Characterization of Cu in lithiophorite from a banded Mn ore

ALAIN MANCEAU

Laboratoire de Minéralogie-Cristallographie, Universités Paris 6 et 7, CNRS UA09, Tour 16, 2ème étage, 4 place Jussieu, 75252 Paris Cedex 05, France

PETER R. BUSECK, DONALD MISER, JAMES RASK

Departments of Geology and Chemistry, Arizona State University, Tempe, Arizona 85287, U.S.A.

DANIEL NAHON

Laboratoire de Géologie Dynamique et de Pétrologie de la Surface, Université d'Aix-Marseille, Centre de Saint Jérôme, 13397 Marseille Cedex 04, France

ABSTRACT

The structural location of Cu in lithiophorite from a banded Mn ore from the Ivory Coast has been determined by extended X-ray absorption fine structure (EXAFS) measurements. Cu atoms are located within the hydrargillite [Al(OH)$_3$] sheet of lithiophorite and substitute for Al or Li. The Cu location is the same as that of Ni and differs from that of Co, which is in edge-sharing octahedra within sheets possessing a buserite-like structure. High-resolution transmission electron microscopy confirms that the major phase is lithiophorite together with minor hollandite.

INTRODUCTION

Fe and Mn oxides control the budget of numerous trace metals at the Earth's surface, including transition elements, lanthanides, and actinides (Krauskopf, 1956; Jenne, 1968; Paulson et al., 1988). Several mechanisms are responsible for this control: (1) solid solution, in which metal ions replace Fe or Mn in the host crystal structure, e.g., Ge for Fe substitution in Fe oxides (Bernstein and Waychunas, 1987), (2) adsorption onto specific surface sites of crystals, and (3) precipitation of discrete solid phases that are intimately associated with the major Fe or Mn phase, e.g., the Ni- and Co-rich layers in asbolane (Chukhrov et al., 1980; Drits, 1987; Manceau et al., 1987), feroxyhite (δ'FeOOH) domains in vernadite (Manceau and Combes, 1988; Chukhrov et al., 1988), and phyllomanganate domains in Mn-containing goethite (Manceau et al., in preparation).

Recognition of the mechanisms by which Fe and Mn oxides trap trace metals is relevant to several problems: (1) How do oxides influence the distribution of elements near the surface of the Earth? Such information is essential for understanding global geochemical cycles. (2) How can the metals be removed from the Fe-Mn oxide host? This question is especially important for determining the mobility of toxic ions such as Cd, Pb, Cs, Se, Hg, Zn, and Cu and also concerns the availability of trace elements to plants and animals.

Lithiophorite, ideally (Li,Al)MnO$_2$(OH)$_2$, probably contains a wider spectrum of trace elements than other Mn oxides. Microprobe analyses of many natural lithiophorites reveal small amounts of Co, Ni, Cu, or Zn (Ostwald, 1984). Their presence results from its mixed-layer structure, which consists of interlayered MnO$_2$ and (Al,Li)(OH)$_3$ sheets (Wadsley, 1952; Pauling and Kamb, 1982). In this structure cations such as Ni (Manceau et al., 1987) may substitute for Al and Li, elements that do not occur in other Mn oxides. In contrast, Co atoms in lithiophorite occur within edge-sharing octahedra in sheets possessing a buserite-like structure, as they do in asbolane. EXAFS (extended X-ray absorption fine-structure) data strongly support a segregation of Co atoms either in separate CoOOH layers or within the MnO$_2$ layers of lithiophorite (Manceau et al., 1987).

The location of Cu in the lithiophorite structure is not known. All these previous studies have revealed that there is no general rule for predicting the position of transition elements within the structure of Mn oxides. The variety of trapping mechanisms on the scale of crystallographic sites is wide and apparently must be examined in detail on a case-by-case basis. The goal of the present study is to determine whether immobilization of Cu in lithiophorite resembles either that of Ni or that of Co, or whether it results from yet another mechanism.

EXPERIMENTAL

Material

The lithiophorite we studied comes from the Ziemougoula area, northwest Ivory Coast, West Africa. It is from the pisolitic horizon of the lateritic mantle developed on Mn^{2+}-bearing Precambrian metamorphic parent-rock (Nahon et al., 1983, 1984). The pisolites consist of concentric layers of lithiophorite and hollandite. Microprobe analyses of monomineralic bands show that the Cu is associated with the lithiophorite; the average Cu content is 1.2 wt%. Material extracted for transmission electron microscopy (TEM) and EXAFS studies was hand-picked un-

der a binocular microscope to minimize contamination from the hollandite.

