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Evidence for the inclusion of Al saponite in the chlorite-like group of minerals. Nota II. Thermal analysis and IR spectroscopy

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Mineralogia. — *Evidence for the inclusion of* Al *saponite in the chlorite-like group of minerals.* Nota II. *Thermal analysis and* IR *spectroscopy* (*). Nota di NORIS MORANDI e LUCIANO POPPI, presentata (**) dal Socio P. GALLITELLI.

RIASSUNTO. — Vengono riportati i risultati delle analisi termiche (DTG e DTA) e di spettroscopia di assorbimento IR condotte su campioni di clorite, interstratificati clorite–saponite e Al saponite, raccolti da un unico affioramento di serpentinite (Casermone, Valle F. Taro, Parma), recante manifesti segni di idrotermalismo e di degradazione superficiale. Questi risultati hanno fornito elementi per individuare in tutti i campioni una unità strutturale di tipo brucitico, interlaminata con le unità micacee e progressivamente idratata; hanno inoltre permesso di ordinare i campioni secondo una successione continua di minerali strutturalmente e chimicamente inseribili tra la Mg clorite e la saponite. Con questo contributo si propone quindi di considerare la Al saponite non più come termine delle montmorilloniti triottaedriche ma come membro del gruppo dei minerali tipo clorite.

INTRODUCTION

In a previous work (Morandi and Pirani, 1976) the results of X-ray and chemical analysis of six samples of weathered serpentinite collected at Casermone, Taro valley (Italy) were reported. These show that the Al saponite, in which the tetrahedral-octahedral ratio lies between 2 : 1 : 1 and 2 : 1, although nearer the latter, may be regarded as a stable member of the magnesium chlorite-saponite group.

The mineralogical and chemical composition of the samples is reported by Morandi and Pirani (1976). Differential thermal analysis and infra-red absorption studies of the same samples were made to confirm the presence of a variously hydrated layer of hydroxide with a brucitic structure. A DuPont apparatus (DTA and DTG) and a Grubb Parson Spectrometer (IR spectroscopy) were used in this study.

RESULTS

The DTG curves for the six samples, arranged on the basis of increasing H_2O^- and decreasing H_2O^+ content, are reported in fig. 1. In all samples most of the H_2O^- was lost around 100 °C, and a small amount of residual, interleaved water at and above 200 °C (1).

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(1) The higher rate of temperature increase in DTG (50 °C per minute) give higher reaction temperatures than in DTA (10 °C per minute).

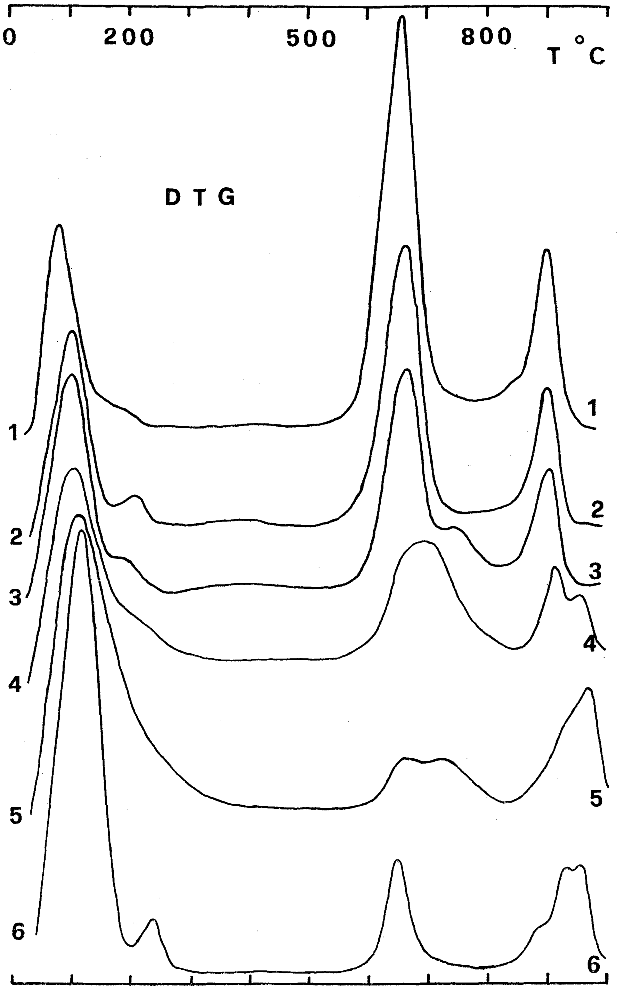

Fig. 1. - DTG curves. Tests carried out with a heating speed of 50 °C/min.

