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INTERLAYER WATER AND SWELLING PROPERTIES OF NATURAL AND HOMOIONIC CORRENSITE

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Abstract—A corrensite-like mineral, from near Borgotaro, Parma (Taro Valley, Italy), was studied by X-ray powder diffraction (XRD) and thermal analysis at different temperatures and water vapor pressures in the natural state and after exchange with ten different cations. In the natural state the mineral is characterized by a basal reflection at ~29 Å shifting to ~24 Å on heating and to ~32 Å by glycerol treatment. The dehydration features of the homoionic minerals show that the stability of the complex of water, compensating cation, and silicate framework depends on the electrostatic energy of the water dipole in the cation field, similarly to smectite.

XRD of the exchanged mineral shows a basal reflection of ~58 Å particularly in the NH_4-, Rb-, and Ba-exchanged states. This value suggests a structure characterized by a regular sequence of silicate layers with different layer charge, that generally results in a *c* periodicity of ~29 Å, but which shifts to ~58 Å, and perhaps higher values, because of small differences in the compensating cation layers.

Key Words—Chlorite, Corrensite, Dehydration, Exchange cations, Smectite, Water, X-ray powder diffraction.

INTRODUCTION

Several minerals from near Borgotaro (Taro Valley) were described as regular chlorite/saponite, chlorite/vermiculite, and/or chlorite/swelling-chlorite interstratifications by Alietti (1957a, 1957b, 1959). Regular interstratification of swelling and non-swelling components, such as found in corrensite or corrensite-like minerals, are well known (Bailey *et al.*, 1982; Brigatti and Poppi, 1984a). It is generally accepted that the non-swelling component of such materials is similar to a chlorite layer, but some confusion exists in the literature regarding the swelling component because of the different names (saponite, vermiculite, swelling-chlorite, or undefined smectite) that have been used to describe it (Lippmann, 1954; Bradley and Weaver, 1956; Martin Vivaldi and MacEwan, 1960; Lippmann and Johns, 1969; Bailey *et al.*, 1982). The distinction between the different types of swelling components reported for corrensites and corrensite-like materials is based on the layer charge and hence on the chemical composition of the 2:1 silicate layer (Brindley and Brown, 1980).

Thus, in corrensite, more attention has been paid to interlayer chemical features of the swelling component than to those of the brucitic layers of the non-swelling component because of its charge variability. A regular interstratification involves the presence of two components (swelling and non-swelling in corrensite), each with an imperfect structure balanced by the imperfections of the neighboring layers, so that the amount of layer charge depends on the charge unbalance of the whole of the interstratification. In corrensites the chemical variability of the non-swelling component is greater than that of the swelling component (Brigatti and Poppi, 1984a), a situation that does not allow reliable layer-charge values to be determined for the swelling layer. In addition, Veniale and Van der Marel (1969) showed that infrared (IR) and thermal analyses cannot be used to characterize the swelling component of corrensite.

From investigations of the interlayer configuration of montmorillonite, hectorite, saponite, and vermiculite (Graham *et al.*, 1964; Calvet, 1972; Hougardy *et al.*, 1976; Prost, 1976; Suquet, 1977; Suquet *et al.*, 1977; Poinsignon and Cases, 1978; Fornes, 1979), the equilibrium water content appears strongly dependent on the temperature and water vapor pressure imposed on the mineral and on the nature of the compensating cation. Detailed studies of the interaction of H_2O, the compensating cation, and the silicate framework show that the stability of the complex at a given temperature and water vapor pressure depends on the magnitude and site of the layer charge and on the electrostatic energy of the water dipole in the cation field (Del Pennino *et al.*, 1981). The XRD features of a homoionic smectite with respect to the interlayer water can, therefore, be used to characterize the smectite itself.

Thus, the behavior of interstratification with respect to hydration can provide useful information about the features of the interstratification. In the present study, a regular interstratification of chlorite and smectite from near Borgotaro (Taro Valley) was examined, both in

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the natural state and in the exchanged state at different temperatures and water vapor pressures to characterize such interlayer configurations.

