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LI-BEARING STEVENSITE FROM MOLDOVA NOUĂ, ROMANIA

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Abstract—Li-bearing smectite minerals occurring as hydrothermal alteration products of magnesium silicate minerals in skarns associated with the Moldova Nouă, Romania, porphyry copper deposit were examined by X-ray powder diffraction, infrared spectroscopy, and thermal and chemical analyses. Li-bearing smectite containing 0.45–0.50 Li/unit cell is common, whereas smectite containing 0.21–0.33 Li/unit cell is less common. Both materials coexist with talc and kerolite. The Li-bearing smectite minerals (b = 9.111 Å) contains semi-ordered or ordered stacking and is highly crystalline, similar to saponite. After 3-yr storage under laboratory conditions in an air-dried state (RH = 50%) or after heating for 2 hr at 100°, 200°, 300°, or 400°C, the Li-bearing smectite minerals showed characteristics of a regular 1:1 interstratification of anhydrous and dihydrate layers. Some segregation of the anhydrous, monohydrate, and dihydrate layers was noted.

The amount of Li-for-Mg substitution was found to be close to that in hectorite, and the number of octahedral vacancies was similar to that in stevensite. This Li-bearing smectite apparently formed directly from colloidal suspensions at atmospheric temperature and pressure.

Key Words—Hectorite, Hydration, Interstratification, Lithium, Smectite, Stevensite.

INTRODUCTION

Li-bearing smectite minerals containing as much as 0.12 Li/unit cell were first reported by Neacşu (1970) from Moldova Nouă, Romania, as low-temperature, low-pressure hydrothermal alteration products of wollastonite, diopside, grossularite, vesuvianite, and, locally, talc, serpentine-group minerals, and sepiolite. Materials having properties and compositions consistent with Li-bearing smectite, saponite, and stevensite were identified, but not described in detail in that work. Conflicting views about the nature of Li-smectites in general with or without fluorine, their thermal and hydrothermal stabilities, and their degree of interstratification prompted a much more thorough examination of these materials by X-ray powder diffraction, infrared spectroscopy, and chemical and thermal analyses. The relationship between the Moldova Nouă materials and hectorite, Li-saponite, and Li-stevensite was also ascertained.

GEOLOGIC SETTING

The Moldova Nouă porphyry copper deposit in southwestern Romania occurs with both contact metasomatic rocks (skarn, limestone and/or dolomitic limestone, hornfels) and eruptive rocks (granodiorite, diorite, quartz andesite, dacite). These rocks have been altered by zeolitization, argillization, carbonatization, and anhydritization (Neacşu, 1970). Common hydrothermal alteration products of the magnesium metasomatic silicates are Li-bearing smectite, saponite, stevensite, kerolite, talc, serpentine-group minerals, Mg-chlorite, sepiolite, vermiculite, thomsonite, heulandite, calcite, and quartz. The trioctahedral Li-bearing smectite was deposited in fissures or in pockets, 0.4–1 m wide, in crystalline limestone. The smectite masses are white or greenish-white and occur in more-or-less argillitized zones in skarn bodies (Neacşu, 1970). They apparently were formed by precipitation from colloidal suspensions in the presence of Mg^{2+}, Ca^{2+}, Li^{+}, and Na^{+}.

ANALYTICAL PROCEDURE

Fifty samples of Li-bearing smectite, four samples of saponite, and two samples of stevensite from the Moldova Noua deposit and one sample of hectorite from Hector, California from the Source Clay Repository of the Clay Minerals Society were studied by X-ray powder diffraction (XRD), thermal analysis, infrared (IR) spectroscopy, and chemical analysis. Five representative samples are characterized in this paper by means of particle-size, Li, and saturating cation data (Table 1).