A peak at 650°-670 °C is attributed to the loss of brucitic hydroxyls and its intensity decreases regularly from chlorite (no. 1) to Al saponite (no. 6). The broad reflections at about 700°-740 °C in samples no. 3, 4 and 5 occur when the X-ray results show randomly interstratified chlorite and Al saponite to be present.

The loss of hydroxyls from the mica-like layer occurs at 900 °C in the chloritic samples (no. 1, 2 and 3) and at 930°-960 °C for the samples (no. 4, 5 and 6) in which the Al saponite is dominant. The double effect in sample no. 4 is ascribed to the two co-existing minerals (partially hydrated chlorite and Al saponite). The Al saponite (no. 6) shows highly characteristic effects due to the high crystallinity of the material, and the two peaks above 900 °C are presumably due to the high Al content of the mica-like layer.

The DTA and derivative curves (fig. 2) show that the dehydration reaction and the loss of hydroxyls from the brucitic layer are complementary. The

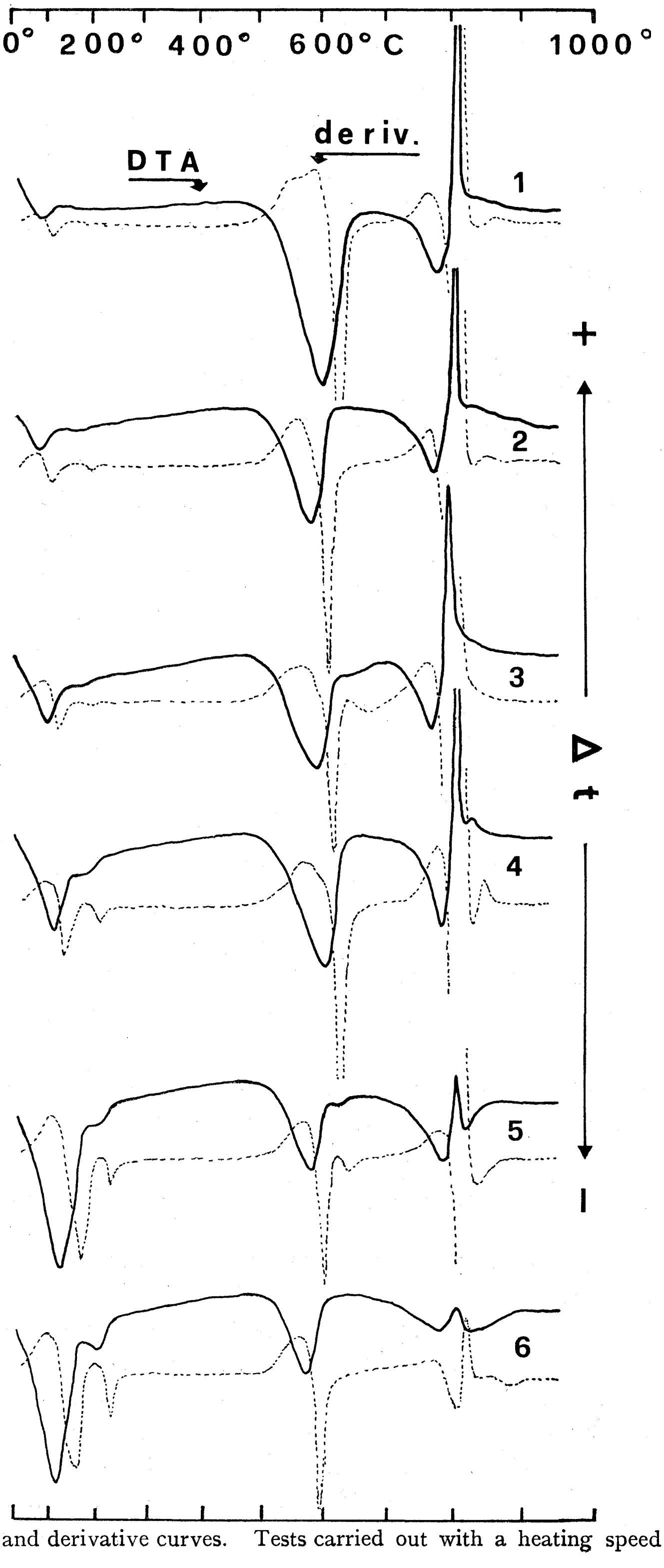

Fig. 2. – DTA and derivative curves. Tests carried out with a heating speed of 10 °C/min.

intensity of the exothermic peak decreases simultaneously with the decrease in chlorite, i.e. as the amount of aluminium decreases. The derivative curves help to explain the broad DTA reactions which closely follow those of the DTG.

Thermal analysis results can be correlated with those of X-ray analysis and though they provide useful additional data, in this case they do not lend themselves to the drawing of conclusions on the crystal-chemistry of the samples.

