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EXTENDED X-RAY ABSORPTION FINE-STRUCTURE STUDY OF COBALT-EXCHANGED SEPIOLITE: REPLY

Key Words—Cobalt, Extended X-ray absorption fine-structure spectroscopy, Kerolite, Loughlinite Sepiolite.

The comments of Manceau and Decarreau (1988) are important to clear the limitations of extended X-ray absorption fine-structure analysis (EXAFS) and to avoid misleading to wrong models by EXAFS. The discussions concerning the limitations were insufficient in the original paper by Fukushima and Okamoto (1987).

Because many unknown parameters are necessary for analyzing EXAFS data, the final results are not the only solution, but one of many possible solutions, as pointed out by Manceau and Decarreau (1988). For the second neighbor in Co-sepiolite, overlapping of many pairs, Co-Co, Co-Mg, and Co-Si, makes the analysis more complicated. Final solutions, coordination number, and neighbor distance by EXAFS will depend on the method of data processing and the initial values used for curve-fitting calculation. Moreover, these problems are more serious for the second neighbor shell than for first neighbor shell. The model proposed by Manceau and Decarreau (1988) should be one of the solutions of the EXAFS data presented by Fukushima and Okamoto (1987) and appears to be the most reasonable solution. Such detailed discussion in their comment, however, may be beyond the limitations of EXAFS method. The models for kerolite discussed in the comment were based mainly on X-ray powder diffraction (XRD) results, and the EXAFS results were used to confirm the XRD results. The limitations should be taken in consideration, and other methods, such as XRD, should accompany EXAFS investigations, if available.

The results of XRD and chemical analyses in the experiments of Fukushima and Okamoto (1987) also support the EXAFS results, which are not the absolute values obtained by curve fitting, but the fact that Co was substituted for Mg or Na in octahedral sites near the crystal edge of sepiolite and loughlinite. As discussed by Manceau and Decarreau (1988), sepiolite, loughlinite, talc, and kerolite should possess a similar local structure in the crystal; however, Co ions in Co-sepiolite and Co-loughlinite in the experiment of Fukushima and Okamoto (1987) are probably located on the crystal edges of the outer surface and in the tunnels of sepiolite. The local structure around the Co ion is probably not similar to that of the octahedral cations in the crystal. The data for kerolite shown in the comment are inadequate for the discussion of local structure near crystal edges of phyllosilicates.

For the curve-fitting calculation of EXAFS data, Co-Co and Co-(Mg, Si) pairs should be separated because of the difference between phase shifts of Co and Mg/Si and the difference between their back scattering amplitudes. This is the only reason that Co-Co and Co-(Mg, Si) were listed separately in the Table 3 of Fukushima and Okamoto (1987). The values listed in Table 3 should be interpreted to mean that Co, Mg, and Si are in the second neighbor shell of Co, at distances of 2.9–3.4 Å. Other experimental results and more detailed analyses are necessary for the discussion of differences between neighbor distances in Co-sepiolite and Co-loughlinite.

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