EXPERIMENTAL

Material

The Borgotaro sample studied was described by Brigatti and Poppi (1984b). Its structural formula is:

$$(Ca_{0.34}Na_{0.06}K_{0.01})$$
$$(Mg_{7.65}Fe^{2+}_{0.55}Fe^{3+}_{0.44}Al_{0.40}Mn_{0.02}Ti_{0.06})^{VI}$$
$$(Si_{6.06}Al_{1.94})^{IV}O_{20}(OH)_{10}$$

Methods

Basal X-ray powder diffraction (XRD) spacings, d(00*l*), were measured on oriented samples with a Philips diffractometer (Ni-filter, CuKα radiation) using quartz and $C_{14}H_{29}OH$ as standards at controlled temperatures and water vapor pressures. The temperature (T) was raised in 20°C increments from 20° to 400°C, and the water vapor pressure (p/p_s) was raised in steps of about 0.10 p/p_s from 0.05 to 0.90 (at 22°C). Data were taken at each temperature and pressure after equilibrium had been reached.

Simultaneous thermogravimetric (TGA) and derivative thermogravimetric analyses (DTG) were carried out with a DuPont thermal analyzer on 10 mg of powder at a heating rate of 20°/min in air and in argon gas at a flowing rate of 50 ml/min.

Homoionic samples of Li, Na, K, Rb, Cs, NH_4, Mg, Ca, Sr, Ba, and La were obtained by shaking the mineral in Teflon tubes filled with repeatedly renewed 1 N solutions of superpure chloride reagents at ~40°C and at pHs between 7.5 and 8. The excess chloride solution was removed by repeatedly washing with distilled water. All solid and solution products were analyzed to check the completeness of the ion exchange and/or for evidence of hydrolysis.

RESULTS

X-ray powder diffraction (XRD) measurements

The XRD behavior of the natural and homoionic minerals, at controlled temperature and water vapor pressure (p/p_s), is shown in Figure 1. The mineral exhibits several orders of basal reflections both in the natural and the exchanged state. The shift of the basal reflections as a function of ethylene glycol solvation and p/p_s values demonstrates the swelling nature of the mineral, whereas the contraction of the *c* dimension on heating excludes the presence of swelling-chlorite layers in the structure.

In many products a basal reflection at ~58 Å was noted, particularly after the starting sample was exchanged with Rb, Ba, or NH_4. For the Rb-exchanged material, the reflection was best observed at p/p_s 0.50–0.90 (T = 22°C); and for the Ba-exchanged mineral, after heat treatment. For NH_4-exchanged mineral, it tended to disappear on heating. The reflection at ~58 Å was sharp or in the form of a broad band. When it was sharp, it was always accompanied by several sharp basal reflections suggesting that the layer packing was affected by the nature of the compensating cation.

The behavior of the mineral at different p/p_s values and temperatures as a function of the compensating cation can be summarized as follows: K, Rb, and Cs caused the largest contraction at $p/p_s = 0.10$ (T = 22°C), whereas Na, La, Sr, Ca, Mg, and Ba showed three different *c* dimensions at $p/p_s = 0.30$, T = 22°C; at $p/p_s = 0.10$, T = 22°C; and after heat treatment at 200°C. In every sample the collapsed state was reached at ~200°C, but the contraction was always reversible (irreversibility occurred only after heating to 600°C for several hours). XRD patterns taken at room temperature after the sample had been heated at a given temperature between 100° and 500°C commonly did not reveal any contraction because of the immediate rehydration at room conditions.

