

Reply

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IN OUR recent publication¹ we illustrated (1) that the 980°C exotherm in the kaolinite-to-mullite series is caused by the formation of a γ - Al_2O_3 spinel phase alone and (2) that this spinel phase contains not more than 10 wt% silica in solid solution. Chakraborty and Ghosh² agree with us on the first issue but question the appropriateness of the experimental procedure we followed in assigning the 980°C exotherm to the formation of the spinel phase. On the second issue, they dispute our findings in favor of their earlier results³ on the grounds that our composition analysis was not performed on the γ - Al_2O_3 -type spinel phase but on χ - or κ -alumina phases that might have formed during alkali leaching. We will reply to both of these issues in detail in an effort to eliminate Chakraborty and Ghosh's concerns about our results.

On the first issue, our heat treatments of kaolinite at 850°C were done solely for the purpose of isolating the spinel phase from the mullite phase to determine to what extent spinel and/or mullite is responsible for the 980°C exotherm. Otherwise, if the samples are heated to or above the 980°C exotherm, the exotherm cannot solely be assigned to the spinel phase due to the simultaneous formation of spinel and mullite. In fact, Chakraborty and Ghosh's results on Georgia kaolinite agree with our observation that samples heated to the completion of the exothermic peak show small amounts of mullite with mostly spinel phase. As properly indicated by them,² when a mixture of the two is observed, the partial contribution of the mullite phase to the 980°C exotherm will be in question. With our approach there is no doubt that the spinel phase alone is the cause of the exotherm. We agree, however, that our findings should not be generalized to all the kaolin group minerals or to synthetically prepared aluminosilicates. Our work was only on Georgia kaolinite. As illustrated by Okada *et al.*,⁴ not all the kaolin group minerals behave in the same way as the kaolinite examined in our study.

On the second issue, the main claim of Chakraborty and Ghosh that our NaOH leaching treatment affected the composition of the spinel phase and/or possibly modified the structure to a zeolitic phase and χ - or κ -alumina is clearly a misinterpretation of our data. Contrary to their claim, all our samples were first analyzed

by X-ray (p. 840 of Ref. 1) and electron diffraction prior to any microanalysis by energy-dispersive X-ray spectroscopy (EDS). The formation of a zeolitic phase and/or χ - or κ -alumina was not observed. To reiterate this point, in Fig. 1 we provide a transmission electron microscope image and the microdiffraction patterns of a sample first annealed at 850°C for 7 d and then subjected to a 40-min-leaching treatment with 10 wt% boiling NaOH solution. The presence of the γ -type spinel phase is confirmed by microdiffraction patterns taken in $\langle 111 \rangle_{\text{fcc}}$ and $\langle 001 \rangle_{\text{fcc}}$ zone-axis orientations. The compositional analysis by EDS reported in our study was performed on samples as in Fig. 1 after first checking the structure by microdiffraction. It is important to note that a leaching treatment very similar to ours was also used by Okada *et al.*⁴ without any change in the spinel structure. A careful examination of Chakraborty and Ghosh's Fig. 2 in Ref. 2 illustrates that the peaks corresponding to γ - Al_2O_3 type spinel at 67.2° and 46° are still present even after their 40-min-leaching treatment. What has disappeared, however, are the peaks corresponding to the mullite phase, not the spinel. Thus, Chakraborty and Ghosh's own experiments also support our finding that the structure of the γ - Al_2O_3 type phase is not modified within the time period of our leaching experiments. Similarly, in their earlier publication,³ Chakraborty and Ghosh illustrated that under their standardized leaching condition, although the mullite phase is affected, the spinel phase is not affected by the leaching treatment (see Table I, columns 2 and 4 of Ref. 3).

In view of the additional evidence provided here, our compositional analysis of the spinel phase (i.e., <10 wt% SiO_2) appears to be correct.

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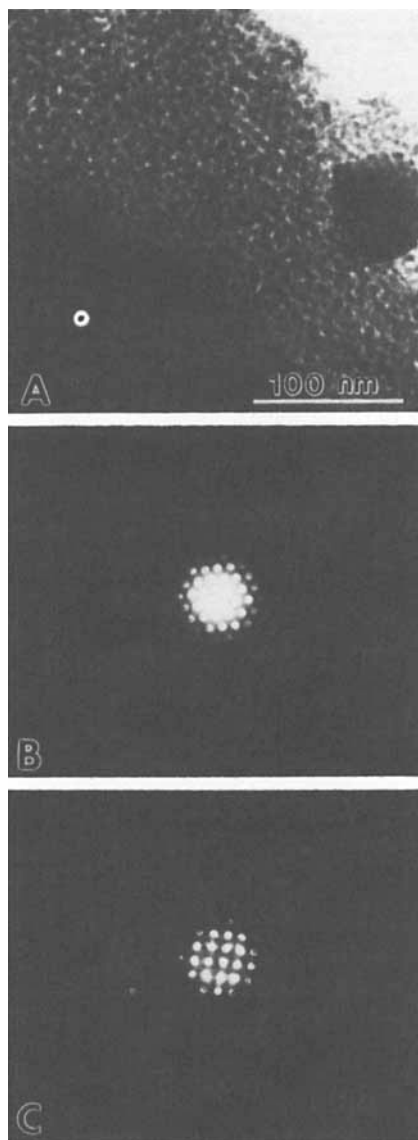


Fig. 1. (A) Bright-field (BF) image of the sample heat-treated at 850°C (7 d) and leached (40 min) in boiling 10 wt% NaOH. (B) and (C) are microdiffraction patterns in $\langle 111 \rangle_{\text{fcc}}$ and $\langle 001 \rangle_{\text{fcc}}$ zone-axis orientations, respectively, from the spinel phase after heating under the electron beam.

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