The samples were analyzed in bulk and separated into the following particle size fractions: >20, <10, <1, and <0.08 μm. The samples were saturated with Na^{+}, K^{+}, Ca^{2+} and Li^{+}, glycolated or glycerolated, hydrated, heated at various temperatures (100°–800°C), and stored in a vacuum desiccator in the presence of $CaCl_2$. The samples were saturated with various cations by exposing them to 1 N solutions of NaCl, KCl, $CaCl_2$, and LiCl for 24 hr. The samples were glycolated by placing oriented films on glass slides in a desiccator over an ethylene glycol solution under vacuum conditions for 24 hr. They were glycerolated by adding a few drops of a glycerol-ethyl alcohol mixture (2:17 V/V) to the surface of oriented aggregates.

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Table 1. Size fraction, lithium content, and saturating cation of samples of Li-bearing smectite from Moldova Nouă, Romania.

Sample	Size fraction (μm)	Li_2O (wt. %)	Saturating cation
2	bulk	0.59	Ca^{2+}
	<10	0.73	Na^+
4	bulk	0.25	Ca^{2+}
	<10	0.33	Na^+
7b	bulk	0.39	Ca^{2+}
	<10	0.48	Na^+
12c	bulk	0.66	Ca^{2+}
	<0.08	0.83	Na^+
H[1]	bulk	0.70	Na^+
	<10	0.83	Na^+

[1] Hectorite, Hector, California.

A structural formula was calculated from analyses of a <0.08-μm fraction of sample 12c which was separated by centrifugation.

The chemical analyses were made by atomic absorption spectrometry on Na-saturated samples (Iosof and Neacşu, 1980); fluorine was determined by the pyrohydrolytic method (Newman, 1968), and the cation-exchange capacity (CEC) was determined by the T_{NH_4} method (Stoica *et al.*, 1979).

X-ray powder diffraction (XRD) analyses were made with a DRON 2.0 diffractometer at a scanning speed of 1°2θ/min and using Ni-filtered CuKα radiation at 35 kV and 20 mA. Glass holders were used for random powder mounts and oriented aggregates. The amounts of calcite, quartz, and the dolomite in the chemically analyzed samples were estimated by XRD, using the external standard method and the measurement of mass attenuation coefficients (Brindley and Brown, 1980).

Thermal analyses were carried out on 0.3-g samples using an MOM Budapest derivatograph, a heating rate of 10°C/min, and a Pt-Pt10%Rh thermocouple.

The infrared absorption spectra (IR) were recorded in the spectral region from 400 to 4000 cm^{-1} on 0.8 mg samples in KBr with a UR-20 Carl Zeiss Jena double-beam spectrophotometer, using KBr, NaCl, and LiF prisms. Internal standards used for calibration were kaolinite (Cornwall, United Kingdom), calcite, and quartz for XRD and polystyrene for IR measurements.

Table 2. Basal spacings (Å) of Ca-saturated, Li-bearing smectites from Moldova Nouă, Romania.

Basal reflections	Ca-saturated	Solvated with ethylene glycol	Heated at 200°C for 1 hr	After heating for 3 hr at 300°C
001	15.06	17.22	9.66	9.48
002	7.57	8.60	5.00	4.74
003	5.02	5.70	3.228	3.171
004	3.673			
005		3.414		
006		2.840		
007		2.439		
008		2.130		

[1] Solvated with ethylene glycol, heated for 1 hr at 200°C, and 3 hr at 300°C.

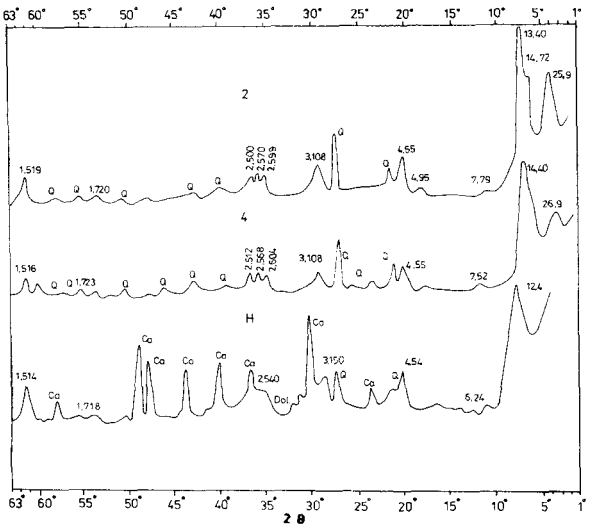


Figure 1. X-ray powder diffraction traces of Li-bearing smectites and hectorite. 2 = Li-bearing smectite having 0.46 Li/unit cell; 4 = Li-bearing smectite having 0.21 Li/unit cell; H = hectorite; Ca = calcite; Q = quartz; Dol = dolomite; CuKα radiation.

