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CATION MIGRATION IN MONTMORILLONITES

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Previous studies (Hofmann and Klemen, 1950; Greene-Kelly, 1955) have shown that lithium-saturated dioctahedral montmorillonites lose their expandable character and exhibit greatly reduced exchange capacities following heat treatment at 200–300° C. These investigators proposed that lithium ions migrated from interlayer positions into montmorillonites at these moderate temperatures, possibly into vacant octahedral positions. This report represents preliminary results obtained from an infrared absorption study designed mainly to examine the foregoing hypothesis.

Separate portions of two dioctahedral montmorillonites (from Cheto, Arizona and San Juan, Argentina) which have different exchange capacities and a trioctahedral montmorillonite (hectorite) were prepared with Li^+, Mg^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Mn^{2+}, Na^+, Ca^{2+}, Sr^{2+}, K^+, and Ba^{2+} in exchange sites. The samples were sedimented and air-dried on silver chloride platelets and infrared spectra recorded from 2–25μ before and after heat treatment at 300° C. for 8 hours. Parallel X-ray diffraction studies were conducted.

Typical absorption patterns of the $<2\mu$ fraction of dioctahedral specimens are shown in Fig. 1. The 8.5–14μ region is of primary interest. No differences were noted on spectra recorded before heat treatment; Fig. 1a is representative of all Cheto specimens at room temperature.

Many of the absorption bands have been assigned to various metal-oxygen linkages by Farmer (1958) and Stubican and Roy (1961). The assignment of bands in this study was patterned after their determinations. The band at 1125 cm^{-1} was attributed to Si-O (apical oxygen) stretching vibrations, the large band centered at 1035 cm^{-1} to Si-O (basal oxygen) combined stretching and bending vibrations, and the band at 918 cm^{-1} to H-O--Al^{VI} bending vibrations (Serratosa, 1960); the band at 840 cm^{-1} has not been assigned definitely.

Spectra of heat-treated clays compared with spectra of unheated clays indicated the following (Fig. 1a–g): 1) the band at 1125 cm^{-1} remained unchanged; 2) the band at 1035 cm^{-1} shifted to higher frequencies (largest shift was to 1055 cm^{-1}) with cations smaller than zinc and the magnitude of the shift increased with decreasing radius of the interlayer cation; no shift was evident with cations larger than zinc; 3) the intensity of the band at 918 cm^{-1} (also band at 840 cm^{-1}) was decreased when calcium

