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# Experimental study of clay mineral, greenschist, and low-pressure amphibole facies in the system $Na_2O–Al_2O_3–MgO–SiO_2–H_2O$

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SUMMARY. Compositions concerning sodic amphiboles (glaucophane) in the system $Na_2O–Al_2O_3–MgO–SiO_2–H_2O$ have been studied at $P_{H_2O} \leqslant 3$ kb, $380\ ^\circ C < T < 700\ ^\circ C$. The study attempts to establish the mineral parageneses under these physical conditions as they define the clay mineral (saponite–hectorite smectite) and greenschist (chlorite–albite) facies. The occurence of sodic amphiboles is defined by compositional parameters. Glaucophane does not appear in the present investigation.

The method of 'reaction reversal', i.e. using precrystallized mineral assemblages to form new ones, has been used to establish the three reactions: albite+chlorite → paragonite+saponite, paragonite+chlorite → saponite+cordierite, and saponite + paragonite → albite+cordierite. In general, the clay mineral → greenschist transformation is favoured by an increase in pressure in the system studied. The amphibole present is a sodic richterite with the type substitution

$$Na_A + Mg_X + 2Mg_Y = Na_X + 2Al_Y.$$

PREVIOUS studies in the sodium–magnesium–aluminium silicate system have dealt with the occurrence of amphiboles (Ernst, 1961; Maresch, 1973; Iiyama, 1963; Carman, 1974), clay minerals (Iiyama and Roy, 1963*a* and *b*), paragonite (Chatterjee, 1970, 1973, 1974), chlorite (Velde, 1973), and sodic phlogopite (Carman, 1974). From these studies we know that ideal glaucophane is not stable at low pressure but sodic richterites are. We know that sodic trioctahedral montmorillonites are stable to high temperatures at low pressures and that sodium phlogopite is restricted to specific low-silica bulk compositions.

However, the associations of these minerals with chlorites and paragonite are not known yet in the system $Na_2O–Al_2O_3–MgO–SiO_2–H_2O$. The present study attempts to define some of the limits of clay mineral, mica–chlorite, and amphibole assemblages or 'facies' at low pressures and moderate temperatures.

*Experimental method.* Anhydrous 'gels' were prepared for study (fig. 1) by a method described by Luth and Ingamells, 1965. These compositions cover a field from ideal glaucophane (G1) through the solid solution between this mineral and aluminous glaucophane $Na_2MgAl_4Si_6Al_2O_{22}(OH)_2$ (compositions G1, G13, G9, G10, G16, G11). A second series is similar except that 2 $SiO_2$ has been added to these amphibole compositions (GQ1 . . . GQ11).

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Other compositions (G6, G5, G4, G14, G3, G7, G12) were prepared to elucidate phase relations of less sodic assemblages. Compositions R1 . . . R5 represent compositions less aluminous than the glaucophanes in the series glaucophane to MgNa richterite. The study by Iiyama (1963) indicates that in this compositional range one should find amphiboles leading towards glaucophane compositions and those associated with the clay minerals common to the other parts of the system.

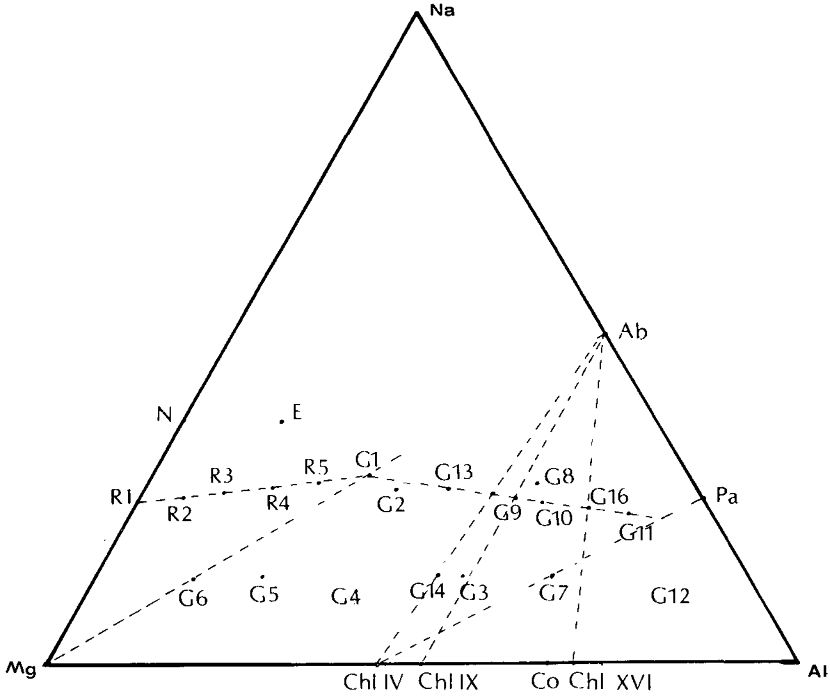

Fig. 1. Compositions investigated in the Na–Mg–Al coordinates. Gels: G1 to G14 and R1 to R5. Mixtures of synthetic minerals: CA9, 13–9, 14, 16 (albite+chlorite), CP7 (chlorite+paragonite). G1 = ideal glaucophane; R1 = NaMg richterite; E = eckermanite; N = sodic richterite $NaNa_2Mg_5Si_8O_{21}(OH)(OH)_2$; T = talc; Pa = paragonite; Ab = albite; Co = cordierite; Chl = chlorites.