RESULTS

X-ray powder diffraction

The >20-μm size fractions of the Li-bearing smectite clays contained mostly apophyllite, quartz, and calcite, as well as appreciable amounts of wollastonite, diopside, and grossularite. Random powder mounts of bulk samples of the Li-bearing smectite, saturated with Ca^{2+}, analyzed one month after sampling, and were found to have retained their natural humidity. The untreated sample solvated with ethylene glycol and heated for 3 hr at 300°C displayed a perfectly regular succession of basal reflections (Table 2).

Samples 2 and 4 were analyzed 3 hr after they were collected; the samples had been stored in the air-dry state under laboratory conditions (RH = 50%). They showed a segregation of the Ca-saturated (natural state) dihydrated layers (15 Å) and regular 1:1 mixed-layer characteristics (25–26 Å, sample 2), or only regular 1:1 mixed-layer characteristics (dihydrated, 15 Å; anhydrous, 9 Å, sample 4), marked by low-angle reflections at 25 Å (Figure 1). Similar results were observed by Brindley (1955) and Shimoda (1971), and were recorded for stevensite from Moldova Nouă, Romania, but not for the saponite from this locality.

Of the 50 Li-bearing smectite samples analyzed in this study, 44 contained 0.45–0.50 Li/unit cell, and 6 had 0.21–0.33 Li/unit cell. Seven contained impurities of kerolite, two of talc, and four of serpentine-group

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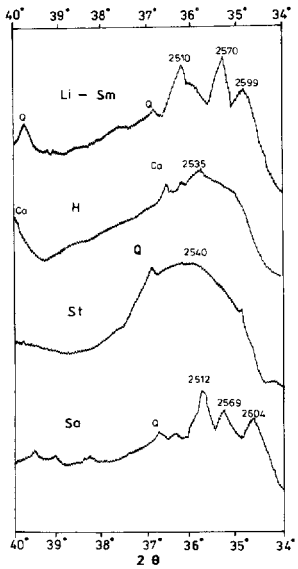


Figure 2. X-ray powder diffraction traces between 34° and 40°2θ of Li-bearing smectite having 0.21–0.50 Li/unit cell (Li-Sm), hectorite (H), stevensite (St), and saponite (Sa). Ca = calcite; Q = quartz; CuKα radiation.

