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Data showing a relation between Li and F in trioctahedral smectites

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INTRODUCTION

Over a period of several years of intermittent work on lithium-bearing smectites, I have observed an apparent correlation between the lithium and fluorine contents of trioctahedral smectites. Foster (1960) had demonstrated that a 1:1 Li:F ratio existed in lithium-bearing micas when the lithium equivalents and the fluorine equivalents were plotted against each other. Such a plot for the trioctahedral smectites seemed appropriate to see if a similar relationship existed.

Smectites are clay minerals consisting of a cation octahedral layer between two silica tetrahedral layers. In dioctahedral smectites two-thirds of the cation positions in the octahedral layer are filled with aluminum which is trivalent; in the trioctahedral smectites all the cation positions in the octahedral layer are filled with divalent cations such as Mg^{+2} or Fe^{+2}. Lithium-bearing smectites are magnesium-rich and a generalized structural formula for this type of mineral is $[M^{+}_{0.33}(Mg, Li)_3Si_4O_{10}(OH,F)\cdot \underline{n}H_2O]$.

Although lithium in smectites has been known since Foshag and Woodford (1936) described the mineral which was later named hectorite by Strese and Hofmann (1941), lithium usually has not been determined in routine analysis of clays unless its presence was known or suspected in the study area.

Even fewer determinations of fluorine in clays have been made; Foshag and Woodford (1936) did not report fluorine in their analysis of hectorite from the type locality. The reason for this shortage of fluorine analyses is the lack of a reliable method of determination until recently. During the past twenty years more lithium and fluorine determinations of clays have been forthcoming, although often the determination of fluorine is overlooked.

This report brings together previously published data with one unpublished analysis to show the relationship between lithium and fluorine content in trioctahedral clays without making an attempt to explain the reason for that relationship.

SAMPLES

The data for the samples listed in table 1 include: the locations, the authors' identifications of the samples, the authors, and the analysts, when known, as listed below.

1. Hector, San Bernardino County, Calif. Hectorite. Reported by Ross and Hendricks (1945). R. E. Stevens, analyst.
2. Hector, San Bernardino County, Calif. Hectorite. Reported by Ames and others (1958). S. S. Goldich, analyst.
3. Djebel Ghassouel mine, Kasaki Province, Morocco. Ghassoulite. Analysis from Faust and others (1959) who equated this mineral to hectorite. J. J. Fahey, J. I. Dinnin, and Sarah Berthold, analysts.
4. Synthetic hectorite. Reported by Granquist and Pollack (1960).

5-12. Spor Mountain, Juab County, Utah. Montmorillonite. Reported by Shawe and others (1964). Wayne Mountjoy and W. D. Goss, analysts.

13-21. Lyles lithium clay deposit, Yavapai County, Ariz. Montmorillonite. Reported by Norton (1965). Wayne Mountjoy, J. I. Dinnin, and W. D. Goss, analysts.

22. Laponite (trade name for a synthetic hectorite-like mineral). Analysis reported by Neumann (1965).

23-28. Spor Mountain, Juab County, Utah. Mixture of hectorite and montmorillonite. Identified by Starkey and Mountjoy (1973). Wayne Mountjoy and J. M. Gardner, analysts.

29. Kings Mountain, Cleveland County, North Carolina. Swinefordite (a dioctahedral-trioctahedral smectite). Described by Tien and others (1975).

30. Southwest side of the Uinta Basin, Duchesne County, Utah. Trioctahedral smectite. Reported by Dyni (1976). Wayne Mountjoy, Violet Merritt, J. M. Gardner, and G. T. Burrow, analysts. Final analysis obtained after calculating out an illite impurity.

31. Hector, San Bernardino County, Calif. Hectorite. Purified by calcite removal by centrifugation. Reported by Starkey and others (1977). Wayne Mountjoy and J. M. Gardner, analysts.

32-43. Pleistocene Lake Tecopa, Inyo County, Calif. Lithian saponite. Reported by Starkey and Blackmon (1979). Violet Merritt and J. M. Gardner, analysts.

44-45. Drainage area of Pleistocene Lake Tecopa, Inyo County, Calif. Lithian saponite. Reported by Starkey and Blackmon (1979). D. R. Norton, J. M. Gardner, and Wayne Mountjoy, analysts.

46. Hector, San Bernardino County, Calif. Hectorite. Unpublished data. Sample collected by J. D. Vine, and purified by centrifugation to remove calcite by H. C. Starkey. Edythe Engleman and Wayne Mountjoy, analysts.

Samples 5-12 and 23-28 are all from the same area and, probably, are all a mixture of hectorite and montmorillonite. Because of the similarities of the X-ray powder diffraction patterns of these two minerals, samples 5-12 were identified as montmorillonite.

Samples 13-21 from Yavapai County, Arizona, also were labeled montmorillonite based on the X-ray powder diffraction pattern. Another sample from the same area of the Lyles lithium clay deposit, collected by A. J. Gude, 3rd, was X-rayed by the present author and, based on the 060 spacing, was determined to be a trioctahedral smectite.