Mixtures of synthetic chlorites and albite or paragonite were prepared for compositions CA14 (chlorite IV+albite), CA9 (chlorite IX+albite), CA16 (chlorite XVI+albite). A precrystallized mixture was made from chlorite IV and paragonite (CP7). Chlorites were crystallized at 480 °C from gel compositions: Chl IV, $Mg_{3.2}Al_{2.3}Si_{4.5}$ (clinochlore); Chl IX, $Mg_3Al_3Si_4$; Chl XVI, $Mg_{1.88}Al_{4.12}Si_4$. Albite and paragonite were crystallized respectively at 700 °C and 600 °C after two weeks' run time.

The experiments were carried out in cold-seal hydrothermal bombs where the temperature was controlled by on–off regulators; variations were found to be ±3 °C. Pressures were estimated to be accurate to ±3 %. It was found that run times of at least one month were necessary to approach equilibrium using gel materials, especially when two phyllosilicates were present. Metastable interlayered phases were often encountered as described by Seifert (1970). Rapid run up times were attempted in order to prevent crystallization of metastable phases.

### *Description of phases encountered*

The major method of identification was X-ray diffraction, supplemented when possible by optical determinations. When clay mineral or phyllosilicates were present, oriented specimens were prepared and were treated with ethylene glycol, heated at 110 °C and 550 °C in air to identify the clay minerals by X-ray diffraction methods. Unoriented preparations were also used to aid in the identification.

*Montmorillonites.* Two series were encountered: hectorite and saponite. They are distinguished by a reflection at 2·29 Å and glycollated spacing of $\geqslant$ 17·2–17·3 Å for hectorite. The 2·29 Å reflection is missing in saponite and the expanded structure has a $\sim$ 17 Å reflection.

*Chlorites* were normally the 14 Å polymorph, but some expanding chlorites were observed (Velde, 1973). These forms contract to near 14 Å at 550 °C (dried in air) and have a 060 reflection near 1·540 Å.

At $T < 300$ °C, some runs produced a 14 Å phase that expands to 17 Å; it is a 'labile chlorite' (Stephen and MacEwan, 1949). The run products produced from gels for many compositions often resulted in interlayered minerals with a chlorite component.

Trioctahedral *vermiculite*, which expands when treated with ethylene glycol and contracts to 9–10 Å at 110 °C was identified after the criteria of Barshad (1949, 1950, 1952), Walker (1950, 1958), Brown (1953), Hathaway (1955), Robert and Barshad (1972).

*Micas.* Two sorts are possible in the chemical system studied: paragonite and sodic phlogopite. The latter phase should not appear in the compositions studied, because of the relatively high silica content (Carman, 1974). The paragonite produced here is not exactly that reported by Chatterjee (1970, 1974) in that the basal spacing is found to be near 10 Å instead of 9·6 Å. However, the reflections 060 = 1·481 Å and 111 = 4·386, 113 = 3·759, and 114 = 3·161 Å indicate a *2M* dioctahedral paragonite. The 10 Å reflection remains even after heating to 110 °C. Solid solution between a sodic-phlogopite and paragonite is suspected (see Carman, 1974).

*Mixed-layered minerals* were found involving talc–montmorillonite, chlorite–montmorillonite, and paragonite–montmorillonite. It was judged that all but chlorite (or expanding chlorite)–montmorillonite mixed-layered minerals were metastable forms. Longer experiments tended to reduce the amount of expanding mineral in most cases. The use of precrystallized mineral mixtures as starting materials also led to this conclusion. The composition–*P*–*T* influences on the chlorite–montmorillonite minerals are treated in more detail in Triboulet (1976).

*Feldspar and feldspathoid.* Diffractograms show that high albite (Smith, 1956) exists at temperatures above 500 °C, and low albite crystallizes below this temperature. Analcime was found below 380 °C for compositions low in silica; X-ray diffraction