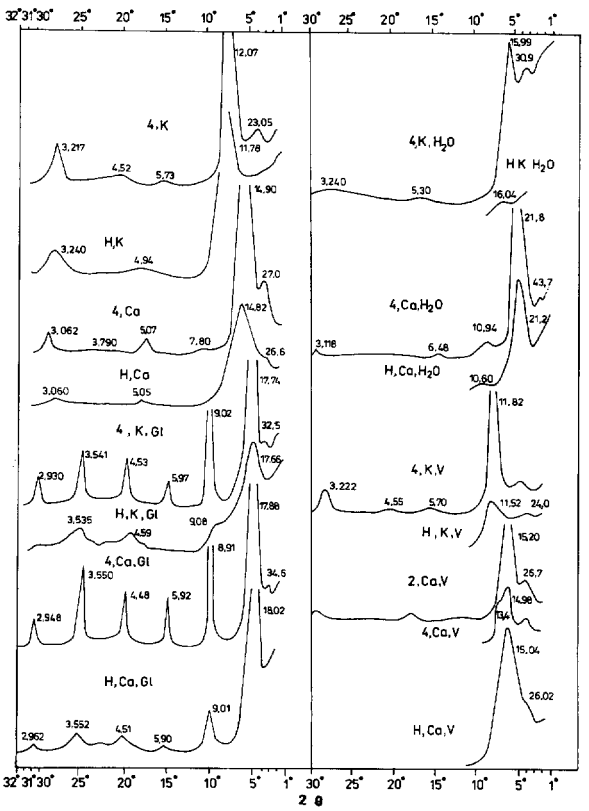


Figure 3. X-ray powder diffraction of Li-bearing smectite having 0.46 Li/unit cell (2), 0.21 Li/unit cell (4), and hectorite (H). Oriented aggregates, CuKα radiation. Ca = Ca-saturated, Gl = glycerolated, H_2O = water treated, K = K-saturated, V = preserved in vacuum for two weeks in the presence of $CaCl_2$.

minerals. Stevensite, kerolite, talc, and serpentine-group minerals have also been shown to result synthetically from hydrothermal treatment of wollastonite, xonolite, pectolite, and bustamite under different hydrothermal conditions (Otsuka *et al.*, 1972, 1979; Suzuki and Otsuka, 1976; Sakamoto *et al.*, 1977, 1982).

The index of crystallinity (half-height width, HHW) and the crystalline perfection (sharpness of XRD peaks) of the Li-bearing smectites were found to be close to those of the saponite from Moldova Nouă, and two to three times greater than those of the stevensite from Moldova Nouă or the hectorite from Hector, California, judging from the area and sharpness of the XRD peaks.

The *hk* reflections of Li-bearing smectite in Figure 1 are asymmetrical and tail towards high diffraction angles. For reflections having $k = 3$, a modulation was noted at 35°2θ, as well as a tendency of reflection to form three *hkl* lines (cf. pattern of saponite), indicating semi-ordered or ordered stacking (Méring, 1975). For stevensite and hectorite, however, only a broad, diffuse reflection was found, indicating fully disordered stacking (Figure 2).

Table 3 compares the range and the means ($\bar{x}$) of the 06 reflections and *b* parameters of Li-bearing smectite, hectorite, stevensite, and saponite samples from Moldova Nouă with those in the literature. This table indicates that the *b* parameter of the Li-bearing smectite samples is between those of hectorite and stevensite.

Hydration of K-saturated Li-bearing smectite and hectorite produced dihydrate (16 Å) phases, whereas hydration of Ca-saturated Li-bearing smectite and hectorite resulted in the formation of tetrahydrate phases

Table 3. 06 reflections and *b* parameters of trioctahedral magnesian smectite materials.

Mineral	06		*b*	
	Range (Å)	$\bar{x}$ (Å)	Range (Å)	$\bar{x}$ (Å)
Li-bearing smectite (50)	1.516–1.520	1.5185	9.096–9.120	9.111
Hectorite (5)	1.512–1.515	1.514	9.072–9.090	9.084
Stevensite (12)	1.518–1.527	1.522	9.108–9.162	9.132
Saponite (14)	1.525–1.533	1.529	9.150–9.198	9.174

$\bar{x}$ = arithmetical means. ( ) = number of the samples.

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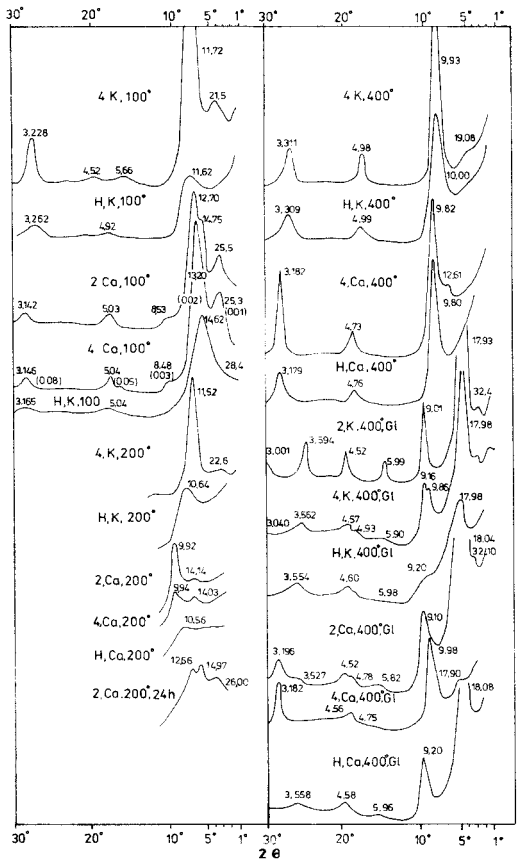