Infra-red spectroscopy, on the other hand, is particularly valuable in providing information on chemical substitutions in layer silicates and the arrangement of cations in their structure. IR analyses were made on both untreated samples and others which had been heated (100°, 200°, 500 °C for 20 hours and 700 °C for 20 minutes) to eliminate the broad water absorption pattern and the brucitic hydroxyls.

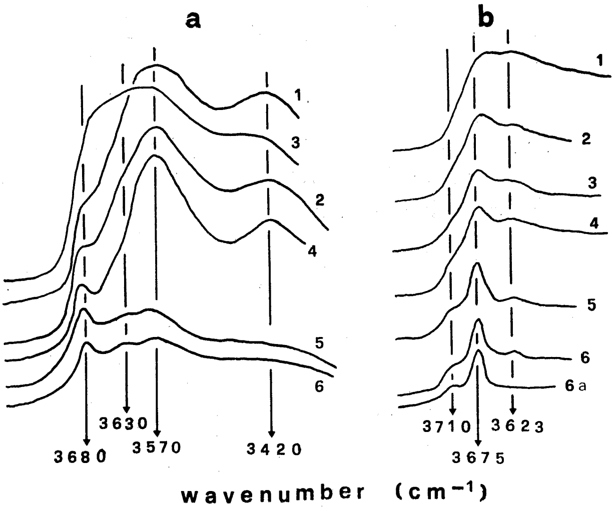

Fig. 3. – IR spectra of: *a*) samples heated at 200 °C for 20^h; *b*) samples heated at 700 °C for 20 min.

The hydroxyl stretching vibrations of the samples when heated to 200 °C (fig. 3 a) show three main absorption effects at about 3680, 3570 and 3420 cm^{-1} respectively. The first is due to the inner hydroxyl group of the mica component and the last two to the interlayer hydroxyl sheets of the minerals. In samples no. 1 and 3 the high intensity of the two lower frequency bands partially masks the first effect. After heat treatment at 700 °C (fig. 3 b) and the consequent first dehydroxylation reaction, the absorption effects are at about 3675 and 3623 cm^{-1}. Due to the loss of the less-strongly bonded hydroxyls of the mica-like layer, the second band disappears after heating at 800 °C for 20 minutes (fig. 3 b, no. 6 a). A broad absorption effect at 3710 cm^{-1} increases from sample no. 3 to sample no. 6.