Swinefordite, sample 29, was included to demonstrate the difference between a dioctahedral-trioctahedral smectite and mixtures of dioctahedral montmorillonite and trioctahedral hectorite, samples 5-12 and 23-28.

Some samples, especially those in which the total sample was analyzed (table 1), contain impurities in varying amounts. None of the recognized impurities normally contain any lithium or fluorine. This does not preclude the possibility that minute amounts of lithium and fluorine are present in undetected impurities.

DISCUSSION

To better illustrate the relation between the lithium and fluorine contents the data presented in table 1 were converted to equivalents ($\text{wt.\%} \times \frac{\text{valence}}{\text{atomic wt.}}$) and plotted on arithmetic graph paper (fig. 1). All but two of the samples plotted close to a curve indicating a $Li_{equiv.}/F_{equiv.}$ ratio of 0.25. The two samples that did not plot near the curve were samples 4 and 29. No. 4 was a synthetic sample about which more will be said later, and No. 29 was a sample of swinefordite, which is classified as a dioctahedral-trioctahedral mineral rather than as a trioctahedral mineral.

It must be borne in mind that most of these samples contained minerals other than the trioctahedral smectite and that if any of these impurities contained lithium or fluorine, the plotting of the points would be affected. If, however, these impurities did not contain either lithium or fluorine, the $Li_{equiv.}/F_{equiv.}$ ratio should not be affected by their presence. A greater source of error should be found in those smectites containing only small amounts of lithium or fluorine. An error of only one digit in the last decimal place would be large enough to affect the plotting of the point for that sample. Considering the possible sources of error, the agreement of the points with a straight line curve is good. An increase in the amount of data, especially for samples containing larger amounts of lithium and fluorine, should lead to better definition of the curve.

Swinefordite, the dioctahedral-trioctahedral smectite, is thought to be an alteration product of spodumene, and it contains a larger percentage of lithium than any other clay but does not have a correspondingly larger amount of fluorine as do the trioctahedral smectites. Mixtures of both trioctahedral and dioctahedral smectites (samples 5-12 and 23-28) fit the curve as well as do the monomineralic samples. This indicates that the lithium and fluorine are in the trioctahedral mineral and are unaffected by the presence of the dioctahedral mineral.

Synthetic hectorites may or may not contain lithium and fluorine in the same ratio as the natural ones do. Granquist and Pollack (1960) produced a synthetic trioctahedral smectite which they termed a hectorite. This is sample No. 4 in table 1. This sample is deficient in fluorine when compared to natural samples. The lithium and fluorine in their starting materials were furnished by LiF. If a larger amount of fluorine had been used in their starting material, a $Li_{equiv.}/F_{equiv.}$ ratio closer to that of natural hectorite might have been obtained.

Miller and Johnson (1962) produced a fluormica for which they calculate a formula similar to hectorite but for which the optical and physical properties are more like fluortaeniolite. The $Li_{equiv.}/F_{equiv.}$ ratio for this product does not fit the curve and is not plotted in figure 1. A byproduct of this synthesis was a water-swelling phase that they called a "lithium fluor-hectorite" but which they did not analyze. This "lithium fluor-hectorite" may have been closer chemically to natural hectorite than was the fluortaeniolite.

Sample No. 22 in table 1 is Laponite. Laponite is a trade name for a synthetic hectorite. As described by Neumann (1965), it has a $Li_{equiv.}/F_{equiv.}$ ratio of 0.29 which is similar to that of the natural smectites. The proportions of the materials in the starting mix were not given.

The only sample found in which fluorine definitely is not found is another synthetic, Laponite CP, described by Neumann and Sansom (1970) which

Table 1.--Lithium and fluorine weight percent obtained from portions of samples analyzed

Sample No.	Percent Li_2O	Percent F	Particle size
1	1.05	5.96	---
2	1.14	4.75	---
3	0.36	3.22	---
4	1.96	1.53	---
5	0.24	1.34	Total sample
6	0.12	0.76	>0.05 mm
7	0.33	1.87	0.05 mm-5 µm
8	0.39	1.88	<5 µm
9	0.19	1.90	Total sample
10	0.13	0.96	>0.05 mm
11	0.21	1.17	0.05 mm-5 µm
12	0.38	3.10	<5 µm
13	0.34	1.07	Total sample
14	0.44	1.20	Total sample
15	0.48	1.36	Total sample
16	0.29	0.88	Total sample
17	0.43	1.28	Total sample
18	0.45	0.96	Total sample
19	0.30	0.96	Total sample
20	0.05	0.21	Total sample
21	0.15	0.33	Total sample
22	1.9	8.3	---
23	0.42	2.38	<2 µm
24	0.44	2.52	<2 µm
25	0.50	4.02	<2 µm
26	0.58	3.84	<2 µm
27	0.57	4.04	<2 µm
28	0.57	4.06	<2 µm
29	4.7	1.49	---
30	0.17	1.06	---
31	1.03	4.60	<0.5 µm
32	0.177	0.50	Total sample
33	0.045	0.11	Total sample
34	0.172	0.74	Total sample
35	0.088	0.29	Total sample
36	0.090	0.10	Total sample
37	0.095	0.37	Total sample
38	0.123	0.35	Total sample
39	0.022	0.04	Total sample
40	0.073	0.31	Total sample
41	0.121	0.43	Total sample
42	0.168	0.78	Total sample
43	0.129	0.50	Total sample
44	0.071	0.48	<2 µm
45	0.095	0.58	<2 µm
46	1.08	5.44	0.5 µm