Figure 4. X-ray powder diffraction traces of Li-bearing smectites (samples 2 and 4) and of hectorite (H), heated at different temperatures. Oriented aggregates, CuKα radiation. K = K-saturated, Ca = Ca-saturated, 100° = analyzed 1 hr after heating for 2 hr at 100°C, 200° = analyzed 1 hr after heating for 2 hr at 200°C, 24 h = analyzed 24 hr after heating for 2 hr at 200°C, 400° = analyzed 1 hr after heating for 2 hr at 400°C, Gl = glycerolated.

(21 Å, Figure 3). K- or Ca-saturated Li-bearing smectite and hectorite solvated with glycerol gave a perfectly regular succession of the basal reflections (samples 2 and 4 had similar XRD patterns).

Sample 4, Ca-saturated, after two weeks storage in a vacuum desiccator in the presence of $CaCl_2$, like stevensite, showed regular mixed-layer reflections (22–26 Å) and a segregation of the normally dihydrated layers (15 Å) from the regular 1:1 mixed-layer (anhydrous-dihydrated). For hectorite and sample 2, only dihydrated layers were observed, having a basal spacing of 15 Å and rational higher order reflections.

The Li-bearing smectites, similar to stevensite, showed reflections at 22–26 Å, which were more intense for the Ca-saturated samples analyzed 1 hr after a 2-hr treatment at 100°, 200°, or 400°C (Figure 4).

Sample 4, 1 hr after heating for 2 hr at 100°C, showed intensified reflections of a mixed-layer phase having regular characteristics (22–26 Å), whereas sample 2 showed segregation of the normal dihydrated layers (15 Å), as well as characteristics of the regular mixed-layer 1:1 (anhydrous-dihydrated). The XRD patterns of K-saturated Li-bearing smectite samples 1 hr after heat treatment of 200°C for 2 hr indicated monohydrate layers; the patterns of the Ca-saturated samples indicated anhydrous layers and a very weak segregation of dihydrate layers. After 24 hr, the hydration of the Ca-saturated samples was significantly greater.

Anhydrous, monohydrate and, dihydrate layers were segregated in Ca-saturated samples by heating at 200° or 400°C; segregation of the trihydrate in K-saturated samples was noted after the samples were heated at 400°C (Figure 4). Otsu and Yasuda (1963) reported similar results on heating stevensite.

The regular succession of basal reflections was obvious in Li-bearing smectite samples glycerolated 48 hr after they had been heated at 400°C; glycerolation was partial in sample 4 (anhydrous or non-expandable layers predominated). Li-saturated, Li-bearing smectites analyzed at room temperature or after being heated at 100°C gave regular mixed-layer reflections at 31.1 (001), 15.50 (002), 7.90 (004), 5.10 (006), and 3.076 Å (0010).

After heating these samples for 2 hr at 200° or 300°C, Li-saturated, Li-bearing smectites showed intense regular mixed-layer reflections at 22.5 (001), 11.84 (002), 5.48 Å (004), etc. After being heated for 2 hr at 600°C, Li-bearing smectite and hectorite were anhydrous, as shown by basal reflections for higher orders of 9.40 Å (001); after calcination for 2 hr at 800°C, only enstatite and quartz reflections were present in the XRD patterns.

