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Evidence for the inclusion of Al saponite in the chlorite—like group of minerals. I: X—ray and chemical analysis

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Mineralogia. — *Evidence for the inclusion of* Al *saponite in the chlorite-like group of minerals.* I: *X-ray and chemical analysis* (*).

Nota (**) di NORIS MORANDI e ROSSANA PIRANI, presentata dal Socio P. GALLITELLI.

RIASSUNTO. — Vengono riportati i risultati di uno studio termico-roentgenografico e chimico su campioni di clorite, saponite, interstratificati clorite-saponite raccolti da un unico affioramento di serpentinite (Casermone, Valle F. Taro, Parma), recante manifesti segni di idrotermalismo e di degradazione superficiale. L'andamento della variazione di riflessi basali ai raggi X, registrato durante il processo di disidratazione e deossidrilazione progressiva dei singoli campioni, e le relazioni scaturite dal confronto tra il chimismo di questi hanno permesso di ipotizzare uno stretto legame genetico e cristallochimico tra i minerali normalmente definiti Mg cloriti, interlaminati clorite-saponite, Al saponite e saponite. La Al saponite, in cui il rapporto strati tetraedrici/strati ottaedrici sta fra 2 : 1 : 1 e 2 : 1 ed è spostato verso il secondo, viene considerata come termine di miscela di una serie a termini estremi clorite e saponite. Su questa base la saponite può essere vista come il prodotto di un processo di idratazione dello strato brucitico di un reticolo tipo clorite in cui si verifica una diminuzione di Al [4], Al [6], Fe, OH e del numero di posizioni ottaedriche occupate.

INTRODUCTION

Aluminium saponite is accepted as a trioctahedral member of the 2 :1 layer silicates, occupying a position in the magnesium group of the montmorillonite (smectite) series (Mongiorgi e Morandi, 1970). Unlike a true saponite, it contains aluminium in both the tetrahedral and the octahedral positions.

This paper shows that Al saponite occupies a place intermediate between the 2 : 1 and 2 : 1 : 1 trioctahedral layer silicates.

MATERIALS AND METHODS

In order to study its secondary minerals, forty samples from an outcrop of a hydrothermalized and weathered serpentinite were collected at Casermone, Taro valley, in the Northern Apennines (Italy). The samples contain serpentine (chrisotite and lizardite), talc, chlorite, interstratified minerals and saponite (Alietti, 1959). These last three minerals were the principal component of the fractions of particle size 0.1 μm. By means of a preliminary diffrac-

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tomectric analysis two chlorites (no. 1 and 2), two interstratified minerals (no. 3 and 4) and two saponites (no. 5 and 6) were selected for detailed examination.

Oriented specimens were prepared on a silica glass slide for X-ray analysis with a Philips diffractometer. Samples were examined untreated, after glyceration and while being heated directly in the specimen holder on a flat heating stage (Morandi *et al.*, 1976). This enabled samples to be examined at selected temperatures, maintained for a minimum of 5′ and controlled to ± 5 °C. Fig. 1, 2, 3, 5, 6 and 7 report the changes in X-ray patterns which occurred at particular temperatures.

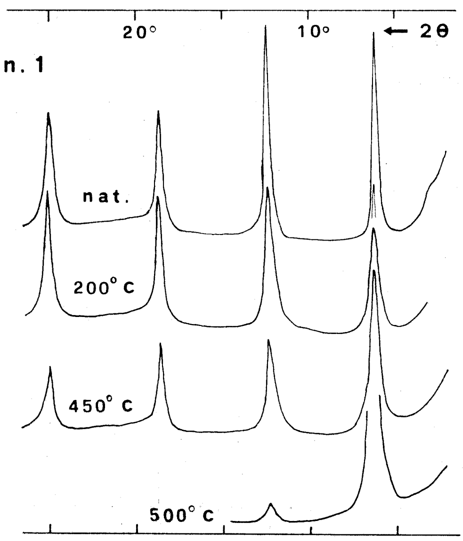

Fig. 1. – X-ray diffractograms of natural and heated sample no. 1. Oriented specimen.