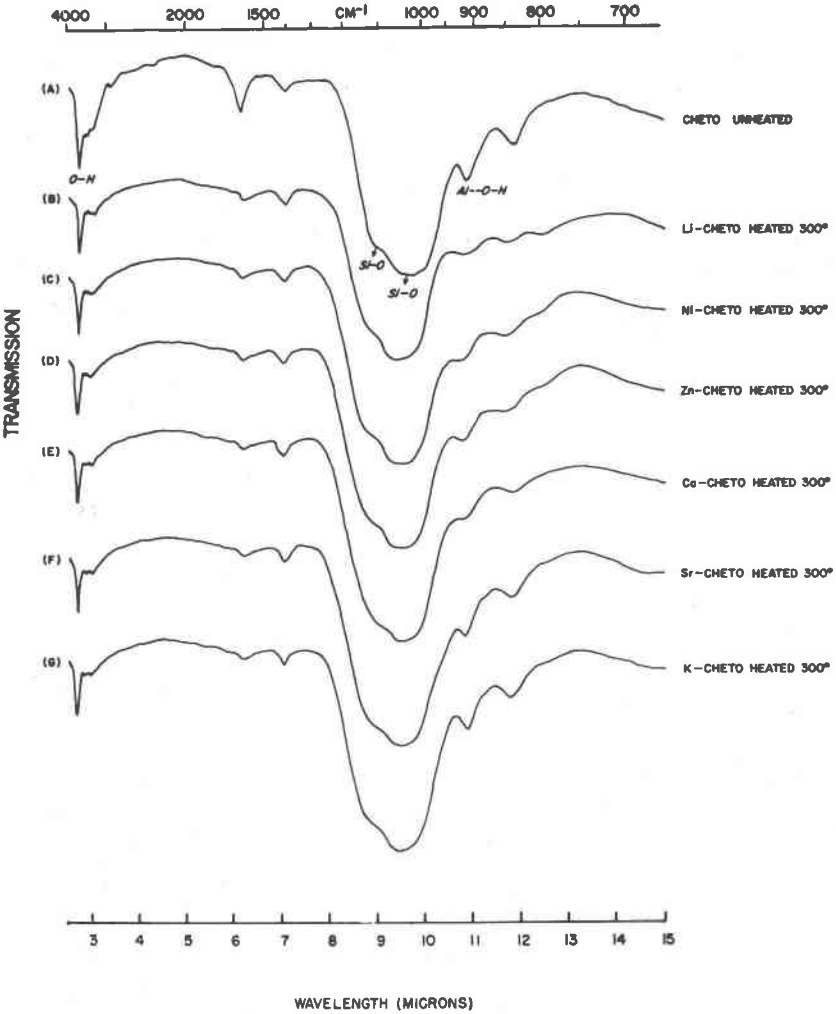

FIG. 1. Typical infrared absorption spectra of dioctahedral montmorillonites.

or smaller ions were present and the magnitude of the intensity change increased with decreasing radius of the interlayer cation; 4) the spectra of clays with ions as large as potassium were unchanged; 5) an additional weak band developed at 810 cm^{-1} on heat-treated specimens containing small ions (Li^+, Mg^{2+}, Ni^{2+}).

Shift of the 1035 cm^{-1} band to higher frequencies and decrease in intensity of the 918 cm^{-1} band indicates that some interlayer cations migrate into the silicate skeleton. *X*-ray diffraction studies support this observation, *i.e.*, irreversible collapse of some layers. Removal of cations bonded to basal oxygens would be expected to shift the 1035 cm^{-1} band to higher frequencies as the Si-O (basal oxygen) bond strength increased. Comparison of spectra of talc and phlogopite (Stubican and Roy, 1961) shows a similar relationship; the large Si-O absorption band centered at about 1000 cm^{-1} occurs at higher frequencies for talc. Intensity changes of the 918 cm^{-1} band (and, perhaps, shift to a lower frequency such as 810 cm^{-1}) would be expected as cations became associated with structural OH groups.

Additional features are: 1) Infrared absorption spectra indicate that ions as large as Ca^{2+} migrate into montmorillonites following heat treatment, whereas *x*-ray studies which employ recognized techniques (Greene-Kelly, 1953) do not suggest this possibility. Apparently, infrared spectra are more sensitive than *x*-ray diffraction patterns to changes described herein. 2) The suggestion that ions as large as Na^{+} and Ca^{2+} migrate into the montomorillonite structure upon heating at 300° C. is not consistent with the presumed size of the empty sites in the octahedral coordination sphere. However, Heller and Kalman (1961) have suggested that Ca^{2+} may fit into these sites after heating to 700° C. 3) Migration of cations of any size into unfilled octahedral sites should tend to shift the 1125 cm^{-1} band to lower frequencies as the metal cations would be associated with four apical oxygens. The absence of this feature may indicate that various interlayer cations, although removed from interlayer positions following heat treatment, do not migrate into unfilled octahedral sites. Additional evidence to support this supposition is A.) lack of increase in the *b*-axis dimension of heat-treated clays, noted by White (1955) and confirmed in this study, B.) reexpansion of Li^{+}-treated dioctahedral clays upon rehydration in a bomb at 250° C., noted by Greene-Kelly (1958) and confirmed in this study, and C.) lack of change in the orientation of the O-H bond axis as reflected in the persistance of the sharp band at approximately 3600 cm^{-1} in Figs. 1a–g. An increase in trioctahedral character should cause a corresponding decrease in the intensity of the O-H stretching vibration as O-H bond axes orient perpendicular to the basal surfaces (Serratosa and Bradley, 1958).