Taken in conjunction with the chemical formulae (Morandi and Pirani, 1976, Tables 2 and 3) these results show that:

1) hydroxyls in a brucitic arrangement are present in all six samples and the amount decreases from chlorite (no. 1) to Al saponite (no. 6);

2) the Al substitution in the interlayer hydroxyl sheets decreases toward the saponitic samples, as shown by the intensity of the 3420 cm^{-1} absorption effect;

3) there is regular increase of aluminium in the mica-like layer, as shown by the behaviour of the 3623 cm^{-1} band in the samples heated to 700 °C;

4) the broad 3710 cm^{-1} absorption band of the material heated to 700 °C may be related to tetrahedral substitutions as it is absent when the Al [4] content is high (sample no. 1) and increases when Al [4] is low as in the saponite-like samples. This absorption band may also be correlated with a new structural arrangement of the mica-like layer following the complete dehydroxylation of the brucitic sheet;

5) the changes in intensity of the hydroxyl absorption bands follow closely the chemical formulae constructed on the basis of the genetic and crystal-chemical analogies between chlorite and saponite (Morandi and Pirani, 1976).

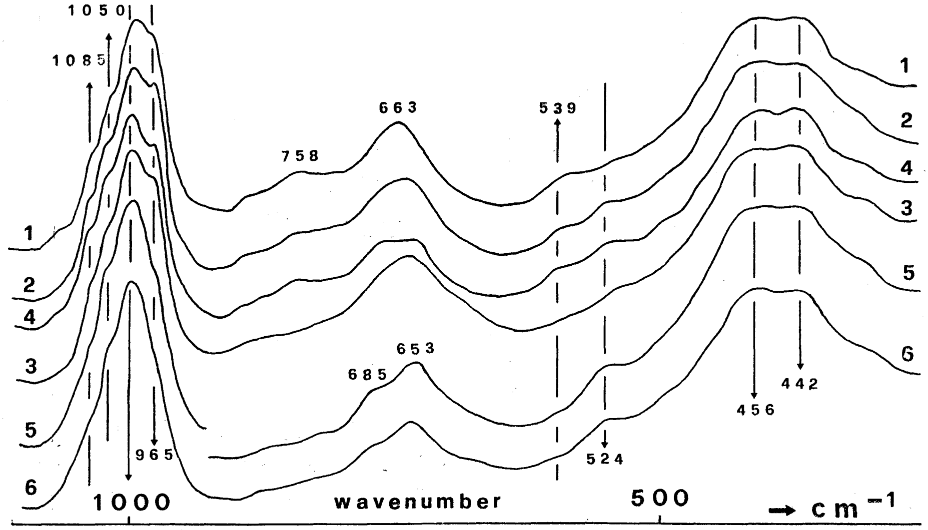

Fig. 4. - IR spectra of samples heated at 200 °C for 20^h.

The IR spectra in the 1200-400 cm^{-1} interval (fig. 4) show that the behaviour of the lattice vibrations in all six samples is very similar and that the main Si—O absorption band at 1000 and 450 cm^{-1} are only slightly affected by tetrahedral substitutions.

The 965 cm^{-1} absorption band, which disappears with heating to 700 °C, is ascribed to OH libration in the brucitic layer: its intensity changes with OH content in the chemical formula. The broad bands at 650–670 cm^{-1} are due to the libration of hydroxyls in the 2 : 1 layers and the hydroxide sheets: their frequency increases slightly with Al [6] content and the intensity is reduced at 700 °C. Sample no. 4 with its two co-existing minerals, containing different amounts of Al, has two absorption bands at 670 and 651 cm^{-1}, respectively.

CONCLUSIONS

X-ray and thermal analysis, the infra-red absorption and chemical data offer evidence of: 1) the existence of a highly hydrated brucitic sheet in the Al saponite lattice and 2) the existence of a continuous sequence of minerals which structurally and chemically lie between Mg chlorite and true saponite.

Our results and the study of Morandi and Pirani (1967) suggest the inclusion of Al saponite in the chlorite-like group of minerals rather than in the trioctahedral montmorillonite group.

REFERENCES

MORANDI N. and PIRANI R. (1976) – *Evidence for the inclusion of* Al *saponite in the chlorite-like group of minerals.* Nota I. *X-ray and chemical analyses*, «Atti Acc. Naz. dei Lincei, Rend. Cl. Sc. fis. mat e nat.», *61*, 284–292.