Chemical analyses

The corrected chemical analyses of four Li-bearing smectite samples and one hectorite sample (corrections were made for the quartz, calcite, and dolomite contents) are shown in Table 4. Structural formulae, calculated on the basis of 22 equivalent oxygens (Deer *et al.*, 1962) are also given in Table 4. Literature data (e.g., Köster, 1982) and our own analytical data were used to compare the crystal chemical features of Li-bearing smectite samples and hectorite, stevensite, and saponite (Table 5). For Li-bearing smectite having 0.47 Li/unit cell, the degree of octahedral Li-for-Mg substitution was only 76% of that of hectorite. In Li-bearing smectite having 0.26 Li/unit cell, the degree of Li-for-Mg substitution was 42% of that of hectorite; no F-for-OH substitution was observed.

The number of octahedral vacancies of Li-bearing smectites were similar to those of stevensite, i.e., the number of octahedral cations (Σ) was 5.75–5.77, compared with 5.78 for stevensite (Table 5). The unbalanced layer charge caused by Li-for-Mg octahedral sub-

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Table 4. Chemical analyses, structural formulae, cation-exchange capacities, and mineralogical impurities of Li-bearing smectite samples from Moldova Nouă, Romania.

Oxide (%)	2	4	7b	12c	H[1]
SiO_2	63.40	64.04	60.07	59.17	46.99
TiO_2	0.00	0.00	0.00	0.00	0.08
Al_2O_3	0.20	0.60	0.20	0.19	1.18
Fe_2O_3	0.17	0.45	0.12	0.61	0.28
MnO	0.07	0.10	0.14	0.12	0.01
MgO	22.55	20.37	22.95	26.15	23.18
Li_2O	0.73	0.33	0.48	0.83	0.83
CaO	2.01	2.24	6.64	1.62	9.58
Na_2O	3.14	3.07	2.51	1.93	2.99
K_2O	0.07	0.04	0.01	0.06	0.19
CO_2	1.57	1.75	5.25	0.36	8.14
P_2O_5	0.13	0.10	0.08	0.08	0.06
H_2O^+	6.70	7.13	1.91	8.48	4.95
F	0.00	0.00	0.00	0.00	2.90
Total	100.74	100.22	100.36	99.60	101.36
O ≡ F					1.22
					100.14
Structural formulae on basis of 22 equivalent oxygens					
Octahedral	5.76	5.48	5.81	5.77	5.94
Al	0.00	0.12	0.00	0.00	0.00
Fe	0.02	0.06	0.01	0.06	0.03
Mg	5.27	5.08	5.45	5.25	5.36
Li	0.46	0.21	0.33	0.45	0.55
Mn	0.01	0.01	0.02	0.01	0.00
Tetrahedral	8.00	8.01	7.99	8.00	7.97
Si	7.96	8.01	7.95	7.97	7.73
Al	0.04	0.00	0.04	0.03	0.23
Ti	0.00	0.00	0.00	0.00	0.01
Interlayer	0.96	1.01	0.78	0.69	0.99
Na	0.95	1.00	0.78	0.51	0.95
K	0.01	0.01	0.00	0.01	0.04
Ca	0.00	0.00	0.00	0.17	0.00
Cation-exchange capacities (meq/100 g)					
T_{NH_4}	113.0	81.5	82.4	124.8	78.4
Ca^{2+}	96.3	68.0			
Mg^{2+}	9.8	7.8			
Na^+	5.7	4.8			
K^+	1.2	0.9			
Mineralogical impurities estimated by X-ray powder diffraction (%)					
Quartz	12.6	16.2	10.2	0.0	0.0
Calcite	3.6	4.0	11.9	0.8	15.0
Dolomite	0.0	0.0	0.0	0.0	3.0

Analyses 2, 4, 7b, and hectorite, on <10-μm fraction.
Analysis 12c, on <0.08-μm fraction.
Samples dried at 105°C.
[1] Hectorite, Hector, California.

stitution and octahedral vacancies generated a high interlayer charge, similar to that of saponite.

