# Lithiophorite from Mazaka, Ashikaga City, Tochigi Prefecture, Japan

By

**Satoshi Matsubara\*, Akira Kato\*, Yasuji Saito\***
and **Tokiko Tiba\***

**Abstract**—Lithiophorite from Mazaka occurs as black dendrites growing on smoother fracture surfaces in massive chert and as the underlying impregnation in bedded chert that overlies a bed of nodular goethite partially coated by kaolinite and sericite. The wet chemical analysis of dendrite gave $SiO_2$ 3.37, $MnO_2$ (total Mn) 52.43, $Al_2O_3$ 21.52, $Fe_2O_3$ 2.75, $TiO_2$ 0.08, MgO 1.04, CaO 0.14, CuO 2.63, NiO 0.85, CoO 0.43, ZnO 0.36, $Li_2O$ 0.61, $Na_2O$ 0.67, $K_2O$ 0.32, $H_2O$ 12.80% (by difference), corresponding to $Mn^{4+}_{0.99}$ $(Al_{0.69}Li_{0.07}Fe^{3+}_{0.06}Cu_{0.05}Mg_{0.04}Na_{0.04}Ni_{0.02}Co_{0.01}Zn_{0.01}K_{0.01})_{\Sigma 1.00}O_{2.59}(OH)_{1.41} \cdot 0.47\ H_2O$ on the basis of total metallic cation$=2$ after deducting $SiO_2$. The X-ray powder pattern is essentially identical with those of known lithiophorites and indexed on a monoclinic cell with $a=5.018$, $b=2.904$, $c=9.585$Å, $\beta=99.8°$.

The dendrites were formed by capilarity conveying the manganiferous material in a watery media from the underlying bedded chert impregnated by lithiophorite that had deposited in an open space as inferrable from the development of minute tablets.

## Introduction

During the survey on siliceous rocks in Ashio Mountainland, thick black dendrites and the underlying impregnation of manganese dioxide are found along fractures of massive chert and in bedded chert, respectively, in the quarry of the Ashikaga mine, Mazaka, Ashikaga City, Tochigi Prefecture, located near the southwestern margin of the mountainland. The wet chemical analysis and X-ray powder diffraction study demonstrated it to be lithiophorite with some metallic elements as minor constituents. The latter study on the impregnation did it to be a mixture composed of lithiophorite with small amounts of quartz, kaolinite and sericite. It is worthy of note that despite the extensive distribution of bedded manganese ore deposits in chert-rich horizons of Mesozoic sedimentary rocks in Ashio Mountainland (Watanabe *et al.*, 1970), no significant concentration of manganese minerals is found nearby the quarry.

Recently Potter and Rossman (1979) identified coronadite, cryptomelane, romanechite, todorokite and hollandite in manganese dendrites of various sources, but lithiophorite is out of their enumeration. Also, some constituents of the present material such as Cu, Zn, Co and Ni are common to those in manganese nodules from oceanic sea bottom, and not recorded in their qualitative chemical analyses of manganese dendrites.

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\* Department of Geology, National Science Museum, Tokyo

Also, a brief discussion is made on the differences from the most Li-rich lithio-phorite structurally studied by PAULING and KAMB (1982), who have derived a trigonal polytypic cell. But the X-ray powder pattern of the present lithiophorite can be ex-plained by a monoclinic cell of WADSLEY (1952), although the $b$-tripled supercell could not be confirmed. The present lithiophorite can be compositionally given better by the ideal formula of the latter author as $Mn^{4+}(Al, Li, Fe^{3+}, ...)(O, OH)_4 \cdot nH_2O$ where $Al > Li, Fe^{3+}, ... ; O > OH$ and n about 1/2.

## Occurrence

Geologically Ashio Mountainland is composed of thick accumulation of Paleozoic to Mesozoic sedimentaly pile represented by chert, slate and limestone together with the products of basic volcanic activities and minor sandstone and conglomerate. From the northern to western parts of the mountainland are some intrusives of granite and their offsets accompanying contact metamorphic rocks up to the grade of pyroxene hornfels facies (WATANABE et al., 1970). In the sedimentary rocks are more than 200 bedded manganese ore deposits of various dimensions dominantly accompanied by chert.

