructural assumption closely approximates the platelet-like morphology of kaolinite. The microstructure of the denser crystalline mullite in amorphous silica is in agreement with the results of the microstructural model and previously published literature. The hierarchical pore network is consistent with other clay systems such as montmorillonite. The agreement of the specific surface areas determined from the four population model and the reported BET measurements shows the validity of the proposed microstructural model in quantifying the morphology of kaolinite. This study illustrates the application of multi-scale X-ray scattering measurements which encompass USAXS / SAXS/ WAXS^{23,24} to connect the thermally induced structural changes in materials with a hierarchical morphology.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.

Changes in the characteristic interlayer basal space as represented by the (a) representative peak corresponding to a basal distance of $7.2 \text{ \AA}$, and (b) the basal distance of kaolinite on heating to 700°C . Vertical bars in Figure 1 (b) represent estimated standard deviation uncertainties.

Figure 2.

Changes in (a) the characteristic kaolinite peak ($q = 3.47 \text{ \AA}^{-1}$, $d = 1.81 \text{ \AA}$, or $\text{CuK}\alpha \ 2\theta = 50.2^{\circ}$) and (b) the integrated peak intensity on heating to 1150°C . The movement of the peak to the left in Figure 2a corresponds to the effects of thermal expansion. The relative integrated intensity represented in Figure 2(b) is the integrated intensity of the characteristic kaolinite peak at a given temperature normalized to the integrated intensity at 30°C . Vertical bars in Figure 2b represent estimated standard deviation uncertainties.

Figure 3.

Changes in the X-ray diffraction patterns of kaolinite on heating where the unlabeled peaks at 30 °C, 308 °C, and 500 °C represent kaolinite. Other phases such as quartz (SiO₂, △), anatase (TiO₂, ○), and mullite (2Al₂O₃·SiO₂, □) are shown. For comparison with other literature, the q-scale has been converted to the CuKα scattering angle, 2θ (applicable for X-ray energy = 8.0415 keV and λ = 1.5418 Å).

Figure 4.

Changes in (a) the characteristic mullite peak ($q = 1.87 \text{ \AA}^{-1}$, $d = 3.36 \text{ \AA}$, or $\text{CuK}\alpha \ 2\theta = 26.5^{\circ}$) and (b) the integrated peak intensity as a function of temperature. Vertical bars in Figure 4b represent estimated standard deviation uncertainties. Small shifts in the diffraction peaks may be attributed to the effects of thermal expansion.

Figure 5.

Calculated scattering contrast factor determined as a function of temperature for quantifying the nanoscale features in kaolinite, based on the combined USAXS/SAXS data. The changes in the scattering contrast are related to the changes in the chemical composition of kaolinite on heating.

Figure 6.

Changes in the combined slit-smeared USAXS/SAXS data on heating kaolinite from ambient temperature to a nominal 1150 °C. (a), (b), (c), (d) show different temperature regimes. The disappearance of the small-angle diffraction peak above 675 °C is apparent, as is the emergence of fine nanoscale features at temperatures above 600 °C, which grow in size above a nominal temperature of 1000 °C. Point scatter uncertainties have been removed for clarity.

Figure 7.

The oblate microstructure of kaolinite assumed to model the USAXS/SAXS data is an approximation of the platelet morphology represented by the TEM image (a). On heating kaolinite at 30 °C (a) to 1150 °C (b), the formation of denser nano-scale crystalline particles in a less dense amorphous alumino-silicate matrix is shown in the white circle in (b).

Figure 8.

Microstructural model fit to a representative USAXS/SAXS curve for kaolinite (a) and the four population model representing the hierarchical porosity in kaolinite are shown in (b). Population 1 represents the nano-scale porosity (mean oblate diameter ~ 30 Å and small dimension ~ 3 – 4 Å). Populations 2 and 3 represent porosities to the order of 500 Å to 600 Å, and ~ 3000 Å, respectively. Population 4 represents the intergranular porosity with dimensions to the order of 2 μm to 3 μm .

Figure 9.

Characteristics of main void populations *versus* temperature: (a) mean oblate diameters, (b) volume fractions; (c) surface areas. Estimated standard uncertainties are indicated by vertical bars. Note parameters for the fine pore population 1 can only be followed until discrete nanoscale features appear.

Figure 10.

Model fits to the scattering from the population of discrete nanoscale features emerging at (a) selected intermediate annealing temperatures; and developing at (b) the highest nominal annealing temperatures. Vertical bars at each data point represent standard deviation uncertainties, and the lines are the fits to the data as discussed in the text.

Figure 11.

Fine feature parameters *versus* nominal temperature: (a) Mean sphere equivalent diameters and nearest-neighbor distances; (b) Volume fractions; and (c) Surface areas. Vertical bars are estimated standard deviation uncertainties of $\pm 10\%$.