Assuming a regular interstratification of chlorite and smectite-like layers with $c = 29$ Å (14 + 15 Å), the d(002) and d(003) spacings at different values of p/p_s (0.50 and 0.05) and temperature (22 and 300°C) appeared to be a function of the ionic radius of the interlayer cations (Figure 2a). At $p/p_s = 0.50$, T = 22°C, the ionic radius value of 1.3 Å was discriminant; below this value d(002) and d(003) were ~14.6 and ~9.8 Å, respectively (Li = 14.5 and 9.65 Å; Na = 14.1 and 9.4 Å); above this value d(002) and d(003) were ~13.5 and ~9.0 Å, respectively. The ionic radius value of 1.3 Å gave rise to two sets of samples also at $p/p_s = 0.05$, T = 22°C. Below 1.3 Å, d(002) and d(003) were ~13.5 and ~8.85 Å, respectively (Na = 13.0 and 8.4 Å); above this value the spacings were not constant but proportional to the ionic radius. At 300°C (collapsed state), the ionic radius value of 1.3 Å was also an important discriminant factor; below this value, d(002) and d(003) were constant (~12.3 and ~8.1 Å, respectively); above this value, both d(002) and d(003) increased with increasing ionic radius.

The d(002) and d(003) spacings at different p/p_s values and temperatures were studied also as a function of the electric field (E) generated by the interlayer cation (Del Pennino *et al.*, 1981). The dependence of spacings on the electric field, is shown in Figure 2b. Assuming the spacing variation to be due to the swelling component, the cations with $E > 3.0$ $Vm^{-1} \cdot 10^{10}$ retained two H_2O molecule layers in the interlayer sheets at $p/p_s = 0.50$ (T = 22°C) and one at $p/p_s = 0.05$ (T = 22°C), whereas the cations with $E < 2$ $Vm^{-1} \cdot 10^{10}$ retained only one H_2O molecule layer at $p/p_s = 0.50$, (T = 22°C) and none at $p/p_s = 0.05$ (T = 22°C). The intermediate behavior of Na (and perhaps Li) can be explained considering that E was close to the discriminant value. The spacing in the collapsed state (T =

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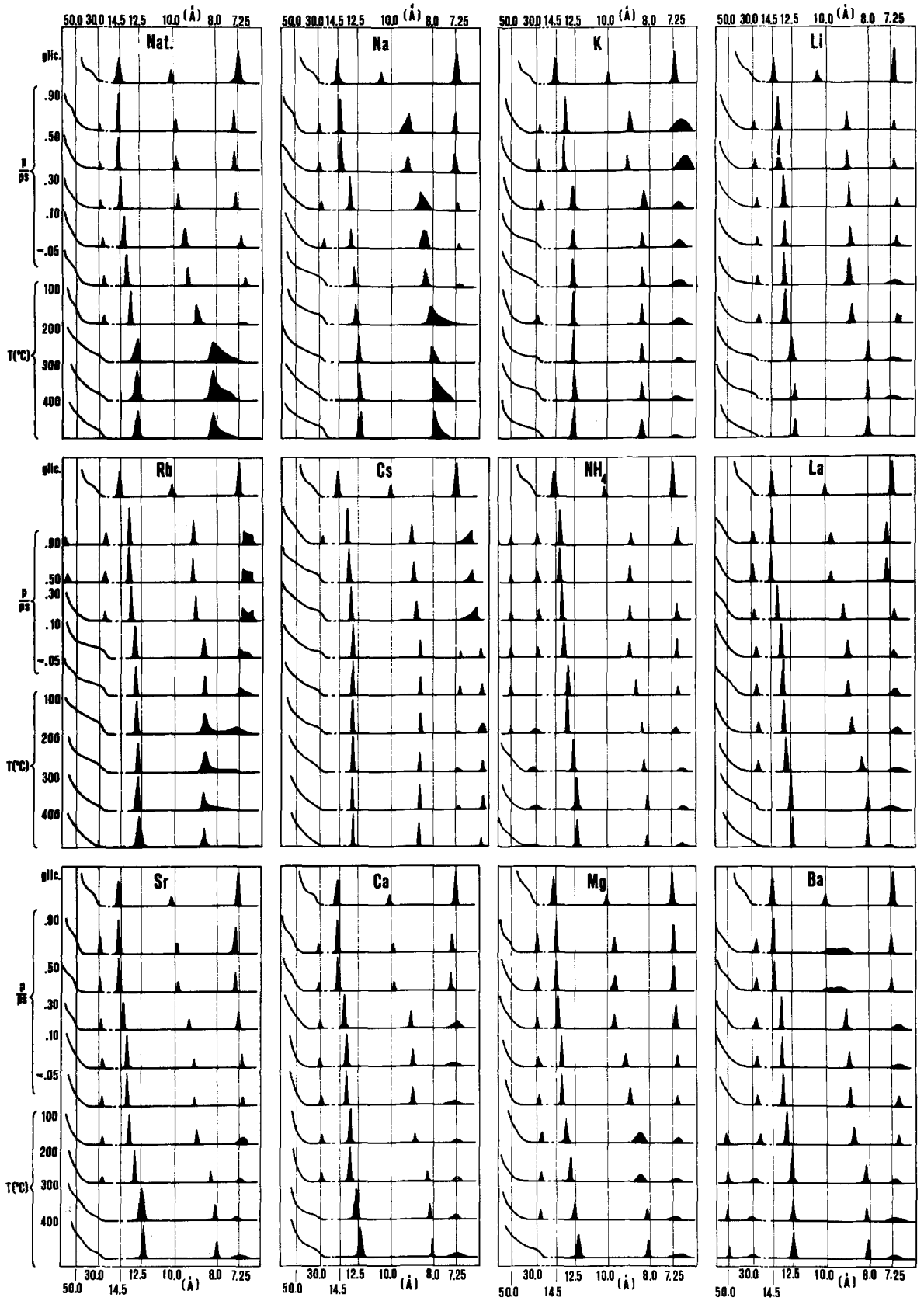