TABLE I. *Results of experiments critical to the establishment of the figures*

| Starting material | $T$ | $P_{H_2O}$ | Time | Phases observed |
|---|---|---|---|---|
| Curve (Ab) paragonite + chlorite $\rightleftharpoons$ saponite + cordierite | | | | |
| Par-Chl (CP7) | 612 °C | 3 kb | 33 days | Cor–Sap–Par |
| Cor–Sap–(Sap–Par)$_0$ | 612 | 3 | 33 | Par–Chl |
| Chl–Par (CP7) | 586 | 2 | 97 | Cor–Par–Chl–(Sap–Chl) |
| Sap–Cor–Par | 582 | 2 | 32 | Chl–Cor–Par |
| Chl–Par (CP7) | 555 | 1 | 30 | Par–Cor–(Sap–Chl) |
| Ab–Cor | 542 | 1 | 30 | Chl–Par–Ab–Cor |
| | | | | |
| Chl–Ab (CA14) | 586 | 2 | 97 | Cor–Sap–Par |
| Chl–Ab (CA14) | 630 | 3 | 30 | Cor–Sap–Par |
| Cor–Sap–Chl | 530 | 1 | 28 | Par–Chl–Cor–Sap |
| Chl–Ab (CA16) | 582 | 2 | 30 | Par–Ab–Sap |
| Chl–Ab (CA13–9) | 582 | 2 | 30 | Ab–Par–Sap |
| Chl–Ab (CA9) | 582 | 2 | 59 | Par–Sap–Ab–Cor |
| gel GQ3 | 563 | 2 | 59 | (Par–Sap)$_s$ |
| Curve (Cor) albite + chlorite $\rightleftharpoons$ saponite + paragonite | | | | |
| Ab-Chl (CA14) | 583 | 3 | 29 | Ab–(Vm–Par)$_0$ |
| Sap–Par | 580 | 3 | 32 | Chl–Ab–Par |
| Chl–Ab (CA14) | 540 | 2 | 30 | Par–Chl-Sap |
| Ab–Par–Sap | 530 | 2 | 31 | Ab–Chl |
| Ab–Chl (CA13–9) | 479 | 1 | 30 | Ab–Par–Sap |
| Ab–Chl (CA9) | 479 | 1 | 30 | Ab–Par–Vm |
| Ab–Sap–Par | 463 | 1 | 32 | Ab–(Chl–Sap)$_0$ |
| | | | | |
| Chl–Ab (CA14) | 472 | 1 | 30 | Chl–Ab–Par |
| Chl–Ab (CA14) | 586 | 2 | 97 | Cor–Sap–Par |
| Cor–Sap–Par | 528 | 2 | 31 | Ab–Chl–Cor–Par |
| Chl–Par (CP7) | 480 | 1 | 31 | Par–Vm |
| Cor–Par–(Sap–Chl) | 530 | 2 | 31 | Par–Chl |
| Ab–Chl (CA16) | 479 | 1 | 30 | Ab–Chl–Par |
| Ab–Chl (CA16) | 582 | 2 | 30 | Sap–Par–Ab |
| gel GQ9 | 584 | 3 | 30 | Par–Ab–Sap |
| gel GQ9 | 470 | 1 | 30 | Ab–(Par–Sap)$_s$ |
| gel GQ10 | 584 | 3 | 30 | Ab–(Par–Sap)$_0$ |
| gel GQ13 | 490 | 1 | 27 | Ab–Sap |
| gel GQ13 | 584 | 3 | 30 | Ab–Par–Sap |
| Curve (Chl) saponite + paragonite $\rightleftharpoons$ albite + cordierite | | | | |
| Sap–Par–Cor | 659 | 3 | 31 | Ab–Cor–Sap |
| Cor–Ab–(Par–Chl) | 645 | 3 | 30 | Ab–Chl–(Par–Sap)$_0$ |
| Ab–Cor–Chl–(Sap–Chl)$_0$ | 645 | 3 | 30 | Ab–Sap–Par–Cor |
| Ab–Cor–Sap–Chl | 648 | 2 | 30 | Ab–Sap–Par–Cor |
| Ab–Sap–Par | 656 | 3 | 30 | Par–Sap |
| Par–Ab–Sap | 694 | 1 | 30 | Ab–Cor–Sap |
| Sap–Par–Cor | 663 | 2 | 30 | Ab–Cor–Sap |
| Cor–Ab | 694 | 1 | 30 | Ab–Cor–Par–Sap |
| Cor–Ab–Sap | 683 | 1 | 30 | Cor–Par–Sap |
| | | | | |
| Chl–Par (CP7) | 672 | 1 | 31 | Cor–Ab–Par |
| Chl–Par (CP7) | 654 | 2 | 7 | Cor–Par–Sap |
| Chl–Par (CP7) | 659 | 3 | 30 | Cor–Ab–Sap–Par |