Thermal analysis

The differential thermal analysis curves of Li-bearing smectite samples and hectorite are shown in Figure 5. The thermograms of Ca-saturated Li-bearing smectite samples show the endothermic effects of losing the two layers of hydration water of Ca^{2+} at 120°–125°C and 170°–180°C, whereas for the Na-saturated samples hydration water was lost at 136°–140°C (Mackenzie, 1957). The dehydroxylation temperature depended strictly on the extent of Li-for-Mg octahedral substitution, values of 678°, 725°, and 741°C being determined for Li-bearing smectite samples having 0.46, 0.33, and 0.21 Li/unit cell (Figure 5).

The temperature of the exothermic effect at 802°–880°C depended on the nature of the interlayer cation, being 844°–880°C for Ca^{2+} and 802°–824°C for Na^+. The weak exothermic peak at 802°–880°C represents the formation of enstatite. No such exotherm was noted for the stevensite or hectorite samples; thus, its pres-

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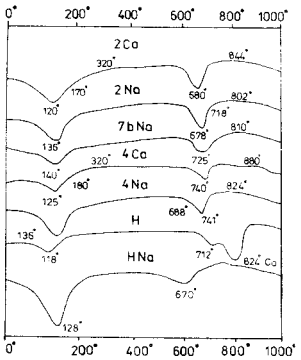


Figure 5. Differential thermal analysis curves of Li-bearing smectite samples and hectorite.

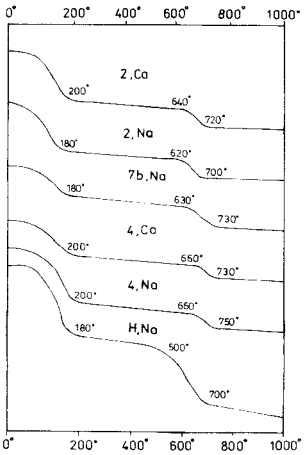


Figure 6. Thermogravimetric curves of Li-bearing smectite samples and hectorite.

ence may have been due to the high degree of crystallinity of Li-bearing smectite or to the lack of octahedral fluorine (see Granquist and Pollack, 1960). The differential thermal analysis curve of hectorite from Hector, California, had a low-temperature peak at 118°–128°C and a dehydroxylation endotherm at 670°C. Mackenzie (1957) and Deer *et al.* (1962) reported a dehydroxylation temperature of 800°C for this hectorite.

The TGA curves (Figure 6) showed a displacement of the dehydroxylation domain towards higher temperatures for Li-bearing smectite having 0.21 Li/unit cell and the initial dehydroxylation effect towards lower temperatures for hectorite, than for the Li-bearing smectite.

Infrared absorption spectroscopy

Infrared absorption (IR) spectra of Li-bearing smectites and hectorite are shown in Figure 7. Quartz bands at 788 and 802 cm^{-1} and carbonate bands at 880, 1420–1440, and 1715–1735 cm^{-1} were present in the IR patterns of the natural samples, in addition to the absorption bands of smectite. OH-vibration bands at 3698 and 3640–3650 cm^{-1} have been reported for Li-bearing smectites (Farmer, 1958, 1974). Si–O vibrations (ν_3) at 1007–1008 cm^{-1} had the same position for Li-bearing smectite samples, stevensite, and saponite, whereas Si–O vibrations (ν_1) at 1084 cm^{-1} were at the same position for Li-bearing smectite and hectorite (Figure 8).

The position of the Mg–O bands (ν_7), which occur as a doublet of magnesian smectite, is of the utmost significance. Hectorite displayed a band at 469 cm^{-1}, and stevensite, a band at 450 cm^{-1}, whereas the intense absorption band of saponite was at 465 cm^{-1}, with a shoulder at 453 cm^{-1}, closer to the wavelength of the IR bands of hectorite and Li-bearing smectite having 0.47 Li/unit cell. For Li-bearing smectite having 0.21 Li/unit cell, a band was present at 455 cm^{-1}, with a shoulder at 471 cm^{-1}, similar to the bands of stevensite.

SUMMARY AND CONCLUSIONS

In the Moldova Nouă area magnesian silicates have been hydrothermally altered to fluorine-free, Li-bearing smectite having 0.21–0.50 Li/unit cell. The XRD patterns of Li-bearing smectite samples suggest an obvious layer segregation and the formation of a regular 1:1 mixed-layer phase (dihydrated-anhydrous), especially after the samples were heated between 100° and 300°C and saturated with Ca^{2+} or Li^{+}. Anomalous dehydration phenomena, similar to those of stevensite, were also observed.