Methods

Impurities are common in Mn oxides, and so it was necessary to determine whether Cu is present as microscopic inclusions such as those within biotite (Ilton and Veblen, 1988). High-resolution transmission electron microscopy (HRTEM) and chemical analyses using in situ X-ray fluorescence energy-dispersive spectroscopy (EDS) were performed using Philips 400T and JEOL 2000FX microscopes to check the purity of the samples. We did not observe submicron inclusions such as those in the biotite. Over 30 grains were analyzed qualitatively using Ti grids as substrates. All contain minor amounts of Cu. Quantitative spectra from 14 grains were obtained and did not show any trends or correlations of other elements with the Cu.

The CuK EXAFS spectrum was obtained at LURE (Orsay, France) on the experimental set-up EXAFS IV. The synchrotron was operated at 1.85 GeV and about 250 mA. A Si (311) monochromator crystal (two reflection) was used. Under these experimental conditions the intensity of harmonics is negligible at the CuK edge. Because of the low concentration of Cu, the EXAFS spectrum was recorded in fluorescence mode using a multiwire proportional counter, with a counting time of 10 s per point. Double Fourier transform filtering was used for data reduction (e.g., Teo, 1986). The first Fourier transform (k → R space) was performed using a Kaiser window to minimize sidelobes created by the finite data range of the raw experimental spectrum (Manceau and Combes, 1988). The Cu-Al distance was calculated using phase shifts tabulated by Teo and Lee (1980) to be consistent with our previous work on lithiophorite containing Ni and Co.

TEM RESULTS

To minimize electron-beam damage, the lithiophorite was studied by using rapid exposures at low electron densities. HRTEM images suggest that most of the sample has a layered structure, consistent with the interpretation given by Wadsley (1952) for lithiophorite. Figure 1A shows lattice fringes with an approximate spacing of 9.3 Å, closely matching the value of 9.4 Å determined from the data of Wadsley for the (001) spacing. The (002) planes with a spacing of 4.7 Å are also resolved, as seen in the enlargement (Fig. 1B). This spacing corresponds closely to the projected separation along c* of sheets, viewed edge on, of edge-sharing MnO_6 and $(Li,Al)(OH)_6$ octahedra.

HRTEM images indicate that tunnel and layer Mn oxides are intimately mixed. Some acicular grains show lattice fringes with a spacing of about 9.4 Å, which is also consistent with images of Mn oxides having tunnels that are three octahedra wide, such as occur in todorokite and romanechite (Turner and Buseck, 1979, 1981). Moreover, the needlelike morphologies of some of these grains are suggestive of tunnel rather than layer Mn oxides. The

lattice fringes in Figure 1C provide good evidence for the presence of tunnel Mn oxides associated with the lithiophorite. Fringes in the narrow, darker regions of Figure 1C have spacings of approximately 6.7 Å, consistent with tunnels two octahedra wide, as occur in hollandite and romanechite. EDS analyses provide further evidence that the darker, needlelike regions represent tunnel structures. These analyses show that regions of Mn oxide that contain few of the acicular crystals have little or no Ba, whereas regions with abundant needlelike areas have substantial Ba peaks. Hollandite typically contains Ba as a tunnel cation, suggesting the needles are hollandite crystals.

The Cu contents of 14 randomly selected grains are fairly constant. Therefore it seems unlikely that Cu is associated with the tunnel sites. The constancy of the Cu analyses suggests that the element occupies a specific crystallographic site within the lithiophorite. Co analyses, on the other hand, display wide variations and may be distributed along defects at domain boundaries or within tunnels.

EXAFS RESULTS

The CuK EXAFS spectrum is shown in Figure 2 together with those of a Ni- and Co-bearing lithiophorite from New Caledonia. The close resemblance of Mn and Co EXAFS spectra on the one hand and of Ni and Cu EXAFS on the other is significant. The first spectral likeness originates from the similarity between the Mn and Co sites; Manceau et al. (1987) showed that in phyllomanganates Co atoms are located in sheets of edge-shared octahedra that are probably Mn-free. In lithiophorite Ni atoms are in the hydrargillite sheet, and Manceau et al. (1987) demonstrated that the presence of Al near Ni atoms gives rise to a typical EXAFS structure in the 3–5 $Å^{-1}$ range, which has not been observed for other Mn oxides. As the structure of EXAFS spectra directly models the short-range order around the probe atom, the similarity between the NiK and CuK EXAFS spectra implies a similar site location for Ni and Cu.