TABLE I (*cont.*)

| Starting material | $T$ | $P_{H_2O}$ | Time | Phases observed |
|---|---|---|---|---|
| Ab–Par | 641 | 3 | 30 | Cor–Par–Sap–Vm |
| Chl–Ab (CA13–9) | 674 | 2 | 30 | Ab–Cor–Sap–Chl |
| Chl–Ab (CA13–9) | 664 | 3 | 30 | Cor–Ab–Sap–Chl |
| Chl–Ab (CA9) | 690 | 3 | 36 | Ab–Cor–Chl–(Sap–Chl)$_0$ |
| Chl–Ab (CA16) | 676 | 1 | 31 | Cor–Par–Sap–Ab |
| Cor–Par–Sap–Ab | 619 | 1 | 30 | Par–Cor–Sap |
| Cor–Ab–(Vm–Par)$_0$ | 641 | 3 | 30 | Par–Cor–Sap |
| gel GQ10 | 695 | 1 | 30 | Cor–Ab–(Par–Sap)$_0$ |
| gel GQ10 | 688 | 2 | 35 | Cor–Ab–Sap–Par? |
| gel GQ16 | 671 | 1 | 30 | Cor–Ab–(Par–Sap)$_0$ |
| gel GQ16 | 677 | 2 | 30 | Ab–Cor–(Par–Sap)$_0$ |
| gel GQ16 | 681 | 3 | 30 | Ab–Cor–(Par–Sap)$_0$ |

Chl, chlorite (14 Å); Ab, albite; Cor, cordierite; Par, paragonite; Sap, saponite; Vm, vermiculite; ( ), randomly interstratified clay; o, ordered interstratification; s, interstratification showing a superstructure reflection.

patterns indicated a Si content between 20 and 32 atoms per unit cell, for a cell dimension between 13·732 and 13·780 Å (Saha, 1959).

High temperatures produced *cordierite* in many assemblages. It is assumed to be $Mg_2Al_4Si_5O_{18}$ in the graphic representations.

*Amphiboles* are restricted to compositions less aluminous than glaucophane for the *P–T* conditions of the experiments. Optical examination was particularly useful to distinguish amphiboles, due to their higher relief compared with phyllosilicates. They generally have a small extinction angle (~ 10°) and sometimes they appear to be orthorhombic. The 3·44, 3·28, 2·813, 2·70, and 2·60 Å reflections were used to determine the presence of amphibole by X-ray diffraction. The doublet 9·00 and 8·4 Å was not used since it could be due to a combination of montmorillonite–chlorite interlayered mineral and cordierite (Sudo and Kodama, 1957; Van Moort *et al.*, 1966).

*Stilpnomelane.* Koizumi and Roy (1959) proposed the sodic stilpnomelane, which has been restudied by Triboulet (1975). It is stable between 630 and 650 °C at 2 kbar.

### *Mineral assemblages and their stability*

*Talc–albite–paragonite–chlorite compositional domain.* Mixtures of precrystallized minerals and gel starting materials were used, with the result that the two methods are roughly concordant in the assemblages produced. Compositions CP7, CA14, CA16, and CA13–9 were used to understand the mineral relations leading to the univariant reactions chlorite+albite (or paragonite)→saponite+cordierite. The results of the experiments are listed in Table I. Interpretation of the experimental results, based principally upon runs using mixtures of synthetic minerals, permits the determination of three reactions in *P–T* space:

$$\text{(Cor)}\ 7{\cdot}15\ \text{albite}+9\ \text{clinochlore} = 0{\cdot}75\ \text{paragonite}+6{\cdot}4\ \text{saponite}+3{\cdot}25\ H_2O+21{\cdot}3\ \text{quartz}$$

(Ab) 8·2 paragonite+20 clinochlore

= 8·2 saponite+11·5 cordierite+47·2 $H_2O$+7·9 quartz

(Chl) 4 saponite+20 paragonite+41 quartz = 24 albite+11 cordierite+40 $H_2O$

These equations assume a saponite composition of maximum hydration such as $Na(Mg_{4\cdot5}Al_{1\cdot5})(Si_{5\cdot5}Al_{2\cdot5})O_{20}(OH)_4,3H_2O$. Using this formula, the reactions as written are all ones of dehydration of the solid phases toward high temperatures,