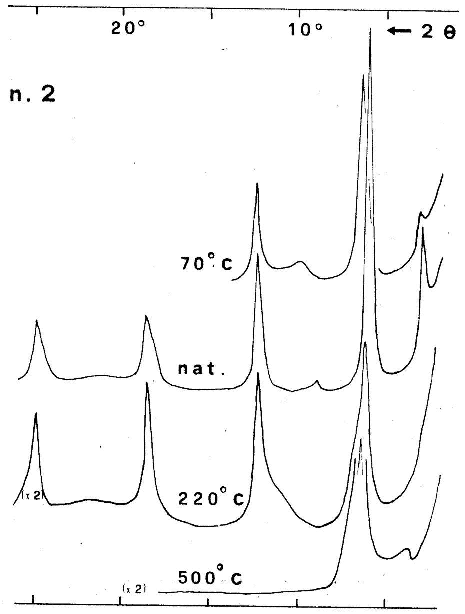

Fig. 2. – X-ray diffractograms of natural and heated sample no. 2. Oriented specimen.

The chemical composition was obtained by analysis of fused samples using X-ray spectrography (Norrish and Hutton, 1969).

X–RAY RESULTS

The main characteristics of the samples are as follows:

no. 1 – unswelling material, showing four basal reflections as in chlorite (fig. 1). The intensity of the first and second peaks is reduced between 150° and 200 °C. The first peak increases between 430° and 500 °C and at the some time all other peaks disappear;

no. 2 – partially swelling material which shows six basal reflections (fig. 2) as in randomly-interstratified minerals. Above 50 °C the peaks broaden and reduce in intesity; above 200 °C, when H_2O^- is lost, the mineral displays

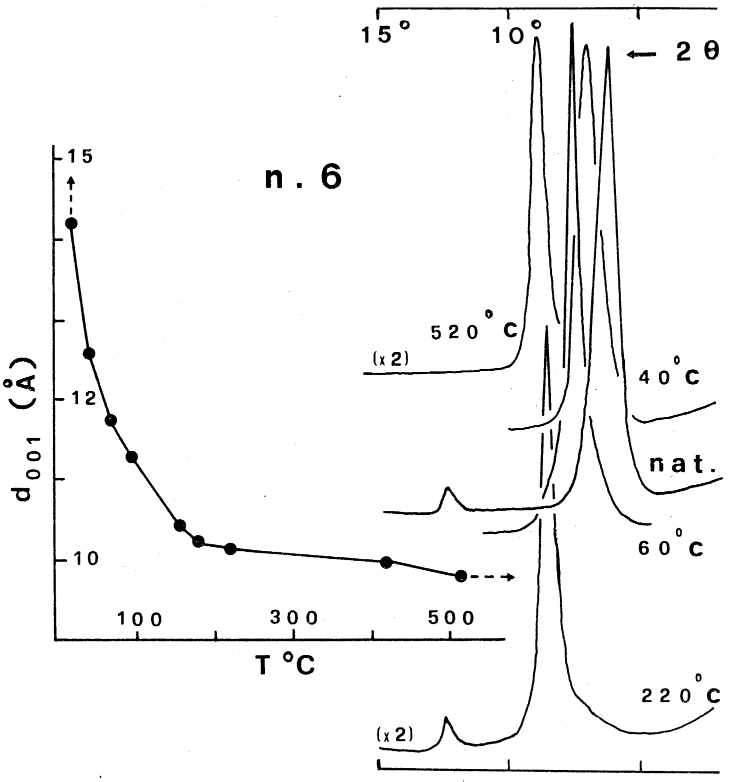

Fig. 3. – X- ray diffractograms of natural and heated sample no. 6. Oriented specimen. The behaviour of $d_{(001)}$ on heat treatment is visible.