The modulus and imaginary parts of the k → R Fourier transforms of Ni and CuK EXAFS spectra are extremely similar (Fig. 3). They consist of two peaks attributed to the anionic and cationic nearest atomic shells. The most important result at this stage of the data reduction is that the imaginary parts of the next nearest contribution at both the Ni and CuK edges are in phase, suggesting that Cu atoms are surrounded by cations with low atomic weights, such as Al. The presence of neighbors with high atomic weights, such as Mn or Cu, would have resulted in an out-of-phase situation (Fig. 9b in Manceau et al., 1987). This assignment of the structural location of Cu atoms is reinforced by the similarity of the Fourier-filtered Cu cation (Fig. 4) and Ni-Al contributions (Fig. 9c in Manceau et al., 1987). The Cu-Al atomic distance, as determined by a least-squares fit of the Fourier-filtered atomic pair contribution, is equal to 2.96 Å and is slightly
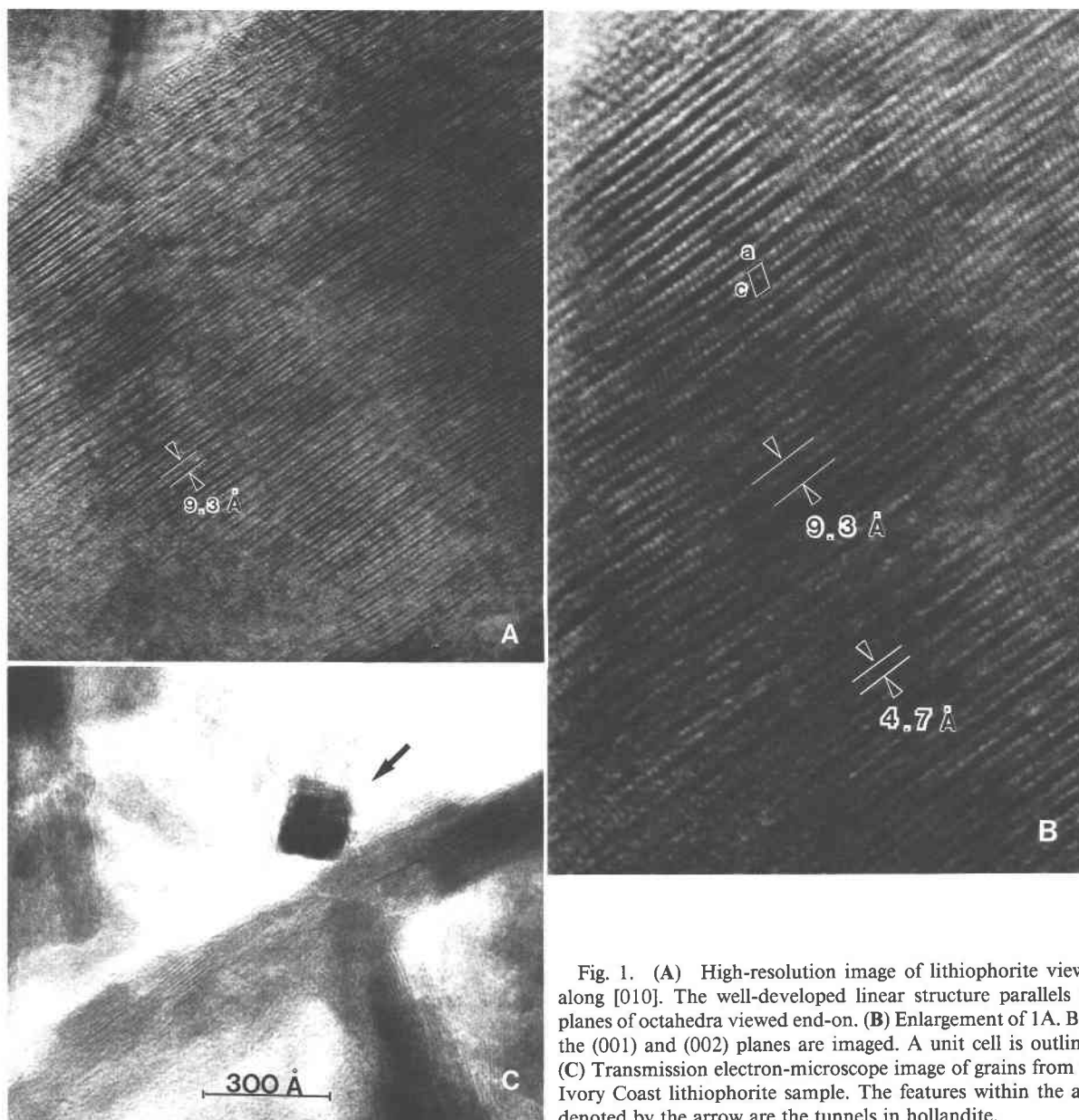
Fig. 1. **(A)** High-resolution image of lithiophorite viewed along [010]. The well-developed linear structure parallels the planes of octahedra viewed end-on. **(B)** Enlargement of 1A. Both the (001) and (002) planes are imaged. A unit cell is outlined. **(C)** Transmission electron-microscope image of grains from the Ivory Coast lithiophorite sample. The features within the area denoted by the arrow are the tunnels in hollandite.