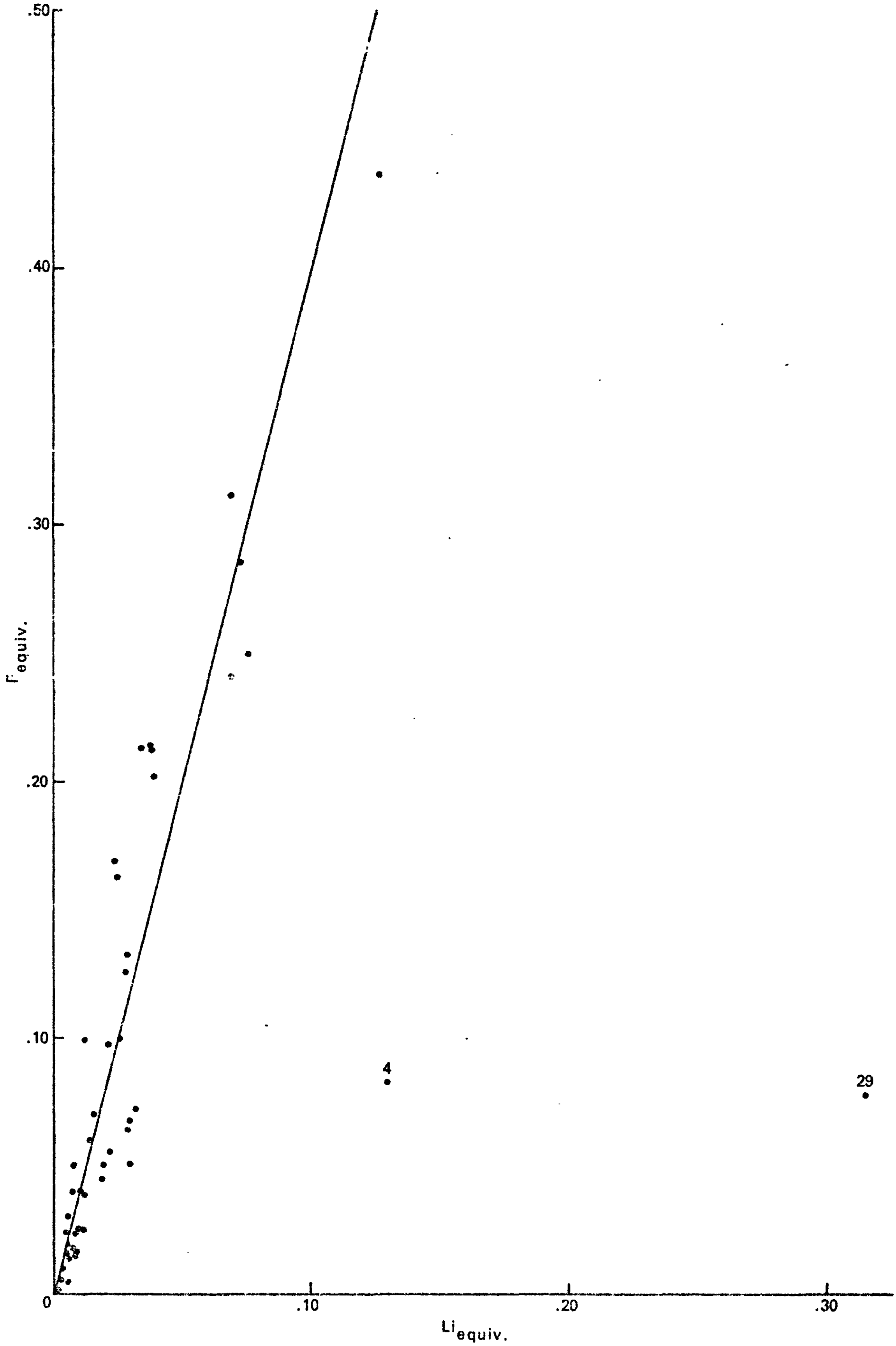

Figure 1.--Relation between Li and F in trioctahedral smectites.

they maintain contains no fluorine, structural or otherwise. This product is the result of attempts to create a clay with particular characteristics, and not of an attempt to duplicate a natural clay by synthesis.

The constant relationship between lithium and flourine in trioctahedral smectites from different sources suggests that the structure or the chemistry of the mineral rather than the environment is the determining factor in the amount of these elements present. Further studies, especially of the waters associated with these smectites, are needed to confirm this hypothesis.

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