Two absorption bands were noted in the 15–25μ region, located at 525 cm^{-1} and 467 cm^{-1} on spectra of untreated Argentina clays and at 515 cm^{-1} and 463 cm^{-1} on spectra of untreated Cheto clays. The band at approximately 520 cm^{-1} has been attributed to a Si-O-Al^{VI} vibration while the band at approximately 465 cm^{-1} has been attributed to a Si-O vibration (Stubican and Roy, 1961). The band near 520 cm^{-1} was not changed following heat treatment in any instance while the band near

465 cm^{-1} was shifted to 470 cm^{-1} and 467 cm^{-1} with heat-treated Li-Argentina and Li-Cheto clays, respectively. Shift of the Si-O absorption band to higher frequencies may indicate that this vibration is of the type Si-O (basal oxygen). Lack of change in the Si-O-Al^{VI} absorption band further suggests little association of the mobile metal cations with apical oxygens, which is reasonable if there is no migration to unfilled octahedral sites after heating.

No change was noted in the *x*-ray or infrared patterns of any metal cation-trioctahedral clay combination. The location of the proton on the structural OH groups may prevent migration of cations into the hexagonal holes in trioctahedral specimens.

In conclusion, the size of interlayer cations determines the extent to which they migrate into montmorillonites. The extent of migration is affected little by the charge or polarizing power of the cation. Under the conditions employed in this study, the results are consistent with migration of cations from interlayer positions into the hexagonal holes rather than a deeper penetration into the unfilled octahedral sites. Attenuation of H-O--Al vibrations may be a consequence of the proximity of the metal cations, which are located in the hexagonal holes, and the structural OH groups. Lack of association of metal cations with apical oxygens is in accordance with a position in the hexagonal holes. Although cations migrate into hexagonal holes of montmorillonite units at 300° C., they may be difficult to exchange with other inorganic cations at room temperature for at least two reasons, *i.e.*, 1) they are closer to the locus of the charge deficiency and consequently are more tightly held, and 2) the basal oxygen layers of adjacent units are closer, because the cations migrated from the interlayer positions, which would tend to seal off the avenues of exchange.

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NICKELIFEROUS LAZULITE FROM BARABOO, WISCONSIN

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In 1958 the writer collected a specimen of Baraboo Quartzite containing a thin (2 mm) vein of light blue-green lazulite. The locality is about 5 miles south of the town of Baraboo, Wisconsin in Sec. 30, T. 11N., R. 7E. on a talus slope above Devils Lake. Other than representing a new locality for lazulite the specimen was of little interest until a qualitative scan of the emission *x*-ray spectrum indicated significant nickel and cobalt as well as iron.

Only about 200 mg was contained in the whole sample, of which it was possible to separate about 45 mg by hand picking both in reflected and transmitted light. A partial analysis by *x*-ray emission for Fe, Co, Ni was carried out using a lithium borate fusion method, with Cr_2O_3 as an internal standard, for the unknowns and a series of artificially prepared standards. The working curves (scaled intensity ratios *vs.* per cent oxide) were linear over the range of 12% to 0%.

In addition, two lazulites were analyzed for comparison, one of which (Graves Mt., Ga.) has an analysis published in the literature (Pecora and Fahey, 1950). Also an analyzed olivine and W-1 were included as checks. Fe and Co are arbitrarily reported as FeO and CoO. For each of the analyzed samples ferrous and ferric are recalculated to total as FeO for comparison. The results are given in Table 1. Considering all the oxides together the maximum analytical error is ±3%.

The Baraboo lazulite is higher in Ni and Co by an order of magnitude than any member of the lazulite-scorzalite series reported on by Pecora and Fahey (1950). They list semiquantitative results which place Ni in the .0X% to .00X% range, and Co in the range of .00X% to .000X%.

The optical properties (Table 2) were determined in NaD light. When all FeO, NiO, and CoO of the Baraboo sample are calculated to an equivalence in FeO the result is FeO = 2.39% and the implied ratio Mg/Mg+Fe is 0.898. With the exception of the γ index, which is