larger than the distance between Ni and Al (2.91 to 2.94 Å).

DISCUSSION

The present study highlights the complementary results of EXAFS and HRTEM for investigating chemically and structurally complex materials such as Mn oxides. We have demonstrated that Cu atoms, like Ni, are located in the hydrargillite sheet of lithiophorite. However, we do not yet know whether Cu and Ni substitute for Al or Li.

Numerous chemical analyses have shown that lithiophorite containing first-series transition elements are depleted in Li (Ostwald, 1984), which supports a substitution of (Cu,Ni) for Li. Our observation of a lack of correlation of Cu with any element detectable by EDS analyses is consistent with such a substitution. Cu is incorporated in lithiophorite differently than in birnessite; i.e., Arrhenius et al. (1979) showed that in birnessite Cu is adsorbed at layer surfaces. The energy for Cu release probably differs for these two trapping mechanisms, so that it presumably
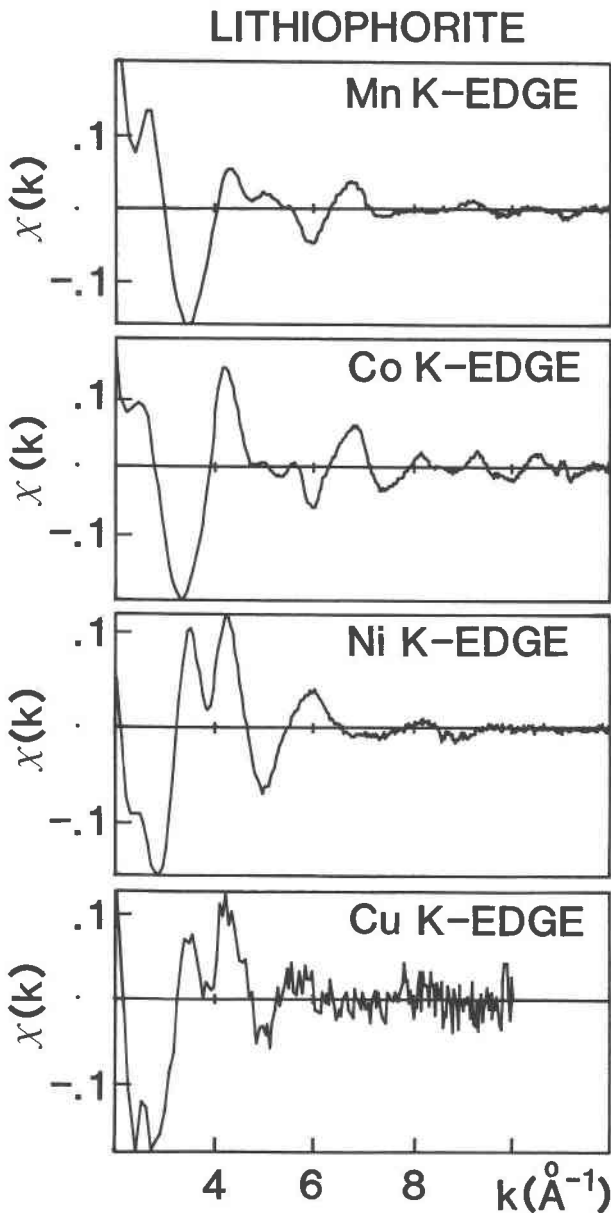
Fig. 2. EXAFS spectra of lithiophorite at the Mn, Co, Ni, and CuK edges. The close resemblance of the Mn and Co EXAFS spectra and of the Ni and Cu EXAFS spectra suggests that the site locations of Mn and Co and of Ni and Cu are similar.
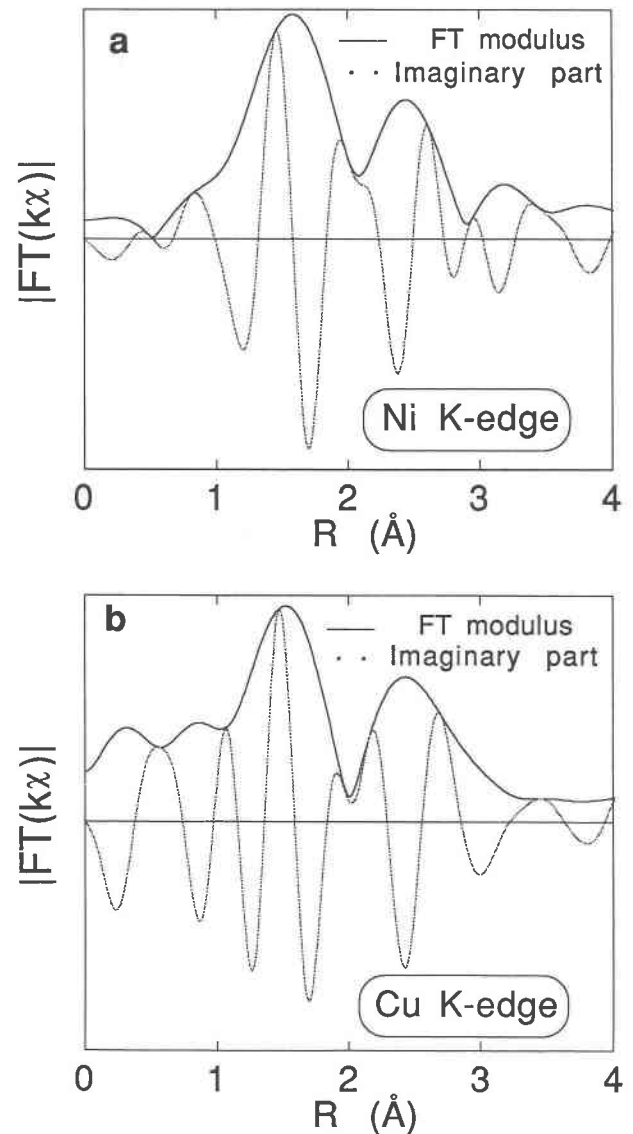

