EXTENDED X-RAY ABSORPTION FINE-STRUCTURE STUDY OF COBALT-EXCHANGED SEPIOLITE: COMMENT ON A PAPER BY Y. FUKUSHIMA AND T. OKAMOTO

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

Fukushima and Okamoto (1987) reported structural data obtained by X-ray absorption spectroscopy on Co-exchanged sepiolite and loughlinite. Extended X-ray absorption fine-structure (EXAFS) analysis led these authors to conclude that Co atoms were substituted for Mg or Na in the octahedral sheet, with the following intercationic distances: d(Co–Co) = 3.16–3.17 Å and d(Co–Mg, Si) = 2.82 (sepiolite)–3.45 Å (loughlinite). We disagree with these conclusions for the following reasons:

1. The distances reported by Fukushima and Okamoto (1987) are not consistent with clay structures. Inasmuch as sepiolite and 2:1 phyllosilicates possess similar local structures, intercationic distances should be very close. For example, in ferrous micas, d(Fe–Fe) = 3.11 Å and d(Fe–Si) = 3.28–3.29 Å (Takeda and Ross, 1975; Hazen and Burnham, 1973); in talc, d(Mg–Mg) = 3.06 Å and d(Mg–Si) = 3.25 Å (Rayner and Brown, 1973). Because the ionic radius of 6-fold coordinated Co^{2+} is between those of Mg^{2+} and Fe^{2+}, intercationic distances should range between the values reported herein. Furthermore, Manceau and Calas (1985, 1986) found by EXAFS that Ni–(Ni, Mg) and Ni–Si distances were 3.05 and 3.21 Å in both sepiolite and kerolite. Finally, Fukushima and Okamoto (1987) noted that their measured Co–Co distances were similar to those known for hydroxides. Because of the necessary fit between tetrahedral and octahedral sheets of phyllosilicates, these distances must always be shorter in phyllosilicates.

2. To the first approximation, fourier-filtered $\chi(k)$ spectra of the second atomic shells of sepiolite and loughlinite are very close (Figure 8 of Fukushima and Okamoto, 1987). We have carefully enlarged, digitalized, and plotted these two curves without spectral distortion. The replotted curves are *exactly in phase* over the entire k-range. Given EXAFS formulae, this phase concordance unambiguously indicates that intercationic distances are identical in sepiolite and loughlinite; Fukushima and Okamoto, however, reported different distances.

We show below how EXAFS analysis can lead to incorrect structural interpretations. We then discuss the problem of EXAFS data reduction of phyllosilicates spectra.

Table 1 shows data based on a theoretical partial EXAFS spectrum (S1) that corresponding to Co atoms surrounded by 6 Co at 3.16 Å and 4 Si at 3.45 Å. This spectrum can be least-square fitted assuming Co and Si atoms at 3.17 Å and 2.82 Å, and a ΔE_0 value (−0.7 eV) roughly equal to the relative variation reported by Fukushima and Okamoto (−6.0 to −5.5) = −0.5 eV) (Spectrum S2, Table 1 and Figure 1). This fit proves that the difference of Co–Si distances found for sepiolite and loughlinite corresponds to two distinct mathematical solutions for two nearly identical spectra. This result can be readily explained by the fact that if the Co–Si distance varies by 0.6 Å, the photoelectron wave moves by about 2π in the low k-range ($2k\Delta r = 2\pi$, with $\Delta r \approx 0.6$ Å). The phase accordance between

Table 1. Parameters of photoelectron waves.

	Scatterer	R (Å)	N	σ (Å)	Γ (Å-2)	ΔE (eV)	Q2
Spectrum S1	Co	3.16	6	0.10	1.0	0.0	
	Si, Mg	3.45	4	0.10	1.0	0.0	
Spectrum S2	Co	3.17	9	0.11	1.0	−0.7	5.410-2
	Si, Mg	2.82	3	0.15	1.0	−0.7	
Co-kerolite	Co	3.08	6	0.09	1.0	0.0	6.110-3
	Si	3.25	4	0.11	1.0	2.2	