The mine has been operated at Mazaka, about 5 km ENE of Ashikaga Station, Ryōmō Line, Japan National Railway (Fig. 1), and lithiophorite is exclusively found within chert overlying a nodular goethite bed exposed in the northern part of the open pit.
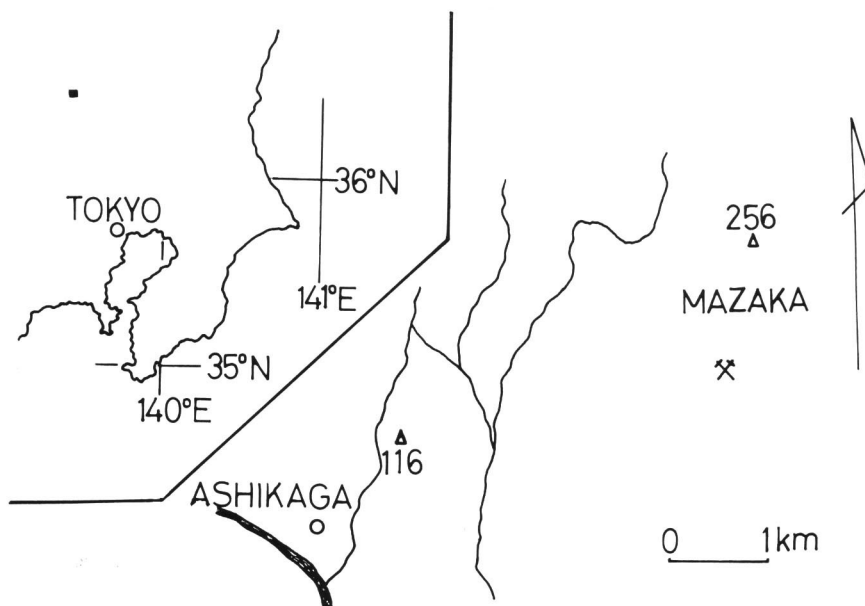


Fig. 1. The index map of the locality (crossed hammar mark).

Lithiophorite has at least two different modes of occurrence. One is black dendrites of various dimensions and shapes, the largest one reaching 70 mm long and a millimeter thick. The other is an impregnation of black manganese dioxide along the bedding of chert just above the nodular goethite bed, and the impregnated part reaches 40 mm thick. Its lateral extension is unknown, since above description comes from the reconstruction of materials in debris and not from the direct observation on exposure. The development of dendrite is restricted in the lower part of chert adjacent to the underlying goethite bed within the portion of about 300 mm above from the boundary between chert and goethite bed. The total thickness of chert will be a few meters and that of goethite bed is more than half a meter. On account of purity of material, the dendrite was subjected to the chemical and X-ray powder studies.

The fracture embodying dendrites are with rather smooth walls and generally stained by yellow brown iron hydroxide, which is a clue to find dendrite in the exposure. Most of dendrites have deep chocolate brown to black colour, but if underlain by pale cream thin film composed of kaolinite and minor sericite on the fracture surface, dendrites are less developed, thinner and shorter, and have lighter colour. Besides lithiophorite, fragments of chert coated by manganese dioxide are found in the debris under the exposure. A metallic-lustred thicker coating of smaller dimension without any dendritic form was identified as cryptomelane and less metallic and thinner but wide one as pyrolusite. However, the direct relations to lithiophorite were unknown because of the absence of any lithiophorite in the specimens comprising them.

Just below the chert bed containing lithiophorite dendrites, a nodular goethite bed is developed with the maximum thickness of more than half a meter, and the average size of nodule is 100 mm across. They are slightly deformed into oval shape in conformity with the bedding structure, and the profile has a well developed concentric texture through the development of regular fractures with a shell-like crust of a few millimeters thick. The nodules have khaki brown to dark brown colour and consist of goethite, quartz, kaolinite and sericite. The wet chemical analysis of bulk nodule after the fourth author gave $SiO_2$ 40.70, $TiO_2$ 1.48, $Al_2O_3$ 15.55, $Fe_2O_3$ 21.59, MnO 4.37, MgO 0.79, CaO 0.31, $Na_2O$ 0.13, $K_2O$ 3.08, $H_2O^+$ 7.49, $H_2O^-$ 4.02, $P_2O_5$ 0.41, $CO_2$ 0.13, total 100.05% in weight. The geothite is of rather low crystallinity. The outermost part of nodule is covered with a cream white powdery film composed of kaolinite, sericite and quartz in some parts. As compared with the film of clay overlain by lithiophorite dendrites on the fracture surface of chert, the relative amount of sericite to kaolinite is smaller, suggesting a preferential deposition of kaolinite to sericite.

