

## ELECTRON DIFFRACTION EVIDENCE FOR C-CENTERING OF NON-HYDROGEN ATOMS IN KAOLINITE

**Key Words**—Atomic positions, C-centering, Crystal structure, Electron diffraction, Kaolinite, Transmission electron microscopy.

A crystal structure refinement of kaolinite reported by Suitch and Young (1983) concluded that the kaolinite structure is not C-centered, principally because the two inner-hydroxy O–H bonds were found to be differently oriented. This result was obtained using X-ray and neutron powder diffraction data and the Rietveld method (Rietveld, 1969), and was notable in its discordance with all previous authors on the subject, who had either concluded or assumed kaolinite to be C-centered, i.e., the condition  $[hkl]: h + k = 2n$  holds.

In response to the Suitch and Young (1983) result, we examined via electron diffraction the (001) zone-axis of kaolinite (Thompson and Withers, 1987). No violation of the C-centering condition was observed. Calculation of relative intensities ( $hkl$ ):  $h + k = 2n + 1$  based on the Suitch and Young (1983) model demonstrated that violation of C-centering by non-hydrogen atoms in the kaolinite structure would be readily observable in this zone-axis electron diffraction pattern. Furthermore, for a thick crystal (~100 unit cells thick), even positional symmetry violation by the hydrogen atoms *alone* would generate observable intensity in reflections forbidden by C-centering.

The reexamination of the kaolinite structure by Young and Hewat (1988) and Young (1988) reproduced the earlier result of Suitch and Young (1983). Our selected-area electron diffraction (SAD) result (Thompson and Withers, 1987), which required at the very least the non-hydrogen atoms to obey C-centering, was disregarded on the basis that the principal deviation from C-centering occurred in the  $z$  parameters. This argument implies that, in projection along the  $c$ -axis, the structure is essentially C-centered. To test the existence of a  $c$ -axis deviation from C-centering, further electron diffraction patterns were made and are discussed below.

The kaolinite used in the present work has been described previously (Thompson and Withers, 1987). A TEM specimen was prepared from kaolinite powder dispersed in epoxy resin, densified and oriented by means of centrifuging, sectioned appropriately, and finally thinned by an argon ion-beam. Electron diffraction patterns were recorded using a Philips 430 transmission electron microscope. Due to the relatively small

size of coherent domains in this specimen of Georgia kaolinite, electron diffraction patterns were collected using a convergent beam with a 15- $\mu\text{m}$  condenser aperture and a probe size of 500 Å.

Convergent-beam diffraction patterns (CBPs) were recorded for  $[hk0]$  zone-axes. Given the non-C-centered model of Suitch and Young (1983) and Young and Hewat (1988), such diffraction patterns, including  $h00$  or  $0k0$  type reflections (i.e.,  $[010]$  and  $[100]$  zone axes, respectively), should sufficiently test their hypothesis (see Figure 1). According to these authors, such zone-axis diffraction patterns should display rows of reflections demonstrating the lack of C-centering. Caution must be exercised when indexing  $[hk0]$  zone-axes in kaolinite due to the extreme similarity of inequivalent zone-axis diffraction patterns, e.g.,  $[0\bar{2}0]$  and  $[310]$ . Zone-axes from a single crystal, however, can be distinguished and, therefore, uniquely indexed by recording at least three neighboring major  $[hk0]$  zones, which occur every  $30^\circ$  if the crystal is tilted about  $c^*$ .

Figure 2 shows the  $[100]$  and  $[010]$  zone-axis CBPs of kaolinite. Clearly, there is no observable intensity for reflections ( $hkl$ ):  $h + k = 2n + 1$ . As in our earlier work (Thompson and Withers, 1987), reflection intensities were calculated for these zone-axes, this time based on the Young and Hewat (1988) structural refinement. These calculations indicated that intensity should have been readily observable for reflections ( $hkl$ ):  $h + k = 2n + 1$  if the Young and Hewat model were correct. In practice, the present results show that, for these two projections of the structure (as well as for  $[001]$  projection), non-hydrogen atoms obey the C-centering condition. Furthermore, given the thickness of crystals in these directions ( $>1000$  Å), the complete absence of intensity in reflections ( $hkl$ ):  $h + k = 2n + 1$  makes it highly unlikely that the hydrogen atoms violate the C-centering (see Thompson and Withers, 1987).

Bish and von Dreele (1989) recently discussed the structure refinement of Suitch and Young (1983) and Young and Hewat (1988) using their own X-ray powder diffraction data and the Rietveld method. Our conclusions are entirely in accord with theirs, arrived at independently and by different methods.