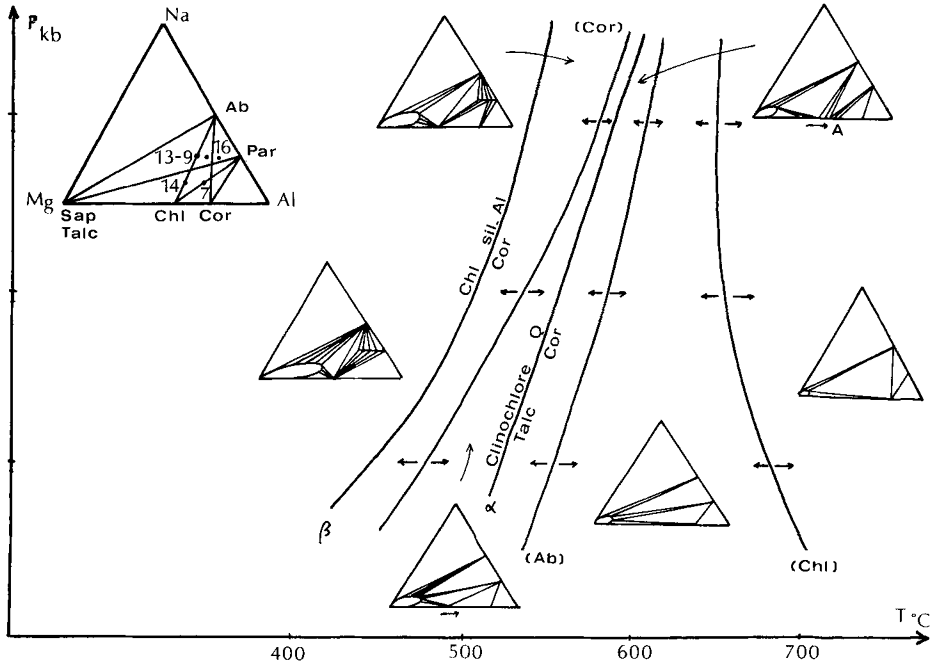

FIG. 2: (a) Position of key compositions used to determine (b) the univariant reaction positions in pressure-temperature space. Curve α from Fawcett and Yoder (1966) and Velde (1973). Curve β from Seifert (1970). Arrrows show points of reaction 'reversal', i.e. where the assemblage on the other side of the curve was recrystallized (data in Table I). Sap = saponite; A = amesite; Chl = chlorites; Ab = albite; Cor = cordierite; T = talc; Par = paragonite. Solid solution extension of chlorites and saponites are discussed in the text. The four phase reactions on the univariant curves (Cor), (Ab), and (Chl) are displayed in the text. The areas drawn from the Mg pole are saponite areas.

despite the fact that saponite is found on the dehydration side in two cases. The stability of paragonite+chlorite (curve (Ab) in fig. 2) represents the highest temperature conditions at which the assemblage chlorite+quartz was found. This univariant curve is found at higher temperatures than the clinochlore+quartz curve of Fawcett and Yoder (1966). However, subsequent work by Velde (1973) indicates that clinochlore is not the chlorite of highest thermal stability. A more aluminous phase (→ Amesite A, fig. 2) is stable to higher temperatures.

*Albite–saponite–paragonite–sodic-hectorite relations.* Lacking precrystallized mineral mixtures, crystallized gel compositions were used to establish the stabilities of assemblages containing expanding minerals.

In fig. 2 one finds that the tie-line albite+saponite (or hectorite) is stable throughout the range of physical conditions investigated. However, this is true for the quartz-rich compositions only. The alternative assemblage analcime+hectorite is present below 480 °C at $P_{H_2O} = 1$–$3$ kb for certain compositions that contain less $SiO_2$. Depending upon the bulk composition (fig. 3) the alternative, high-temperature assemblages albite+saponite and albite–saponite–paragonite can be formed. This necessitates that in the parageneses analcime+hectorite (compositions in $Si_8$) and albite+saponite (compositions in $Si_{10}$), hectorite and saponite do not have a maximum substitution in the octahedral site, but that they do have a maximum interlayer charge ($\approx$ 0·66 Na); otherwise the tielines cut each other (fig. 3). The decrease in silica substitution in