Between chert and goethite beds is a narrow zone where chert is bedded and fractured forming more debris under the exposure. In the debris a few pieces of bedded chert fragments are found to be impregnated by lithiophorite. A densely impregnated part reaches 40 mm in maximum thickness where the bedding is more emphasized by the presence of argillaceous material with less black colour than lithiophorite. On account of the occurrence as fragment only, the lateral extension of the impregnated part was unmeasurable. However, seeing from the situation of lithiophorite of this

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Table 1. X-ray powder diffraction pattern of lithiophorites.

| 1. | | 2. | | 3. | | 4. | | 5. | | | 6. | | 7. | | 8. | | 9. | | 10. | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| d(Å) | I | d(Å) | I | d(Å) | I | d(Å) | I | d(Å) | I | hkl | d(Å) | I | d(Å) | I | d(Å) | I | d(Å) | I | d(Å) | I |
| 9.45 | 90 | 9.50 | 80 | 9.45 | 30 | 9.68 | s | 9.43 | 35 | 001 | 9.54 | s | 9.42 | 70 | 9.45 | 50 | 9.42 | 40 | 9.45 | m |
| | | 6.90 | 10 | | | | | | | | | | | | | | | | | |
| | | | | | | 5.15 | vw | | | | | | | | | | | | | |
| 4.73 | 100 | 4.76 | 100 | 4.715 | 100 | 4.72 | vs | 4.722 | 100 | 002 | 4.72 | vs | 4.70 | 100 | 4.71 | 100 | 4.72 | 100 | 4.70 | s |
| | | 4.20 | 10 | | | | | | | | | | | | | | | | | |
| 3.15 | 50 | 3.16 | 40 | 3.122 | 10 | | | 3.149 | 8 | 003 | 3.13 | w | 3.13 | 20 | 3.14 | 10 | 3.15 | 10 | 3.123 | mw |
| 2.50 | 30 | 2.48 | 30 | 2.505 | 10 | | | 2.507 | 5 | 110, $\overline{2}$01 | | | 2.50 | 20 | 2.49 | 30 | 2.503 | 10 | | |
| 2.37 | 70 | 2.36 | 70 | 2.371 | 60 | 2.39 | s | 2.370 | 20 | 111 | 2.37 | m | 2.38 | 80 | 2.37 | 70 | 2.375 | 50 | 2.385 | mw |
| 2.30 | 20 | | | 2.295 | 50 | | | 2.296 | 5 | 112, 201 | | | 2.24 | 10 | 2.28 | 10 | | | | |
| 2.14 | 20 | 2.14 | 10 | 2.134 | 5 | | | 2.136 | 3 | 112 | | | | | 2.13 | 10 | 2.131 | 10 | | |
| 2.04 | 10 | | | | | | | | | | | | 2.05 | 10 | 2.05 | 10 | | | | |
| 1.884 | 60 | 1.88 | 60 | 1.889 | 50 | 1.88 | s | 1.880 | 20 | 113 | 1.87 | m | 1.886 | 70 | 1.88 | 70 | 1.884 | 40 | 1.882 | m |
| 1.578 | 30d | | | 1.576 | 10 | 1.57 | m | 1.576 | 10 | 115, $\overline{006}$ | 1.572 | w | 1.573 | 20 | 1.57 | 50 | 1.578 | 10 | | |
| | | | | | | | | | | | | | | | | | | | 1.508 | w |
| 1.450 | 40d | | | 1.454 | 20 | 1.47 | m | 1.452 | 15 | 020 | 1.469 | w | 1.462 | 60 | 1.45 | 50 | 1.458 | 20 | 1.459 | vw |
| | | | | | | | | 1.447 | 10 | 115, $\overline{311}$ | | | | | | | | | 1.445 | vw |
| 1.387 | 20d | | | 1.390 | 10 | 1.40 | w | 1.388 | 10 | $\overline{116}$ | 1.388 | w | 1.397 | 40 | 1.39 | 50 | 1.395 | 10 | 1.396 | vw |
| 1.236 | 40d | | | | | 1.24 | vw | | | | | | 1.234 | 10 | 1.23 | 50 | | | 1.229 | w |

| 1. | 2. | 3. | 5. | 8. | 9. | 10. |
|---|---|---|---|---|---|---|
| a 5.02Å | | a 5.077 | a 5.018 | a 5.05 | a 5.12 | a 5.06 |
| b 2.90 | | b 2.907 | b 2.904 | b 2.91 | b 2.915 | b 2.91 × 3 |
| c 9.60 | | c 9.583 | c 9.585 | c 9.55 | c 9.588 | c 9.55 |
| β 100°50' | | β 99°48' | β 99.8° | β 100°30' | β 100°25' | β 100°30' |

