

## The zeolite facies, with comments on the interpretation of hydrothermal syntheses

D. S. COOMBS, A. J. ELLIS,\* W. S. FYFE and A. M. TAYLOR  
Departments of Geology and Chemistry, University of Otago, New Zealand

(Received 20 September 1958)

**Abstract**—Field, petrographic and experimental evidence is presented on assemblages involving Ca–Al and Na–Al silicates, warranting recognition of a zeolite facies. This facies largely bridges the gap between diagenesis and conventional metamorphism. The metamorphic geology of the New Zealand Geosyncline is reviewed and zeolite facies rocks are shown to be of regional extent. They include lower grade heulandite–analcime–quartz assemblages and higher grade laumontite–albite–quartz in tuffs and volcanic greywackes. Thomsonite is found in basic igneous rocks of the Otama Complex. Separating the zeolitic rocks from typical greenschists is a broad belt with quartz–prehnite and quartz–pumpellyite assemblages.

The significance of zeolite sequences in amygdales is often a matter of doubt, but zeolite occurrences in sedimentary rocks, active thermal areas, alkaline igneous rocks and miscellaneous joints and cavities lend some support to two broad generalizations: firstly the water content relative to  $(Ca,Na_2)O \cdot Al_2O_3$  tends to increase for lower temperatures of formation in accordance with theoretical expectations based on entropy; secondly zeolites can be divided into three groups based on silica content: those whose occurrence is favoured by an environment supersaturated in silica, those that often coexist with quartz, and those favoured by silica-deficient environments.

The common species in the Wairakei thermal area are mordenite and wairakite, both of which are readily synthesized whereas laumontite and heulandite, typical of regional metamorphism, are not readily synthesized. This fact, together with the profound influence of starting materials on reaction products in hydrothermal syntheses, emphasizes the lack of equilibrium in our experiments, even in runs of 30 days. The field of high-silica phases such as mordenite is extended when the silica activity is higher than that of quartz. The effect of differing  $P_{load}$  and  $P_{H_2O}$  on important transitions such as analcime + quartz = albite + water is explored on theoretical grounds. Experiments place the reaction temperature at 280°C at 1000 bars water pressure, but the equilibrium temperature may be much lower. Preliminary solubility work indicates a reaction temperature near 200°C at saturated water vapour pressure. Under conditions where load pressure equals three times the water pressure the temperature may be lowered by about 200°C. The upper limit of the zeolite facies is believed to be about 300°C, when water and load pressures are approximately equal.

Fields of synthesis are given for the following: analcime–wairakite series, Na–Ca mordenite series, epistilbite, prehnite and an unidentified phase Z. Phillipsite was synthesized from chabazite. The upper limit of thomsonite is considered to be near 300°C where it breaks down to anorthite.

The range of composition and density of naturally-occurring zeolites is reviewed. New analyses and optical data are given for heulandite from Cape Blomidon, Nova Scotia, and for prehnite from Prospect Quarry, New South Wales.

### 1. INTRODUCTION

(W. S. F., D. S. C.)

THE writers consider that mineral assemblages in which zeolites are characteristic are of such widespread occurrence that a new mineral and metamorphic facies, the zeolite facies, should be recognized, as has recently been proposed by TURNER (in FYFE *et al.*, 1958). Field and laboratory studies indicate that the range of conditions under which the mineral assemblages of this facies form are at least as extensive as for other recognized major facies. The zeolite facies bridges a wide gap between sedimentary processes and the hitherto recognized metamorphic facies and it allows a more complete model of the evolution of metamorphic rocks in progressive regional metamorphism to be developed.

\* Now at Dominion Laboratory, D.S.I.R., Wellington.

TURNER wrote as follows: "ESKOLA (1939, p. 345) discussed the possibility of erecting a zeolite facies to include the many and varied assemblages of zeolites and associated minerals formed by deuteric and hydrothermal processes at low pressures and relatively low temperatures. He rejected the idea, however, on the supposition that such assemblages do not represent systems in equilibrium. He noted, moreover, that because of their hydrothermal origin, their nature 'depends largely upon the composition, reaction and concentration of the introduced solution'." Largely on the basis of field and petrographic studies in southern New Zealand (COOMBS, 1954) TURNER then proceeded to revive the "zeolitic facies" (hereinafter referred to as the zeolite facies) "to cover only regionally developed zeolitic assemblages that largely replace the pre-existing rocks and conform to the mineralogical and chemical requirements of a metamorphic facies as specified in Chapter I."