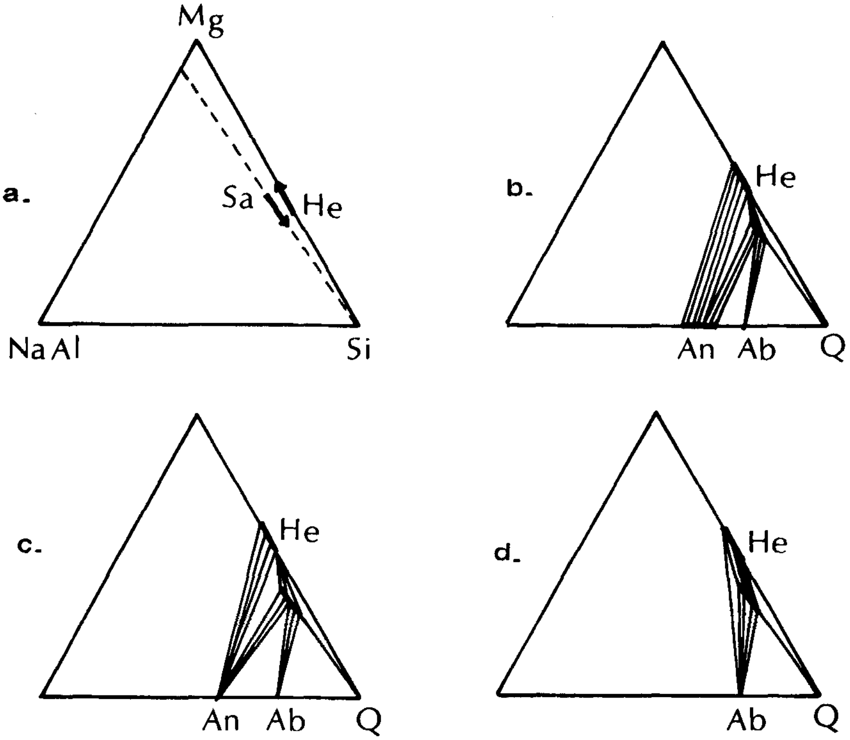

FIG. 3. Feldspar, feldspathoid, hectorite, and saponite phase relations are illustrated as a function of increasing temperature (< 480 °C) from b to d. In Fig. 3*a* the arrows show the compositional field of hectorite and saponite from the most substituted formula, i.e. respectively $(Mg_{5\cdot34}Na_{0\cdot66})\ Na_{0\cdot66}Si_8$ and $Mg_6(Si_{7\cdot34}Al_{0\cdot66})Na_{0\cdot66}$. An = analcime $0\cdot33 \leqslant NaAl/(NaAl+Si) \leqslant 0\cdot44$; He = hectorite $Mg/(Mg+Si) > 0\cdot40$; Sa = saponite $(Mg+NaAl)/(Mg+NaAl+Si) < 0\cdot48$; Q = quartz; Ab = albite.

analcime (Saha, 1959; Sand, Roy, and Osborn, 1957) decreases the hectorite–analcime field (fig. 3c). As it happens, the saponite composition is covered in part by the two-phase zone hectorite–analcime. Thus one must eliminate this join before the assemblage albite–saponite can be found for Si-poor compositions at higher temperatures (fig. 3d). For Si-rich compositions the albite–saponite tie-line is always possible, as shown in fig. 3, for all temperatures.

If one looks closely at the assemblage saponite+albite ($T > 480$ °C) it is apparent that the saponite formed from bulk compositions G13 and G9 necessitates an interlayer occupation of 1·0 cations for $O_{20}(OH)_2$. This is well above that usually found for fully expanded minerals (Grim, 1968), which normally have 0·66 interlayer charges. The conclusion reached here is that some sodium and magnesium remains in the aqueous solution, thus allowing a more normal saponite of lower sodium content to be present. The appearance of paragonite is not solely due to physical conditions but to chemical ones also. The higher the Al content of the charge, the more evident paragonite becomes. However, as temperature increases, the saponite becomes less aluminous and the compositional field over which paragonite is formed is much enlarged. This solid-solution–temperature relation has been noted by Roy and Roy (1955).

Another, somewhat surprising solid solution is that in paragonite, which goes even beyond that proposed by Kiénast and Velde (1968) who found a $\frac{1}{2}\text{Mg}+\text{Al} \rightleftharpoons \text{Si}$ substitution partial in natural paragonites. It appears that there is significant solid solution between sodic phlogopite and paragonite in the synthetic system. However, the bulk composition, being Si-rich, did not permit a precise determination of the solid-solution limits between the two phyllosilicate phases. The mica containing the greatest substitution was deduced by chemiographic relations to be $NaMg_{0\cdot48}Al_{1\cdot52}(Si_3Al)O_{10}(OH)_2$, which was formed at 380 °C, $P_{H_2O}$ 1 kb. The large basal spacing of the synthetic paragonites (~ 10 Å) indicates some type of sodic phlogopite solid solution (see Carman, 1974).

*Relative stabilities of chlorite+saponite and the mixed layered mineral chlorite–saponite.* The association of saponite and chlorite is limited by the univariant curve (Ab) in fig. 2 to the lower range of pressure and temperature. However, in this range an interstratified mineral: saponite–chlorite, indicated as (S–C), is frequently present. This mineral is considered here to represent solid solution between the two better-defined phyllosilicates saponite and chlorite. The extension of this solid solution is indicated in fig. 2 to be function of temperature as it is also a function of pressure. These relations are dealt with in more detail in Triboulet (1976).

### *Talc–albite–Na compositions: sodic-hectorites and amphiboles*

*Sodic hectorites.* The mineral composition join talc–albite divides hectorite and saponite compositions (fig. 1). Maximum solid solution is present at 380 °C and $P_{H_2O}$ 2 kb as seen in the R1 and R4 compositions. This gives a hectorite formula of:

$$a[\text{Na}_x(\text{Mg}_{6-x}\text{Na}_x)\text{Si}_8]+b\ \text{quartz}+\underbrace{[2(1-ax)]\text{Na}^{+}+[6-a(6-x)]\text{Mg}^{2+}}_{\text{solution}}.$$

It is necessary to assume that some Mg and Na is found in the aqueous solution in order to formulate a reasonable formula for this phase.

*Hectorite–talc.* Temperatures above 580 °C at $P_{H_2O}$ 1–3 kb give either talc plus hectorite or talc–hectorite mixed-layered mineral assemblages. This is the result of exsolution in the hectorite mineral. In order to form this assembiage one must divide the bulk composition of the experiment as

$$a[\mathrm{Si_8(Mg_{5\cdot4}Na_{0\cdot6})Na_{0\cdot6}O_{20}(OH)_4}, n\mathrm{H_2O}]+b\ \mathrm{talc}+\underbrace{(2-1\cdot2a)\mathrm{Na^+}+[6-(5\cdot4+3b)]\mathrm{Mg^{2+}}}_{\text{solution}},$$

where $a < 1$.