the characteristics of chlorite but with asymmetric peaks. It is essentially a chlorite with a partially-hydrated brucitic layer;

no. 6 – a swelling trioctahedral (d_{060} = 1.530 Å) material which has an asymmetric basal reflection at 14.2 Å. Fig. 3 shows the uninterrupted

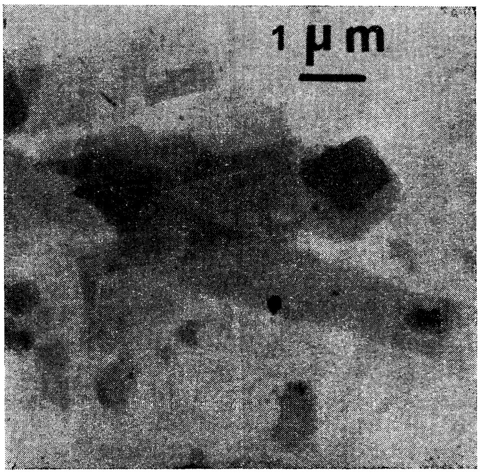

Fig. 4. – Electron micrograph of the clay fraction of sample no. 6.

shift in the basal peak as the temperature is raised. This behaviour and its high crystallinity (fig. 4) show the material to be saponite (Mackenzie, 1956; Mongiorgi and Morandi, 1970);

no. 5 – a trioctahedral (d_{060} = 1.528 Å) swelling material which shows an asymmetric main reflection at 14.6 Å. When heated above 50 °C, the main peak shifts regularly as in sample no. 6 (fig. 5). A supplementary peak at about 12.6 Å appears when the temperature reaches 80 °C. These can be ascribed to random interlayered brucitic sheets in the predominantly saponitic lattice. Small reflections at 7.15 Å and 14.2 Å are probably due to chloritic impurities;

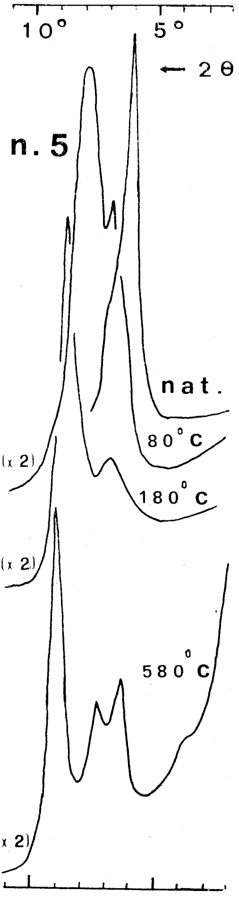

Fig. 5. – X-ray diffractograms of natural and heated sample no. 5. Oriented specimen.

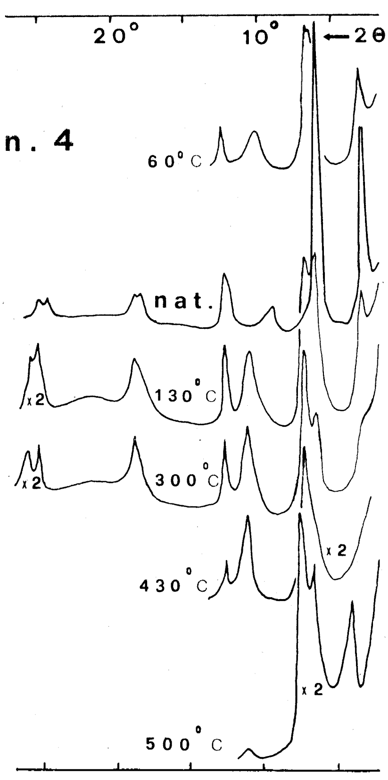

Fig. 6. – X-ray diffractograms of natural and heated sample no. 4. Oriented specimen.