The purpose of this paper is to present field and laboratory evidence bearing on this problem, to explore the extent to which equilibrium is attained, and to suggest that the facies concept can justifiably be extended to the zones of diagenesis and low grade metamorphism.

Irrespective of the exact definition that is used for a metamorphic facies, in our view the stimulus and long-range value of the facies concept rests in the belief that, in time, the physicochemical conditions under which a rock of given bulk composition forms a given assemblage of minerals will be determined within definite limits.

If we wish to follow, say, the complete evolution of a granulite from an unmetamorphosed sediment, we must be prepared to examine each stage in the process and to recognize as markers each observable change of phase. This has been done in some detail for transitions from greenschist assemblages onwards, but lower grades have not been widely recognized.

FYFE (1955a) suggested that it was unlikely that greenschists would form much below 300°C. If there is any substance in this view, then, for so long as we ignore this gap of 300°, we are ignoring about one-third of the possible thermal range of normal regional metamorphism. Field and laboratory evidence, imperfect as they may be, indicate that this neglect is not justifiable and that a large number of important phase changes may occur in this temperature interval. Zeolites are sometimes major rock-forming minerals and show a significant number of such phase changes.

In considering any facies covering the lowest grades of metamorphism it is obvious that certain difficulties will arise which may be less apparent in higher grades. First, at low temperatures, the replacement of pre-existing minerals will tend to be a slow process and may not reach completion.\* The second difficulty arises from the fact that in low-temperature environments metastable phases may have a considerable chance of formation and survival. In the task of reconstructing

\* Partly for this reason it is convenient to consider some zeolitic rocks in terms of the mineral facies concept (ESKOLA, 1920, pp. 145-146), rather than in terms of metamorphic facies, the assemblage of coexisting minerals concerned forming perhaps an interstitial microaggregate in a sediment or a single zone in an amygdale. On the other hand some of the rocks described can appropriately be considered metamorphic in the sense that they are extensively or even completely reconstituted.

a history it may often be possible to draw interesting conclusions from the occurrence of a metastable phase, but kinetic factors must lead to a large degree of uncertainty. For the correlation of physical environment with mineral assemblage to be approached with any certainty, some assurance that equilibrium has been approached is necessary. In the review that follows it will become apparent that similar zeolite-bearing assemblages do in fact appear to form in similar environments. It also appears probable that in some circumstances metastable growth takes place in nature under conditions that may be comparable with those produced in the laboratory.

On the basis of widespread occurrence of zeolitic cements in Russian sedimentary rocks (reviewed below) RENGARTEN (1950) proposed a "geochemical zeolite facies." It was suggested that rather special chemical conditions including the presence of alkaline, colloidal solutions of silica and alumina and a high oxygen potential were necessary for zeolitization to occur. The oxygen potential was believed to distinguish the zeolite facies from a glauconite facies although zeolites and glauconite have subsequently been shown to coexist (BUSILINSKY, 1950; VASIL'EV, 1954). We do not believe that RENGARTEN'S views were justified.

## 2. THE ZEOLITE FACIES IN THE NEW ZEALAND GEOSYNCLINE AND THE TRANSITION TO THE GREENSCHIST FACIES

(D. S. C.)

### 2.1. *Geological setting: the New Zealand Geosyncline* (Fig. 1)

The dominant structural features of New Zealand geology are those related to the New Zealand Geosyncline (WELLMAN, 1956), in which deposition proceeded from pre-Permian times well into the Jurassic. In Otago, early greywackes, siltstones and occasional volcanics of the geosyncline have been metamorphosed into the extensive chlorite-zone schists, made well-known through the work of TURNER (1938) and HUTTON (1940). These schists continue northwards as a narrow belt, the "Alpine Schists," on the western flanks of the Southern Alps. At the south end of this belt, TURNER (1933) established chlorite, biotite and oligoclase zones, while further north in the Franz Josef-Copland River sector LILLIE and MASON (1955) have mapped chlorite, biotite and garnet zones. Boulders of kyanite gneiss in Paringa River and at Hunts Beach to the west have been collected by ODELL (personal communication), and suggest that kyanite-zone conditions were attained at least locally. The Alpine Schists grade progressively eastwards into "unmetamorphosed" (prehnite-zone) greywackes described below.