For bulk compositions containing $Al_2O_3$ (R2 to R5) Na and Mg can be accommodated in the structure so that hectorite+talc becomes:

$$\mathrm{(Si_{8-\mathit{x}}Al_{\mathit{x}})(Mg_{6-(\mathit{x}+\mathit{y})}Al_{\mathit{z}}Na_{\mathit{y}})Na_{\mathit{x}+\mathit{y}+\mathit{z}}}+\mathrm{talc}.$$

For these compositions hectorite would have the same charge and thus a similar expansion to the other phases upon treatment with ethylene glycol (Barshad, 1950). In going from R2 to R5 compositions one calculates a higher proportion of talc component from the bulk composition. This effect is in fact observed on diffractometer traces of the different products. This great range of solid solution in hectorite can possibly explain the equally great range in temperature stability of the phases as noted by Iiyama and Roy (1963*b*) and Ames and Sand (1958). Bulk compositions richer in silica simply produce quartz under the experimental conditions.

*Hectorite–amphibole assemblages.* At 680 °C ($P_{H_2O}$ 1 to 3 kb) the solid solution in hectorite begins to be reduced, and at compositions containing more Na than the line talc–albite, hectorite is accompanied by a sodic amphibole and albite. Within the compositional field studied four amphiboles can be formed:

| | | | | |
|---|---|---|---|---|
| 1. | Na | (NaMg) | $Mg_5Si_8O_{22}(OH)_2$ | NaMg richterite |
| 2. | Na | $Na_2$ | $Mg_5Si_8O_{21}(OH)_2(OH)$ | |
| 3. | Na | $Na_2$ | $(Mg_4Al)Si_8O_{22}(OH)_2$ | eckermanite |
| 4. | | $Na_2$ | $(Mg_3Al_2)Si_8O_{22}(OH)_2$ | glaucophane |

Types 1 and 2 were studied by Witte *et al.* (1969), 2, 3, and 4 by Iiyama (1963), 3 by Phillips and Rowbotham (1968), and 4 by Ernst (1961) and by Maresch (1973).

The present experiments indicate that at 680 °C ($P_{H_2O}$ 2 and 3 kb) substitutions are of the type $Na_A+Mg_X+2Mg_Y = Na_X+2Al_Y$ (fig. 4*b* and *c*). Pressure increases this substitution. Maximum substitution observed would yield an amphibole such as $Na_{0\cdot5}(Na_{1\cdot5}Mg_{0\cdot5})Mg_4AlSi_8$.

The association of amphibole with mixed layered mineral hectorite–talc, present at 580 °C, $P_{H_2O}$ 3 kb, poses a problem. In this assemblage the amphibole would have a composition $Na_2Mg_5Si_8O_{22}(OH)_2$, more sodic than richterite and stable at a temperature lower than the stability of richterite (Witte *et al.*, 1969). If the mixed layered mineral is metastable, a less sodic richterite such as $Na_{0\cdot3}(Na_{1\cdot7}Mg_{0\cdot3})(Mg_{3\cdot6}Al_{1\cdot4})Si_8O_{22}(OH)_2$ would be present. The problem is also present at 680 °C, $P_{H_2O}$ 1 kb, where a very sodic amphibole appears to be present. It was not possible to determine the compositional variations by X-ray diffraction and grain size did not permit