no. 4 – a swelling material which shows the many basal reflections of well-ordered interstratified minerals (fig. 6). This well-ordered pattern is reduced rapidly immediately above room temperature. The co-existence of two interstratified minerals is demonstrated by its behaviour at 130 °C, 300 °C and 430 °C. The first mineral has the main peaks (28 Å, 14.2 Å, 7.1 Å, 4,75 Å and 3.57 Å) and the behaviour, when heated, of sample no. 2; the next shows two broad reflections at 12.6 Å and 8.3 Å which change to three sharp reflections (24 Å, 12.1 Å and 8.0 Å) at the higher temperature (fig. 6). This mineral exhibits the characteristics of the mixed layer chlorite-Al saponite from Rossena (Italy) described by Mongiorgi and Morandi (1970);

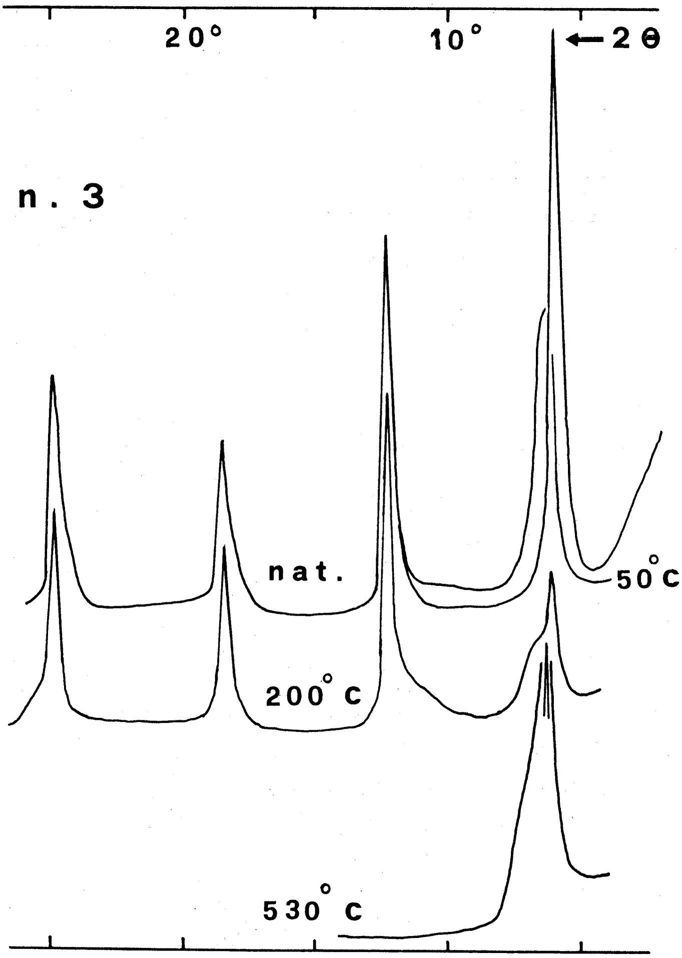

Fig. 7. – X-ray diffractograms of natural and heated sample no. 3. Oriented specimen.

no. 3 – partially swelling material which shows four basal reflections like chlorite (fig. 7). Above room temperature the intensity of the main peak is reduced rapidly and at 200 °C the mineral assumes the characteristics of a chlorite with highly asymmetric basal reflections. This asymmetry may be ascribed to random interlayering of dehydrated mica-like layers. The natural material is essentially a chlorite, like sample no 2, but with a greater number of hydrated brucitic layers.

These results from X-ray diffraction analysis show that the samples contain chlorite, chlorite with the brucitic layer both partially and highly hydrated, saponite and mixed layer chlorite-Al saponite.

CHEMICAL DATA

The results of chemical analysis are reported in Table I. Distinct values for H_2O^+ were obtained from the curves in which three main weight losses are visible (fig. 8). The samples have been arranged on the basis of increasing content of H_2O^- (< 300 °C) and corresponding decreasing content of brucitic hydroxyls (H_2O^+ 300°-800 °C). Similar trends are recorded for SiO_2, Al_2O_3 and FeO_{tot}.

X-ray and chemical analysis indicates that the samples are 2 : 1 layer silicate in which each mica-like layer is interleaved with a single Mg—Al—Fe hydroxide layer.