Figure 1. X-ray powder diffraction behavior of natural and cation-exchanged corrensite at different environmental conditions (CuKα radiation).

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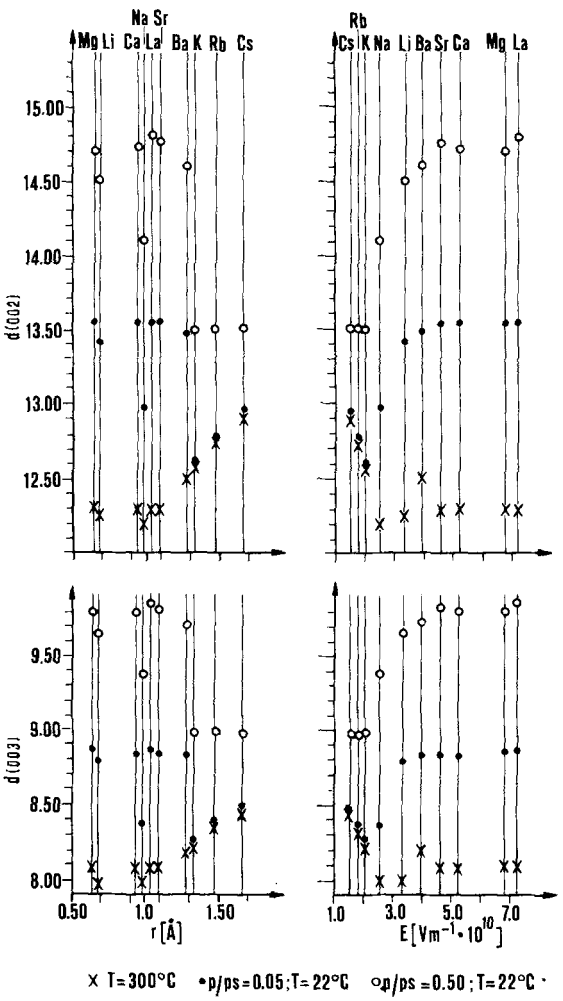


Figure 2. Plot of the experimental values of the basal reflections d(002) and d(003) vs. (a) ionic radius and (b) electric field (E) acting on a solvation water molecule at different p/p_s values and temperatures.

300°C) was not correlatable to the electric field of the compensating cation.

This set of data shows that the interlayer configuration of the interstratification was similar to that described by Del Pennino *et al.* (1981) for montmorillonites. The exchangeable cations were bound to the layer charge of the smectite component; in particular the dehydration features of the homoionic mineral showed that the stability of the complex of water-compensating cation, and silicate framework depended on the electrostatic energy of the water molecule dipole in the cation field. Furthermore, the swelling component of the interstratification was likely a smectite with a well-defined interlayer configuration.