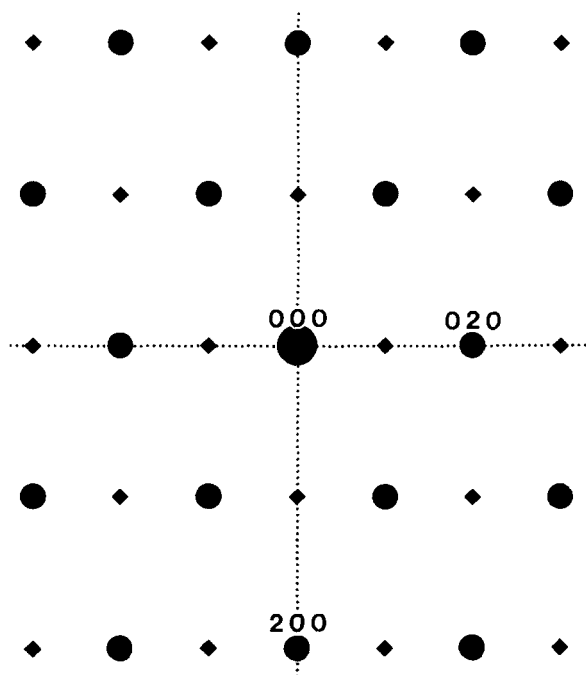


Figure 1. Schematic [001] zone-axis diffraction pattern of kaolinite. Solid circles = reflections allowed by C-centering condition ( $hkl$ ):  $h + k = 2n$  (note pseudo-hexagonal symmetry), and diamonds = reflections violating C-centering. Dotted lines = intersection of the reciprocal lattice plane by [100] and [010] zone-axis diffraction patterns of Figure 2.

Despite the strong evidence from diffraction experiments that the kaolinite structure is C-centered, some spectroscopic evidence (M. Raupach, personal communication, CSIRO Division of Soils, Private Bag No. 2, Glen Osmond, South Australia 5064, Australia) exists that the inner hydroxyl has two orientations with respect to the basal plane. This possibility is not precluded by the present observations due to the small scattering effect for electrons of one hydrogen atom in such a structure. The Young and Hewat (1988) neutron-diffraction-derived result, although incorrect, suggests that inner-hydroxyl hydrogen atoms in some way "misbehave" along the  $c$ -axis.

A resolution of these apparently conflicting data would have the inner-hydroxyl hydrogen distributed randomly about two sites along the  $c$ -axis, while still retaining the overall symmetry. Such disorder would result in streaking along the  $c^*$ -axis and may, in fact, partly contribute to the observed streaking seen in the [100] and [010] zone-axis diffraction patterns of Figure 2 (note that stacking disorder is expected to dominate any  $c^*$  streaking).

As concluded in our earlier work (Thompson and Withers, 1987), the electron diffraction evidence for C-centering of the non-hydrogen atoms in kaolinite is strong. In all probability the hydrogen atoms also pos-

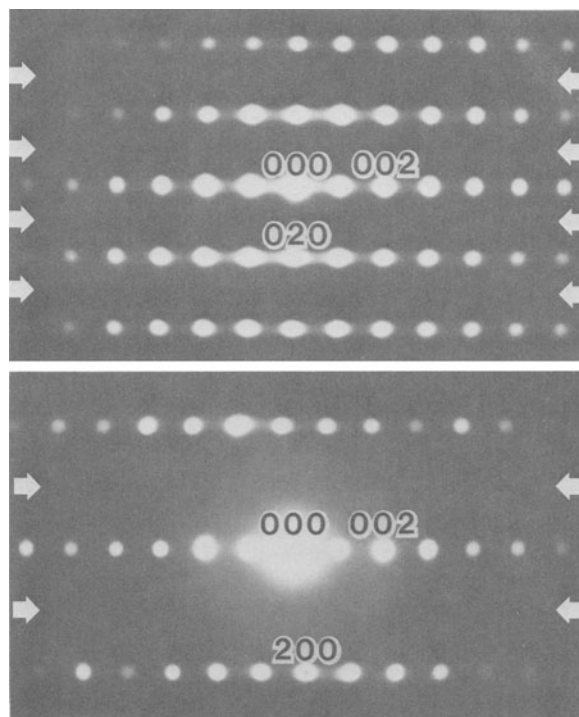


Figure 2. Heavily exposed, convergent-beam electron diffraction patterns (CBPs) of kaolinite along (upper) [100] and (lower) [010] zone axes. Arrows indicate where rows of reflections ( $hkl$ ):  $h + k = 2n + 1$  would appear if kaolinite structure was not C-centered.

sess this overall symmetry, but more careful consideration of neutron powder diffraction data is required to allow confirmation of this.

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