1. Serra do Navio, Brazil (VALARELLI, 1975).
2. New Caledonia (PERSEIL, 1972).
3. Zajecov, Czechoslovakia (DADÁK, 1976).
4. Miyazaki mine, Miyagi Pref., Japan (NAMBU and OKADA, 1963).
5. Mazaka, Tochigi Pref., Japan. This study.
6. Lecht, Banffshire (WILSON *et al.*, 1970).
7. Mihalkovo, Bulgaria (TODOROV and KARADZHOVA, 1974).
8. White Oak Mt., Tennessee, U. S. A. (FLEISCHER and FAUST, 1963).
9. Olesna, Czechoslovakia (DADÁK, 1976).
10. Glouchester Farm, South Africa (WADSLEY, 1950).

The head numbers correspond to those in Table 3, i.e., the order of increasing Li₂O content.

mode of occurrence, this is the source of dendritic lithiophorite, which was derived by capilarity under a superficial condition.

## X-ray Powder Diffraction Study

The X-ray powder diffraction study was made on a black dendrite and the obtained pattern is well coincident with those of known materials as compared in Table 1 despite the quantitative difference in $Li_2O$ content. The unit cell parameters were derived by indexing after the reference to the existing cell as: $a=5.018$, $b=2.904$, $c=9.585$Å, $\beta=99.8°$. No tripling of $b$ found by WADSLEY (1952) could not be ascertained. Therefore, the (hkl) indices are given in terms of the non-tripled cell.

## Chemical Analysis

The complete wet chemical analysis was made on the X-ray studied material by the fourth author. The empirical formula was calculated after the deduction of $SiO_2$ in terms of the ideal formula of WADSLEY (1952) as given in Table 2. The present material satisfies the condition that the ratio $Mn^{4+}$/(total of metallic cations) is unity, provided that all the manganese is in tetravalent state. If a part of manganese is regarded as divalent after the ideal formula of PAULING and KAMB (1982), $Al_{14}Li_6(OH)_{42}$

Table 2.   Chemical analysis of lithiophorite from Mazaka, Ashikaga City, Tochigi Prefecture, Japan.

|  | wt.% | recast to 100% | molecular quotient | cation number | total cation=2 |
|---|---|---|---|---|---|
| $SiO_2$ | 3.37 |  |  |  |  |
| $MnO_2$ | 52.43 | 54.26 | 0.6241 | 0.6241 | 0.99 |
| $Al_2O_3$ | 21.52 | 22.27 | 0.2184 | 0.4368 | 0.69 |
| $Fe_2O_3$ | 2.75 | 2.85 | 0.0178 | 0.0357 | 0.06 |
| $TiO_2$ | 0.08 | 0.08 | 0.0010 | 0.0010 | 0.00 |
| $MgO$ | 1.04 | 1.08 | 0.0268 | 0.0268 | 0.04 |
| $CaO$ | 0.14 | 0.14 | 0.0025 | 0.0025 | 0.00 |
| $CuO$ | 2.63 | 2.72 | 0.0342 | 0.0342 | 0.05 |
| $NiO$ | 0.85 | 0.88 | 0.0118 | 0.0118 | 0.02 |
| $CoO$ | 0.43 | 0.44 | 0.0059 | 0.0059 | 0.01 |
| $ZnO$ | 0.36 | 0.37 | 0.0045 | 0.0045 | 0.01 |
| $Li_2O$ | 0.61 | 0.63 | 0.0211 | 0.0422 | 0.07 |
| $Na_2O$ | 0.67 | 0.69 | 0.0111 | 0.0223 | 0.04 |
| $K_2O$ | 0.32 | 0.33 | 0.0035 | 0.0070 | 0.01 |
| $H_2O$* | (12.80) | (13.25) | 0.7316 | 1.4632 | 2.32 |
| total | 100.00 | 99.99 |  |  |  |

*   by difference

Empirical formula (basis: total cation (except for H)=2)

$Mn^{4+}_{0.99}(Al_{0.69}Li_{0.07}Fe^{3+}_{0.06}Cu_{0.05}Mg_{0.04}Na_{0.04}Ni_{0.02}Co_{0.01}Zn_{0.01}K_{0.01})_{\Sigma1.00}O_{2.59}(OH)_{1.41}\cdot0.47H_2O$.