R = interatomic distance.
N = atomic number.
σ = Debye-Waller factor.
Γ = electron mean free path expressed as $Dj = \exp(-R\Gamma/k)$.
ΔE = shift of the threshold energy. Displacement of the least-square curve.
Q = least square fit parameter. Expression given in Manceau and Calas (1986).
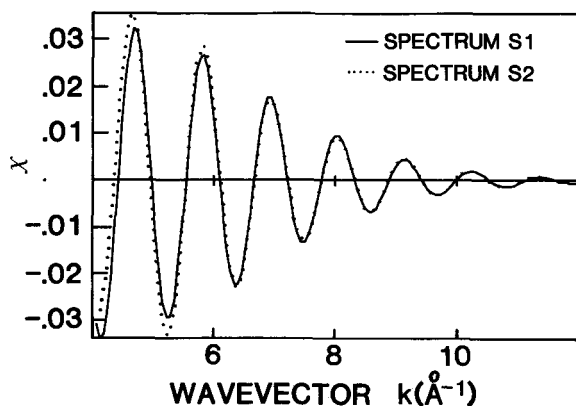Theoretical phase and amplitude functions from Teo and Lee (1979).

Figure 1. Theoretical partial extended X-ray absorption fine-structure spectra S1 and S2.

spectra S1 and S2 is therefore realized by adjusting ΔE_0 and the amplitude of each elementary Co–Co and Co–Si waves (coordination numbers). The difference of atomic numbers between S1 and S2 might be cancelled changing the scaling factor τ (electron mean-free-path parameter). Fukushima and Okamoto (1987) choose to change this scaling factor (D = 1.0 for sepiolite and D = 0.58 for loughlinite), but there is no physical reason to do so (Eisenberger and Lengeler, 1980).

Manceau and Calas (1986) and Manceau et al. (1988) demonstrated that in phyllosilicates EXAFS contributions of octahedral and tetrahedral cations strongly interfere. A quantitative analysis of the EXAFS spectrum of an unknown sample requires, before all, an understanding of how these elementary waves interfere; otherwise, the number of adjustable parameters is too high. This can be achieved by analyzing chemically and structurally similar models. Other work in this laboratory has shown that the Co k-EXAFS spectrum of a synthetic Co-kerolite has a b parameter of 9.20 Å (d(Co–Co) = b/3 = 3.067 Å) (to be published elsewhere). Our EXAFS analysis yields a Co–Co distance of 3.08 Å, in good agreement with XRD data, but different from the findings of Fukushima and Okamoto. The similitude observed between Fourier-filtered χ(k) spectra of the Co-kerolite, sepiolite, and loughlinite suggests that, for the two last minerals, a

third mathematical solution should exist with Co-Mg atoms $\approx$ 3.07 and Si atoms $\approx$ 3.25 Å.

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REFERENCES

Eisenberger, P. and Lengeler, B. (1980) Extended X-ray absorption fine-structure determination of coordination numbers: Limitations: *Physic Review B* **22**, 3551–3562.

Enguehard, F., Decarreau, A., and Manceau, A. (1988) EXAFS study of Ni-Co substitution in synthetic kerolites: *Phys. Chem. Miner.* (in press).

Fukushima, Y. and Okamoto, T. (1987) Extended X-ray absorption fine-structure study of cobalt-exchanged sepiolite: in *Proc. Int. Clay Conf., Denver, 1985*, L. G. Schultz, H. van Olphen, and F. A. Mumpton, eds., The Clay Minerals Society, Bloomington, Indiana, 9–16.

Hazen, R. M. and Burnham, C. W. (1973) The crystal structure of one-layer phlogopite and annite: *Amer. Mineral.* **58**, 889–900.

Manceau, A., Bonnin, D., Frétigny, C., and Kaiser, P. (1988) Polarized EXAFS of biotite and chlorite: *Phys. Chem. Miner.* (in press).

Manceau, A. and Calas, G. (1985) Heterogeneous distribution of nickel in hydrous silicates from New Caledonia ore deposits. *Amer. Mineral.* **70**, 549–558.

Manceau, A. and Calas, G. (1986) Nickel-bearing clay minerals. 2. Intracrystalline distribution of nickel: An X-ray absorption study: *Clay Miner.* **21**, 341–360.

Rayner, J. H. and Brown, G. (1973) The crystal structure of talc: *Clays & Clay Minerals* **21**, 103–114.

Takeda, H. and Ross, M. (1975) Mica polytypism, dissimilarities in the crystal structures of coexisting $1M$ and $2M_1$ biotite: *Amer. Mineral.* **60**, 1030–1040.

Teo, B. and Lee, P. A. (1979) *Ab initio* calculation of amplitude and phase functions for extended X-ray absorption fine structure spectroscopy: *J. Amer. Chem. Soc.* **101**, 2815–2822.