Thermal analysis

TGA and DTG tracings of the natural and exchanged minerals are shown in Figure 3. The thermal effects below 300°C were related to the chemical nature of the interlayer cation. A single effect for the monovalent cations and a double effect for divalent cations were noted, behavior that is typical of smectite (Mackenzie, 1972). In particular, the thermal effect at ~200°C for the Mg-treated mineral suggests saponite-like layers rather than vermiculite layers (Brigatti and Poppi, 1984b).

The dehydroxylation behavior was mainly uniform and did not seem to be affected by the interlayer population. The thermal effect at ~600°C, however, appeared to be broader for monovalent interlayer cations. A plot of the weight loss between 20° and 300°C vs. electric field (Figure 4) shows that the water loss below 300°C was dependent on the electric field which acted on the solvation water molecule; however, the weight loss at ~800°C (linked to OH loss from the octahedral layer) was the same for all interlayer cations.

The thermal analyses suggest that the interstratification components were chlorite- and smectite-like layers: in particular the brucitic layers of the former did not seem to be affected expressly by the exchange treatments.

DISCUSSION AND CONCLUSIONS

The experimental data show that two components of the Borgotaro interstratification can be described as chlorite and smectite. The interstratification is due mainly to the nature of chemical populations in the different coordination sites and thus to the distribution of the electric charges in the interlayer sites. The Borgotaro environment is characterized by a high mobilization of elements such as Mg, Fe, Al, and Si (Brigatti and Poppi, 1984b) perhaps because of hydrothermal (and/or low-grade metamorphic) alteration. The mineral analyzed in this work (like other phases from the same area described in literature) can be considered as a mineralogical phase typical of a genetic environment whose chemical and physical factors do not allow the formation of structures with definitely non-swelling layers (chlorite) and/or swelling layers (smectite). Thus, the mineral, as the other materials described by Alietti (1957a, 1957b, 1959) can be defined as corrensite (as in Bailey, 1982), wherein the smectitic component includes both saponite and vermiculite with a continuous range of layer-charge variation. For those reasons, the identity of the swelling component of corrensite is better defined by physical features such as H_2O-cation interaction. Such interaction is due to their definite correlations with the structural arrangement within the interlayer sites of the swelling component.

In the natural state, the Borgotaro mineral exhibited a structure characterized by a c dimension of ~29 Å; whereas, after cation-exchange treatments, the c dimension generally doubled. In particular, the effect of the nature of the compensating cation on the intensity of the ~58 Å reflection illustrates the tendency of the