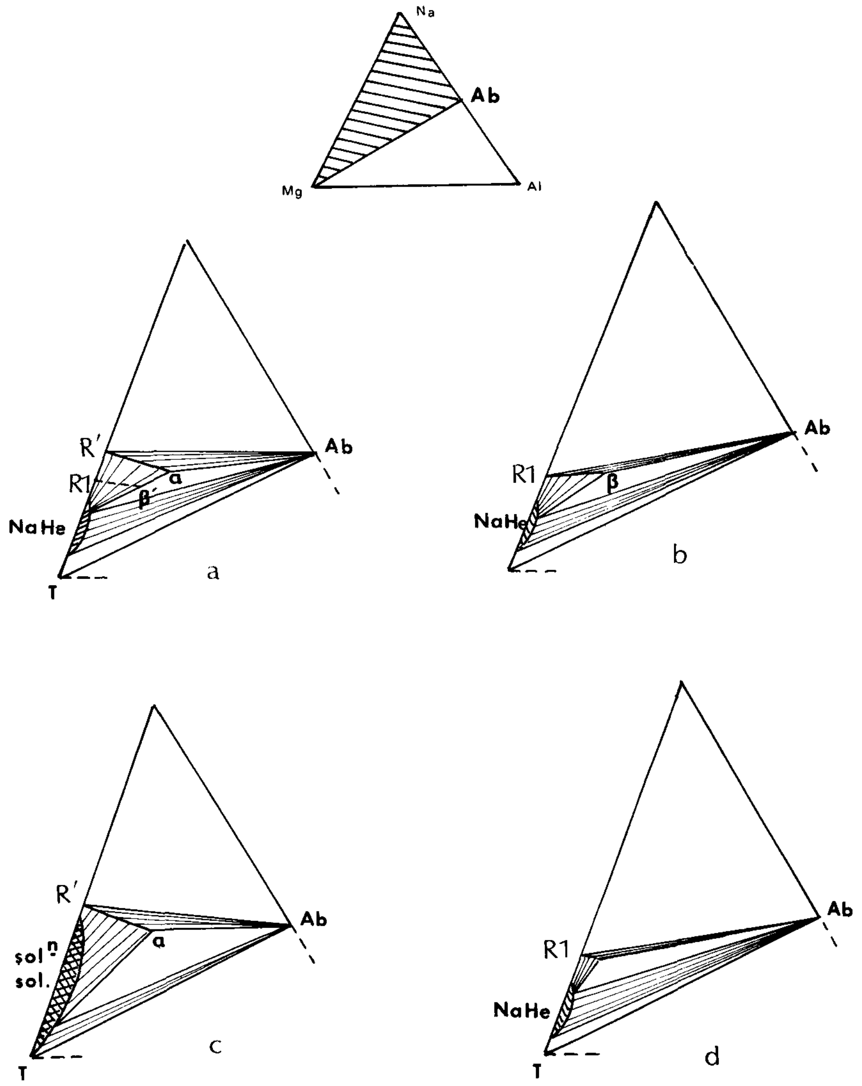

FIG. 4. Amphibole–hectorite relations are shown as determined from crystallization products from gel starting materials. a = 680 °C, 1 kb; b = 680 °C, 2 kb; c = 580 °C, 3 kb; d = 680 °C, 3 kb. R1 = MgNa richterite; α = amphibole $Na_{0.5}Na_2(Mg_{3.5}Al_{1.5})Si_8O_{22}(OH)_2$; β = $Na_{0.3}(Na_{1.7}Mg_{0.3})(Mg_{3.6}Al_{1.4})Si_8O_{22}(OH)_2$; Ab = albite; T = talc; R′ = $Na_3Mg_5Si_8O_{21}OH(OH)_2$ (Witte *et al.*, 1968; NaHe = sodic hectorite solid solutions.

microprobe determinations. The essence of these results is that glaucophane does not occur in the system at these pressures and temperatures. The amphiboles present occur with talc–hectorite and albite. These results were already suggested by the work of Maresch (1973).

## *Discussion*

The geologic applications of this study in the system are rather limited. Most natural rocks contain other elements, which immediately provoke the presence of other phases. Further, most of the information on natural hectorite, saponite, and mixed layered minerals comes from geologic environments of low temperature (Ball, 1964; Veniale and Van der Marel, 1963; Veniale, 1962). However, the simple system can be used as a model for the variation of mineral assemblages from expanding phyllosilicates (clays) to non-expanding phyllosilicates (greenschist facies) and to amphibolite facies assemblages. We see that normal sodic amphiboles, such as glaucophane, do not occur at low water pressures ($\leqslant 3$ kb). Thus the amphibole-bearing assemblages are restricted in bulk composition and cannot be considered as a facies in the normal sense of the term in metamorphic petrology. The existence of sodic richterite amphiboles appears to be controlled by high Na and low Ca contents at $P_{H_2O} \leqslant 3$ kb, $T \leqslant 700$ °C. The passage from clay minerals to greenschist type mineral assemblages (albite–chlorite–paragonite) can be influenced by pressure. The unusual thermal stability of the sodic saponites is perhaps extreme but the principle of diminished clay mineral stability with increasing pressure is perhaps an important one in the evolution of natural mineral assemblages. We see in the system studied that clay minerals pass into cordierite-bearing assemblages at high temperatures and albite–chlorite at high pressures.

The reaction albite+chlorite → saponite+paragonite has a slope of 60°/kb. It is possible that pelitic clay minerals (aluminous) could also be transformed into greenschist facies by increase in pressure. One example of high-temperature expanding minerals has been reported by Wilson *et al.* (1968) and Wilson and Bain (1970). Expanding minerals are found in magnesian carbonate rocks that contain metamorphic minerals such as tremolite, phlogopite, and diopside. It is established that weathering does not cause the formation of the expanding phases. The existence of staurolite–kyanite–sillimanite assemblages in associated rocks places the conditions of metamorphism at rather high temperatures and pressures. It is possible that the expanding minerals in the carbonate rocks were formed at high temperatures by reaction of magnesian silicates with sodic fluids during a period of retrograde metamorphism. The physical conditions of such a process could approach those of the present study, where expanding minerals are stable at high temperatures. Should these assumptions be valid, one would find expanding minerals much more often in magnesian rocks should they be looked for.

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