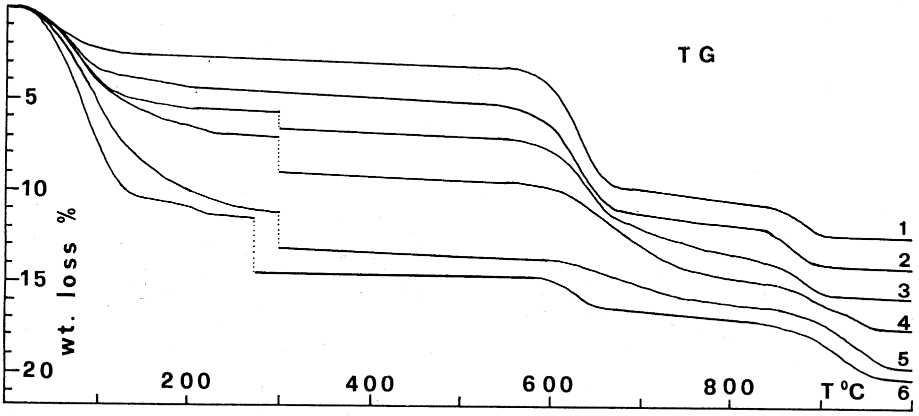

Fig. 8. – TG curve tests carried out with a heating speed of 50 °C/min.

Structural formulas for all the analyses given in Table I were calculated (as in Foster, 1960 and 1962) both on the basis of the theoretical O (OH) content and of valences of 36 oxygens in the half-cell carrying two negative charges (Table II and III).

The formulas show:

1) samples no 1, 2, 3 and 4 in the first calculation turn out to be true chlorites, in the second show a decreasing OH content (until the lower extreme of the Foster (1962) statistic for the chlorites) and confirm the trends recorded for the oxides of the chemical analyses (Table II);

2) samples no. 5 and 6 calculated on the basis of the theoretical O (OH) content of the chlorites, show an OH excess (~ 4) and Si > 4; on the basis of determined H_2O^+ turn out to be OH-enriched saponites with (Si+Al [4]) < 4 (Table III).

The inclusion of those samples in the saponite or chlorite groups is not, therefore, univocal.

According to X-ray diffraction results, samples no. 5 and 6 must be considered in continuous sequence with the other four samples between the theoretical chlorite and saponite. In fact sample no. 1 is a chlorite and closely resembles a structurally ordered clinochlore (Foster, 1962) and samples no. 5 and 6 are aluminium saponites; the three remaining samples (no. 2, 3 and 4) are regularly distributed between those end members.

TABLE I.

	1	2	3	4	5	6
SiO_2	31,51	33,65	34,91	35,57	41,66	41,31
Al_2O_3	17,50	14,61	12,68	13,53	8,13	7,99
TiO_2	0,27	0,06	0,02	0,02	0,26	0,31
$FeO_{(tot.)}$	11,74	10,60	9,66	9,08	5,54	6,12
MnO	0,29	0,15	0,12	0,08	0,05	0,04
MgO	25,10	26,25	27,49	24,76	26,22	25,37
CaO	0,79	0,74	0,73	1,07	0,88	1,00
Na_2O	*abs.*	*abs.*	*abs.*	*abs.*	*abs.*	*abs.*
K_2O	*abs.*	0,01	*abs.*	0,30	0,03	0,11
P_2O_5	0,11	0,08	*abs.*	0,01	*abs.*	0,07
$H_2O^{+(1)}$	7,50	6,70	6,70	5,60	2,30	2,00
$H_2O^{+(2)}$	2,50	3,00	2,50	2,60	2,80	2,80
$H_2O^{-(3)}$	2,60	4,50	5,50	7,00	12,40	12,70
Total	99,91	100,35	100,31	99,62	100,27	99,82
$H_2O^{+(4)}_{(tot)}$	11,30	10,87	10,27	9,21	5,72	5,48
Ion exchange	1	2	3	4	5	6
Ca^{2+}	0,37	0,50	0,51	0,68	0,80	0,86
Mg^{2+}	0,17	0,33	0,38	0,40	0,45	0,45

(1) T < 300 °C

(2) T between 300° and 800 °C.