Fig. 3. Radial distribution functions, uncorrected for phase shifts, of Ni and CuK EXAFS of lithiophorite. Solid line: modulus; dots: imaginary part. Kaiser window with $\tau = 3.0$.

could be remobilized from birnessite much more easily than from lithiophorite.

Results obtained during the last few years on the crystal chemistry of transition elements associated with Mn oxides have revealed a great diversity of behavior, most of which was unsuspected. Because of technical difficulties, the crystal chemistry of trace elements associated with tectomanganates has not yet been studied. The main dif-

ficulty remains the small concentrations of these elements (<1 wt%) as well as the overlap of the X-ray fluorescence of the Mn matrix and of the element under study, which prevents the recording of high-quality EXAFS spectra. This limitation should become less severe in the near future with the current development of energy-dispersive X-ray detectors for fluorescence EXAFS. Such a technical improvement will make comparative crystal chemical studies of trace elements feasible for a wide range of host minerals. Furthermore, by combining EXAFS and transmission electron microscopy measurements, improved estimates of sample purity will be feasible.
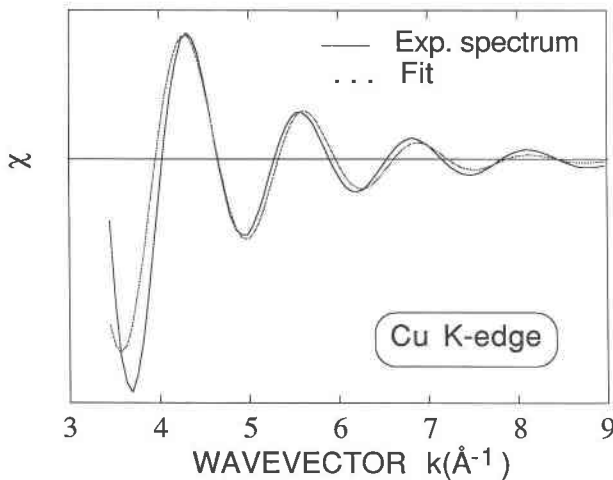
Fig. 4. Fourier-filtered Cu-Al contribution to EXAFS of lithiophorite. Solid line: experimental spectrum; dots: calculated spectrum.

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