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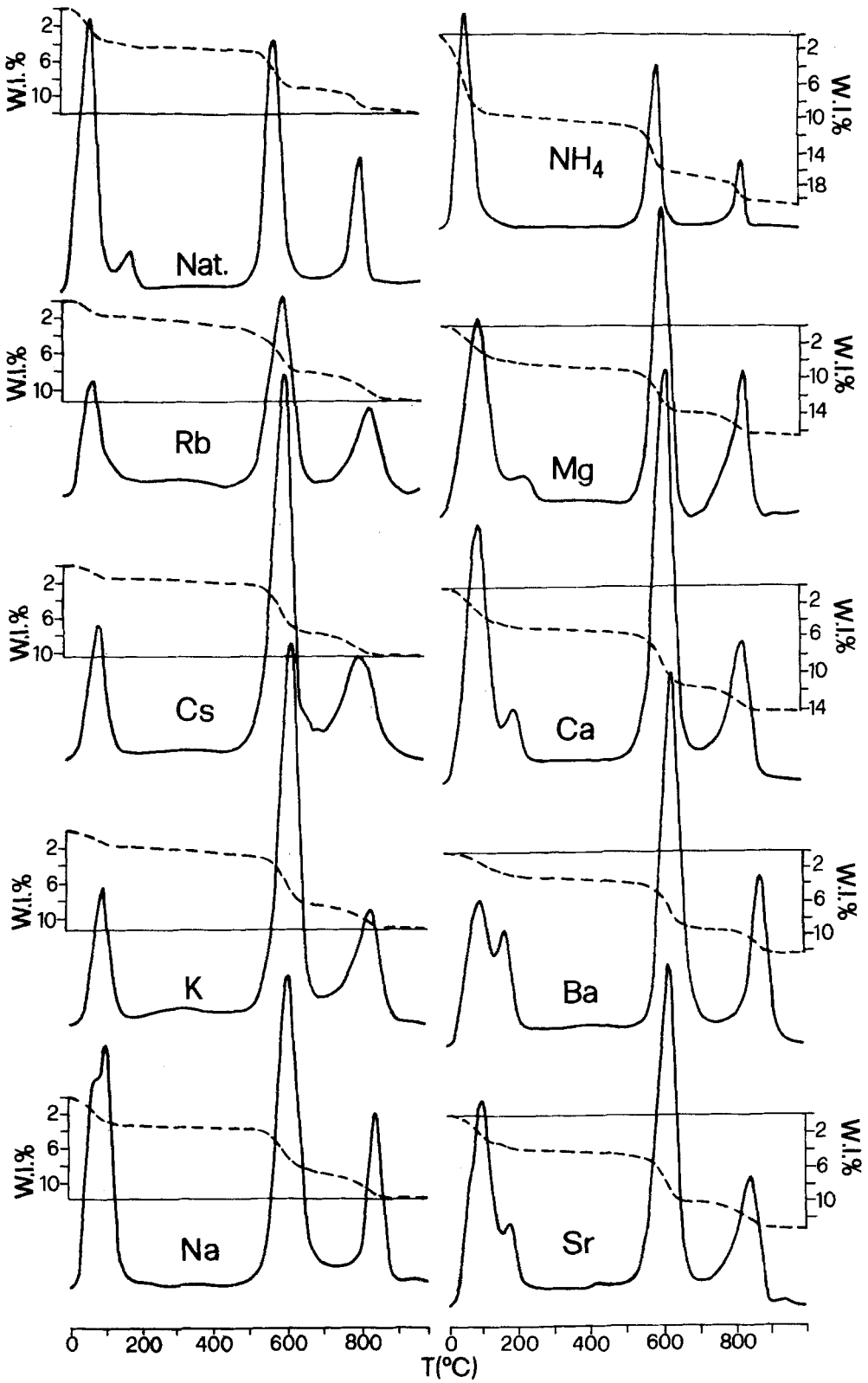


Figure 3. Thermogravimetry (solid line) and derivative thermogravimetry (dashed line) tracings of natural and cation-exchanged corrensite (heating rate = 20°C/min); W.l. = weight loss.

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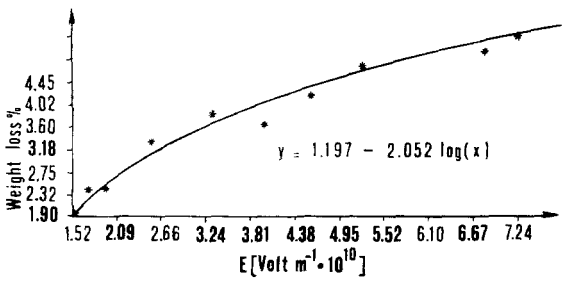


Figure 4. Weight loss below 300°C vs. electric field (E) acting on a solvation water molecule.

interstratification to reach electrical balance by a sequence of several talc-like layers with different charge unbalance. The prevalence of Mg over Ca + Na in the genetic environment (Brigatti and Poppi, 1984b) likely favored the formation of brucitic layers because of the tendency of Mg to fit into octahedral coordination and hence form chlorite-like structural units. The charge of the talc-like layers and/or the insufficient activity of Mg and/or OH probably precluded the formation of a perfect chlorite structure. The charge balance was due to the alternate superposition of different units, some of which were similar to chlorite (and hence non-swelling, although not perfectly electrically balanced) and others of which that possessed variable charge deficits (and hence swelling). The different units were arranged in a structure with perfect electrical balance if the interlayer configurations are also considered. The main periodicity of such a structure appears to be ~29 Å, but smaller differences of layer charges (perhaps of the swelling component) as emphasized by the XRD behavior of the exchanged forms, could shift this value to ~58 Å and perhaps to higher values.