In the southern part of the South Island, the schist belt strikes south-east and is flanked on its south-west side, and apparently overlaid, by folded and steeply-dipping Upper Paleozoic greywackes, siltstones and some volcanics, the thickness of which is given by WOOD (1956) as being greater than 36,500 ft. The Upper Paleozoic rocks are in turn overlaid by Triassic and Jurassic beds in the Southland Syncline which includes at Taringatura the area that prompted TURNER'S re-erection of the zeolite facies. The Triassic sediments vary in thickness along the north limb of the syncline from about 10,000 to 30,000 ft (COOMBS, 1950), but they are much thinner where exposed on the south limb (WOOD, 1953). The thickness



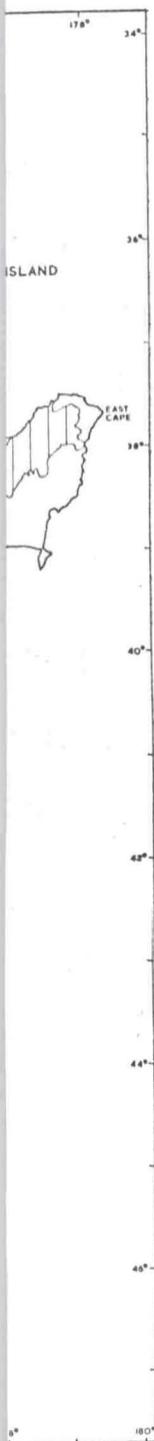
of the Jurassic beds is commonly about 10,000 ft. Petrographically, the Lower and Middle Mesozoic rocks of the Southland Syncline consist almost entirely of volcanic greywackes, siltstones and tuffs with scattered lenses of conglomerate. They belong to the "Hokonui Facies" of WELLMAN (1952), which is also preserved near Nelson and in the coastal regions of the south-west part of Auckland province.

On the north flank of the Otago Schists (MACKIE, 1936), as on the east of the Alpine Schists (WELLMAN, GRINDLEY and MUNDEN, 1952), are semi-schists that locally contain Triassic fossils, followed by an extensive belt of "greywacke" of WELLMAN's "Alpine Facies,"\* largely Mesozoic in age, but including elements containing the Permian fossil *Atomodesma* sp. in South Canterbury. This belt forms the main mountain ranges of Canterbury and Marlborough, and reappears to the north as the basement of much of the North Island. Thicknesses are largely unknown, although WELLMAN *et al.* (1952) consider that for part of the Triassic at least they are greater than in the Hokonui Facies. Graded, greywacke-type sandstones and siltstones are dominant. The volcanogenic fraction is less conspicuous than in the Hokonui Facies, and detrital quartz, potash feldspar and muscovite are correspondingly more abundant. Occasional interbedded volcanics are mostly spilitic pillow lavas, in contrast to tuffs of andesite-dacite-rhyolite affinities and rare andesitic intrusions which occur in the Hokonui Facies.

The concept has grown among New Zealand geologists of a progressive metamorphism consequent upon increasing depth of burial, depth being held to be the main factor controlling temperature. The absence of major intrusives in the New Zealand Geosyncline and, at least in the case of rocks of the zeolite facies, the sequence of mineralogical changes are both compatible with this view. At least three factors may modify this simple conception. First, the geothermal gradient may have varied in different parts of the geosyncline, the gradient being likely to have been lowest where sedimentation was thickest and most rapid. Secondly, structural evidence (GUNN, 1956; LILLIE *et al.*, 1957; ROBINSON, 1958) indicates the possibility that in the higher grade rocks important folding preceded the metamorphic maximum. Thirdly, it is conceivable that internal deformation, which in the schists is often intense, may have affected the position of mineralogically-determined isograds by promoting reactions or by causing slight rises in temperature.

Opinions differ as to the date of the "main" metamorphism and as to whether sedimentation was essentially continuous in the axial regions of the geosyncline. MUTCH (1957) and WELLMAN (1956) have suggested that there is a continuous thickening of formations from the Southland Syncline towards the Otago schist axis, and consider that the maximum grade of metamorphism was attained in the axial region of the geosyncline where these and Lower Jurassic formations were assumed to have achieved their greatest thickness. If this is so, there is a continuous gradation from the zeolite facies through a broad transitional belt into the greenschist and higher grade facies. In two columns, MUTCH indicates 50,000 and 95,000 ft of pre-Jurassic cover for the schists down to the Chl.2 subzone. Evidence of metamorphic grade in the Otama and Kaka Point areas does not altogether

\* Named from the Southern Alps of New Zealand.