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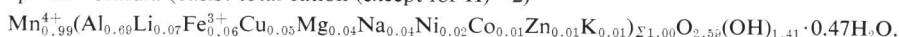
Table 3. Chemical analyses of lithiophorite.

| | 1. | 2. | 3. | 4. | 5. | 6. | 7. | 8. | 9. | 10. |
|---|---|---|---|---|---|---|---|---|---|---|
| $MnO_2$ | 52.10 | 47.00 | 41.72 | 53.11 | 52.43 | 48.5 | 40.28 | 51.07 | 53.03 | 48.95 |
| $MnO$ | 5.90 | 2.90 | 8.70 | 6.55 | | - | 2.31 | 4.61 | 9.63 | 8.21 |
| $CoO$ | 0.07 | 7.41 | 0.39 | 1.18 | 0.43 | 0.07 | 2.36 | 2.83 | 0.10 | - |
| $NiO$ | 0.04 | 2.00 | 0.84 | - | 0.85 | 1.34 | | 1.26 | 0.56 | - |
| $CuO$ | 0.08 | - | 2.36 | - | 2.63 | 0.02 | - | 0.09 | 0.61 | - |
| $ZnO$ | 0.10 | - | 0.10 | - | 0.36 | 2.71 | - | - | 0.26 | - |
| $PbO$ | - | - | 0.01 | - | - | - | - | - | - | - |
| $BaO$ | 0.22 | - | - | 3.99 | - | 0.49 | 0.82 | 0.56 | - | - |
| $CaO$ | 0.19 | - | 0.26 | 1.44 | 0.14 | 0.20 | - | - | 0.26 | tr. |
| $MgO$ | 0.03 | - | 0.05 | 2.69 | 1.04 | 0.49 | - | - | 0.09 | - |
| $Na_2O$ | 0.05 | 0.00 | 0.05 | 1.00 | 0.67 | 0.05 | 0.39 | 0.10 | 0.10 | none |
| $K_2O$ | 0.02 | 0.00 | 0.09 | 0.94 | 0.32 | 0.21 | 0.14 | 0.25 | 0.80 | none |
| $Li_2O$ | 0.04 | 0.08 | 0.48 | 0.56 | 0.61 | 0.86 | 1.29 | 1.59 | 1.93 | 3.30 |
| $Al_2O_3$ | 24.75 | 19.50 | 23.41 | 8.56 | 21.52 | 18.3 | 19.27 | 22.84 | 18.48 | 23.84 |
| $Fe_2O_3$ | 0.31 | 7.25 | 1.65 | 1.19 | 2.75 | 4.95 | 1.21 | 0.32 | 0.21 | 0.96 |
| $V_2O_3$ | - | - | 0.43 | - | - | - | - | - | - | - |
| $SiO_2$ | 0.34 | - | 4.32 | 5.87 | 3.37 | 8.25 | 18.55 | 0.96 | 0.22 | 0.30 |
| $TiO_2$ | 0.06 | - | - | - | 0.08 | 0.07 | - | - | - | - |
| $H_2O^+$ | 12.717 | 14.00 | 14.14 | 10.59 | (12.81) | 13.20 | 10.40 | 13.54 | 13.76 | 13.15 |
| $H_2O^-$ | 3.50 | | 0.90 | 2.46 | | - | 2.60 | 0.67 | 0.66 | 1.45 |
| Total | 100.07 | 100.14 | 100.24 | 100.13 | 100.00 | 99.72 | 99.62 | 100.68 | 100.71 | 100.16 |

1. Serra do Navio, Brazil (VALARELLI, 1975).
2. New Caledonia (PERSEIL, 1972).
3. Zajecov, Czechoslovakia (DADÁK, 1976).
4. Miyazaki mine, Miyagi Pref., Japan (NAMBU and OKADA, 1963).
5. Mazaka, Tochigi Pref., Japan. This study. $H_2O$ is by difference.
6. Lecht, Banffshire (WILSON *et al.*, 1970).
7. Mihalkovo, Bulgaria (TODOROV and KARADZHOVA, 1974).
8. White Oak Mt., Tennessee, U. S. A. (FLEISCHER and FAUST, 1963).
9. Olesna, Czechoslovakia (DADÁK, 1976).
10. Glouchester Farm, South Africa (DE VILLIERS and VAN DER WALT, 1945).