(3) T > 800 °C.

(4) Value obtained from (1)+(2)+iron oxidation.

TABLE II.

Samples	$F_{\text{chlorites}}$ (1)				$F^1_{\text{chlorites}}$ (2)			
	1	2	3	4	1	2	3	4
Si	3,11	3,33	3,45	3,57	3,16	3,41	3,58	3,76
Al [4] . . .	0,89	0,67	0,45	0,43	0,84	0,59	0,42	0,24
Al [6] . . .	1,14	1,04	1,03	1,17	1,23	1,15	1,12	1,44
Ti	0,02	—	—	—	0,02	—	—	—
Fe^{2+}	0,97	0,88	0,80	0,76	0,98	0.90	0,82	0,80
Mg	3,69	3,87	4,05	3,70	3,75	3,91	4,20	3,90
Mn	0,02	0,01	0,01	—	0,02	0,01	0,01	—
OH	8,00	8,00	8,00	8,00	7,56	7,35	7,02	6,49
Σ [6]	5,89	5,80	5,89	5,63	6,00	5,97	6,15	6,14

(1) $F_{\text{chlorites}}$ = gram equivalents of cationic constituents (without hydrogen cation)/28.

(2) $F^1_{\text{chlorites}}$ = gram equivalents of cationic constituents (= 36 charges carried by 18 oxygens in the half-cell)/36.

TABLE III.

Theoretical saponite		$F_{\text{saponites}}$ (1)		$F^1_{\text{saponites}}$ (1)		$F_{\text{chlorites}}$ (3)		$F^1_{\text{chlorites}}$ (4)		Theoretical chlorite
		5	6	5	6	5	6	5	6	
Si	3,67	3,23	3,24	3,11	3,16	4,11	4,12	4,66	4,69	3,00 Si
Al [4]	0,33	0,74	0,74	0,71	0,71	—	—	—	—	1,00 Al [4]
Al [6]	0,00	—	—	—	—	0,94	0,94	1,07	1,06	1,00 Al [6]
Ti		0,01	0,01	0,01	0,01	0,02	0,02	0,02	0,02	Ti
Fe^{2+}		0,36	0,40	0,35	0,39	0,45	0,51	0,51	0,58	Fe^{2+}
Mg	3,00	3,03	2,96	2,91	2,86	3,85	3,77	4,37	4,29	5,00 Mg
Mn		—	—	—	—	—	—	—	—	Mn
OH	2,00	2,00	2,00	2,85	2,72	8,00	8,00	4,27	4,15	8,00 OH
Σ [6]	3,00	3,30	3,37	3,27	3,26	5,26	5,24	5,97	5,95	6,00 Σ [6]

(1) $F_{\text{saponites}}$ = gram equivalents of cationic constituents (without hydrogen cation)/22.

(2) $F^1_{\text{saponites}}$ = gram equivalents of cationic constituents (= 24 charges carried by 12 oxygens in the half-cell)/24.

(3) and (4) see Table II.

CONCLUSIONS

The present study shows that a genetic and crystallo-chemical link exists between the groups of minerals consisting of magnesium chlorite, mixed layer chlorite-saponite, aluminium saponite and saponite.

The aluminium saponite, in which the tetrahedral-octahedral ratio lies between 2 : 1 : 1 and 2 : 1 but nearer to the latter, may be regarded as a stable member of a mineral group in which chlorite and saponite are end members.

Saponite may be considered as the end product of the hydration process of the brucitic layer and is linked with decreasing Al [4], Al [6], Fe, OH and octahedral occupancy in a chlorite-like structure.

Octahedral occupancy in members of the chlorite-saponite series, derived from experimental H_2O^+ values, gives evidence of a positive link between their thermal behaviour and chemical analysis.

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