(Based on  
Geological

support the concept of continuous thickening, and it is conceivable that in Lower Mesozoic times in southern New Zealand there were more or less separate troughs of deposition for the two sedimentary facies.

An upper limit to the date of metamorphism and of erosion deep enough to expose chlorite-zone schists is provided by the deposition of the Kyeburn and Henley formations, the basal members of which may be as old as Upper Jurassic and Lower Cretaceous, respectively (HARRINGTON, 1955). By this time, according to the concept of WELLMAN (1956, pp. 13, 31), new geosynclines were forming on the east side of the North Island and in the north-east part of the South Island to the east of the now firmly indurated welt of older geosynclinal sediments. Pebbles and grains of quartz-sericite-pumpellyite semi-schist in conglomerates and greywackes of probable Lower Cretaceous age (D. HAMILTON, personal communication) in the Hurunui Gorge area are evidence that in North Canterbury the older geosynclinal sediments were providing low grade metamorphic material to a trough in which younger greywacke suites were being deposited.

Similarly, low-grade metamorphics such as actinolitic metavolcanics and quartz-sericite semi-schists are not uncommon as fragments in the Triassic and Jurassic greywackes and conglomerates of Southland. WOOD (1953, 1956), has given evidence from northern Southland for at least three "marginal unconformities" (i.e. marginal to the New Zealand Geosyncline), which exposed successively younger members of the Permo-Triassic sequence to erosion. None of these breaks can be correlated with a general orogeny and metamorphism, but, at least in the case of the break between the Waipahi and Arthurton groups (Permian), the effects extended far from the margins of the geosyncline as is shown by the emplacement at Otama of an igneous complex (described later) which is interpreted as a crudely sheet-like mass nearly 4 miles thick.

Difficulties in unravelling the history of the New Zealand Geosyncline arise from the monotonous uniformity of extraordinarily thick and sparsely fossiliferous greywacke suites, known to range in age from Permian to Cretaceous and commonly preserving general uniformity of strike. The present writer considers that evidence for unrest throughout the mobile belt of the New Zealand Geosyncline is likely to increase with the passage of the years and that the concept of continuous sedimentation, with thickening towards the axis of the geosyncline, is likely to prove at best an over simplification. It is suggested that the locus of most rapid sedimentation may have migrated repeatedly, as indeed it has during New Zealand's later history, and that the metamorphic maximum was not reached simultaneously at all points. The main significance of this interpretation, as far as the present paper is concerned, is that an unchallengable transition from the zeolite facies to typical greenschist facies rocks cannot yet be demonstrated for any one section, nor is it yet possible to state with any great accuracy the depths of cover under which chlorite-zone and higher grade metamorphism occurred. Nevertheless numerous sections of vast thickness are available for study as described below, some of them uncomplicated by unconformities, igneous intrusions or structural disturbance, and from these the general trend of a metamorphic sequence from the zeolite facies through a very broad zone characterized by prehnite and pumpellyite, to the greenschist and hence to higher facies, seems clear.

2.2. *Mesozoic sediments of the Hokonui Facies*

2.2.1. *Taringatua*. In the northern part of the Taringatua district on the north limb of the Southland Syncline is a steeply dipping sequence, approximately 30,000 ft thick, of Hokonui Facies sediments ranging from about Lower to Uppermost Triassic in age (COOMBS, 1950). The area is free from any vents or intrusions of Triassic or later age, and deformation is confined primarily to the simple folding of the syncline, adjustment to which has been accomplished by slip on widely-spaced bedding planes. The amount of post-Triassic overburden that may have been removed is unknown, but it is unlikely to have been more than 10,000 to 15,000 ft, and it may have been much less.