Table 5. Crystallochemical characteristics of trioctahedral magnesian smectite samples from Moldova Nouă, Romania.

Mineral	Tetrahedral sites			Octahedral sites							Interlayer charge (meq/100 g)
	Si	Al	Charge	Al	Fe^{3+}	Ni	Mg	Li	Σ	Charge	
Li-bearing smectite (44)	7.97	0.03	31.97		0.04		5.26	0.47	5.77	11.11	0.92
Li-bearing smectite (6)	7.96	0.04	31.96		0.04		5.45	0.26	5.75	11.28	0.77
Hectorite (5)	7.92	0.08	31.92		0.01		5.38	0.62	6.00	11.41	0.67
Stevensite (5)	7.98	0.02	31.98	0.06	0.04	0.06	5.54	0.06	5.78	11.56	0.46
Saponite (9)	7.13	0.87	31.13	0.09	0.05		5.77		5.93	11.96	0.91

( ) Number of the samples on which were made arithmetical means of the determinations. Cations and charge (tetrahedral, octahedral, interlayer), on the basis of 22 equivalent oxygens.

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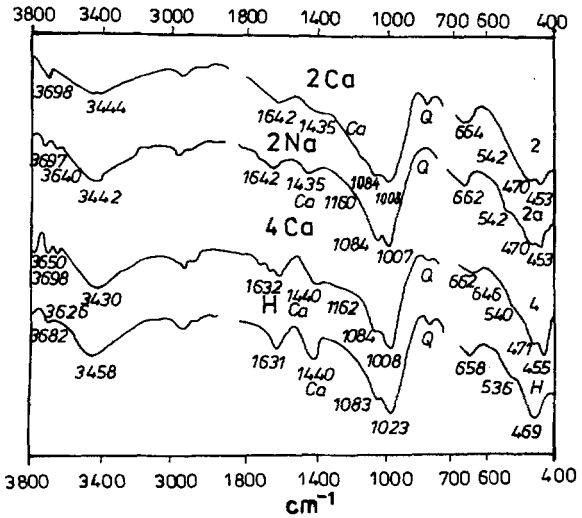


Figure 7. Infrared absorption spectra of Li-bearing smectite samples and hectorite.

The index of crystallinity (HHW), semi-ordered or ordered stacking, and high interlayer charge of Li-bearing smectite samples examined in this study are similar to those of saponite; the number of octahedral vacancies and the phenomena of the segregation and formation of a regular mixed-layer phase (anhydrous-dihydrated) are analogous to those of stevensite. Li-for-Mg substitution is similar to that in hectorite, but no F-for-OH substitution was noted. The reduction of the number of Li-for-Mg substitutions shifted dehydroxylation to higher temperatures and the IR band for Mg–O from 470 to 450 cm^{-1}, towards the stevensite field. Li-bearing smectite can be defined as hectorite without fluorine and having octahedral vacancies, or as Li-bearing stevensite.

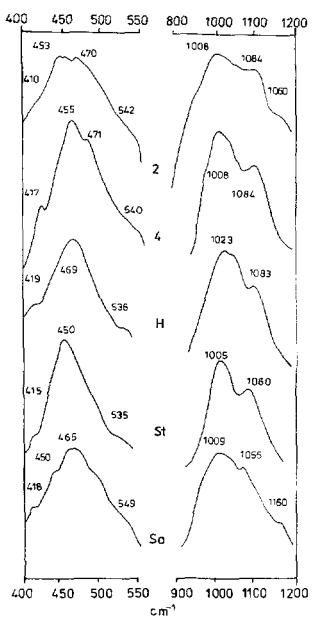


Figure 8. Infrared absorption spectra between 400–550 cm^{-1} and 900–1100 cm^{-1} of Li-bearing smectites, hectorite, stevensite, and saponite.

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