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Резюме—Коррензито-подобный минерал из окрестности Борготаро, Парма (долина Таро, Италия) исследовался при помощи рентгеновской порошковой дифракции (РПД) и термального анализа при различных температурах и давлениях водяного пара в натуральном состоянии и после обмена с десятью разными катионами. В натуральном состоянии минерал характеризуется основным отра-

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жением при ~29 Å, перемещающимся к ~24 Å при нагревании и к ~32 Å при обработке глицерином. Особенности дегидратации гомоионных минералов показывают, что стабильность комплекса воды, компенсационного катиона, и силикатной решетки зависит от электростатической энергии диполя воды в катионном поле, как и в случае смектита.

РПД обмененного минерала показывает, что основное отражение появляется при ~58 Å, в частности в условиях обмена с NH_4, Rb, и Ba. На основании этой величины можно предположить структуру, характеризующуюся регулярной последовательностью силикатных слоев с различными зарядами слоев, что в результате дает величину *c* периодичности ~29 Å, но которая перемещается к ~58 Å и к возможно более высоким величинам вследствие малых разниц в слоях компенсационных катионов. [E.G.]

Resümee—Ein Corrensit-ähnliches Mineral, aus der Nähe von Borgotaro, Parma (Tarotal, Italien) wurde mittels Röntgenpulverdiffraktometrie (XRD) und Thermoanalyse bei verschiedenen Temperaturen und Wasserdampfdrucken in natürlichem Zustand und nach Austausch mit 10 verschiedenen Kationen untersucht. Im natürlichen Zustand ist das Mineral durch einen Basisreflex bei etwa 29 Å charakterisiert, der sich durch Erhitzen nach etwa 24 Å verschiebt und durch Glycerin-Behandlung nach etwa 32 Å. Die Dehydratationseigenschaften der monoionischen Minerale zeigen, daß die Stabilität der Wasserkomplexe, der Gegenkationen, und des Silikatgerüstes von der elektrostatischen Energie des Wasserdipols im Kationenfeld abhängt, ähnlich wie bei Smektit.

XRD-Daten des ausgetauschten Minerals zeigten einen Basisreflex bei etwa 58 Å vor allem nach Austausch mit NH_4^+, Rb^+, und Ba^{2+}. Dieser Wert deutet auf eine Struktur hin, die durch eine regelmäßige Abfolge von Silikatschichten mit unterschiedlichen Schichtladungen charakterisiert ist, die im allgemeinen zu einer *c*-Periodizität von etwa 29 Å führt, die aber aufgrund kleiner Unterschiede in den ladungsausgleichenden Kationenschichten nach etwa 58 Å oder vielleicht höheren Werten verschoben wird. [U.W.]

Résumé—Un minéral semblable à la corrensite, de près de Borgotaro, Parma (Vallée du Taro, Italie) a été etudié par la diffraction des rayons-X (XRD) et par analyse thermale à de différentes températures et pressions de vapeur d'eau à l'état naturel et après échange avec dix cations différents. A l'état naturel le minéral est caractérisé par une réflection basale de ~29 Å se déplacant vers ~24 Å lors de l'échauffement et vers ~32 Å après un traitement au glycérol. Les caractéristiques de déshydratation des minéraux homoioniques montrent que la stabilité du complexe eau, cation compensateur, et charpente de silice dépend de l'énergie électrostatique du dipole d'eau dans le champ de cations de manière semblable à la smectite.

XRD du minéral échangé montre une réflection de base à ~58 Å, particulièrement dans les états d'échange avec NH_4, Rb, et Ba. Cette valeur suggère une structure caractérisée par une séquence régulière de couches de silice avec une charge de couche différente, ce qui résulte généralement en une périodicitée *c* de ~29 Å, mais qui se déplace vers ~58 Å, et peut être vers des valeurs plus élevées, à cause de petites différences dans les couches de cations compensatrices. [D.J.]

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