Chemical analyses are arranged in terms of the order of increasing $Li_2O$ content.

$Mn_3^{2+}Mn_{18}^{4+}(OH)_{42}$, an alternative empirical formula $Al_{14.00}(Li_{1.35}Cu_{1.12}Mg_{0.88}Na_{0.73}$ $Fe_{0.64}^{3+}Ni_{0.39}Al_{0.27}K_{0.23}Co_{0.19}Zn_{0.15}Ti_{0.03})_{\Sigma 6.01}(Mn_{2.91}^{2+}Ca_{0.08})_{\Sigma 2.99}(Mn_{17.48}^{4+}Fe_{0.53}^{3+})_{\Sigma 18.01}O_{46.32}$ $(OH)_{37.68} \cdot 7.79H_2O$ is obtained on the basis of total cation (except for H) to be 41. There is a significant substitution for Li and excess of uncombined $H_2O$.

The compositional variation of lithiophorite is very diverse, comprising at least two characteristic points. One is the variation of $Li_2O$ content, ranging from 3.30% in weight to nearly null and the other is the presence of various kinds of heavy metals such as Ni, Co. Cu and Zn (Table 3), which are common to those found in manganese nodules recovered from oceanic sea bottom.

## Microscopic Textures and Their Interpretation

Microscopic studies include ore microscopic and electron microscopic observation. The mineral is opaque without any internal reflections. The reflection colour is grey white with very faint reflection pleochroism in air. The anisotropic effect between crossed polars is moderate and obviously weaker than the other well-crystallized such manganese dioxide minerals as pyrolusite and ramsdellite. The indentation micro-hardness of impregnated lithiophorite ranges from 61 to 74 $kg/mm^2$ in the fine-grained part and 55–62 $kg/mm^2$ in the coarse-grained part, respectively. The electron micro-scopic observation of cross section of impregnated lithiophorite in the bedded chert disclosed the development of narrow fan-shaped aggregate in the inner and the aggregate of tablets in the outer part, respectively (Fig. 2). These correspond to above grain size difference. Obviously, the tablets are the products in open space probably formed due to the fracturing of chert along the bedding plane. Therefore, the formation is considered to be due to the precipitation of manganiferous material under the condition where the space was kept open, or, near surface condition. Also, it is worthy
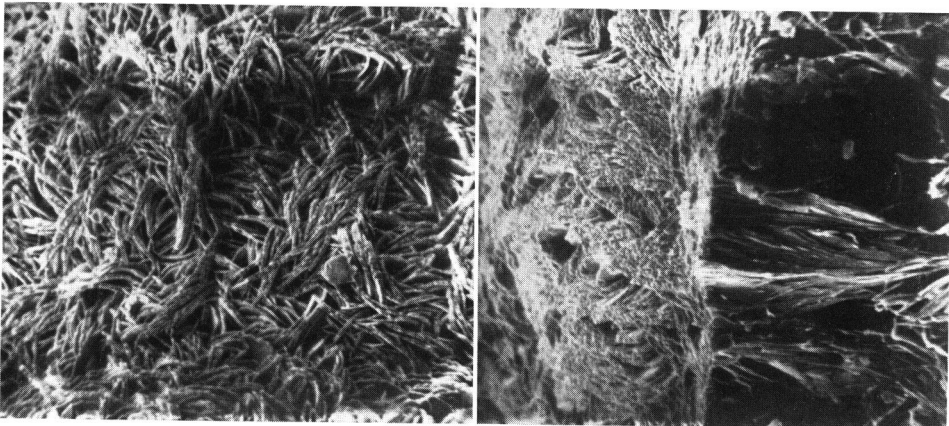


Fig. 2. The scanning electron microphotographs of lithiophorite. Field view, approx. $34 \times 30 \, \mu$. Left: untreated surface possibly facing to an open space, right: lateral fracture.

of note that the associated clay minerals have a good crystallinity, which is not always attained simply through the process of weathering.

The combination of these evidences leads to the conclusion that the mineral assemblage composed of lithiophorite and well-crystallized clay minerals was not simple near-surface precipitates from a meteoritic water but a kind of hydrothermal solution.

## Acknowledgements

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