COOMBS (1954) showed that glass in ash beds in the upper part of the section has been completely replaced by heulandite\* or less commonly by analcime. Both zeolites coexist with quartz and fine-grained phyllosilicates. The great majority

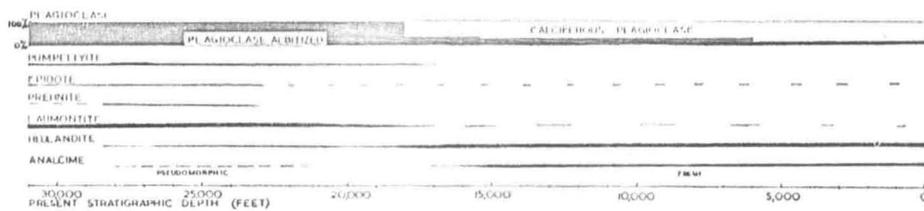


Fig. 2. Mineralogical features in relation to stratigraphic depth below the highest beds at present exposed, Taringatua, Southland, New Zealand (after COOMBS, 1954).

of rocks here contain fresh detrital lime-bearing plagioclase as a major constituent, but from successively lower horizons it is found to be missing from more and more specimens. In its place are pseudomorphs of dusty albite with sericite inclusions, although some "islands" rich in relict andesine persist almost to the base of the section. Simultaneously with the albitization of plagioclase, analcime and heulandite disappear. Analcime has not been observed in rocks from lower than about 17,000 ft below the top of the section, its place being taken mainly by albite, but also in some cases by pseudomorphs of adularia or laumontite. Heulandite persists to greater depths, but it appears to give way to laumontite plus quartz and the lower part of the section contains numerous beds of altered ash, some of them very thick, in which laumontite is the dominant constituent. First pumpellyite, then prehnite appear as accessory minerals. In some cases at least, notably in quartz-albite-adularia-pumpellyite metasomatites, the pumpellyite has clearly formed at the expense of laumontite, magnesium and iron being provided by celadonite and chloritic minerals. Tiny granules of epidote that appear to have grown in place are seen in thin sections from most stratigraphic levels, but they are always quite subordinate in quantity. Stilbite is occasionally found in joints of late formation. It is to be emphasized that with this exception the zeolites occur as essential constituents of the rocks and not as the fillings of veins or joints, although laumontite does occur as a replacement of fossils.

Chemical analyses, including spectrographic data on trace elements, are

\* Including clinoptilolite.

compatible with the conclusion that although the altered rocks deviate notably from their original composition, the metasomatism is complementary and it is unlikely that material was brought in from outside the sedimentary pile.

The sequence of mineralogical changes (Fig. 2) may be summarized as follows:

- (1) Alteration of glass in tuffs to heulandite or analcime.
- (2a) Replacement of the assemblage analcime-quartz by albite-quartz.
- (2b) Replacement of heulandite by laumontite, and of detrital calciferous plagioclase by albite and laumontite.
- (3) Substitution of pumpellyite and prehnite for laumontite.
- (4) Post-tectonic precipitation of stilbite in joints.

It is not possible in the Taringatura district to map sharply-defined zones dependent on the stage of alteration, although beds above the present 17,000 ft level are dominantly in a *heulandite-analcime stage* whereas those below 17,000 ft are dominantly in a *laumontite stage*, while a *prehnite-pumpellyite stage* appears spasmodically towards the base. Observed assemblages of coexisting non-detrital minerals from Taringatura include the following. In each case scaly phyllosilicates of various shades from green to brown and of moderate to high birefringence are further possible phases.

*Stage 1 (heulandite-analcime stage):*

heulandite-montmorillonoid-quartz  
 heulandite-quartz-celadonite  
 analcime-quartz-celadonite  
 heulandite-quartz-celadonite-sphene.

*Stage 2 (laumontite stage):*

laumontite-albite-quartz-celadonite-sphene  
 laumontite-albite-adularia-quartz-celadonite  
 quartz-albite-adularia-montmorillonoid-sphene.

*Stage 2 or 3:*

albite-quartz-chlorite-sphene  
 albite-chlorite-calcite-sphene.

*Stage 3 (prehnite-pumpellyite stage):*

quartz-albite-adularia-pumpellyite  
 albite-chlorite-pumpellyite-sphene  
 albite-chlorite-prehnite-quartz.

*Discussion.* The relation of alteration to depth and hence by inference to temperature, seems clear, although the gross overlapping of zones is to be emphasized. The sequence heulandite, laumontite, pumpellyite, prehnite, epidote is one of decreasing hydration accompanied by release of silica as indicated in Fig. 3, although in the case of the non-zeolites dehydration is complicated by changes in the alumina content which must involve reactions with aluminous minerals such

iate notably  
ry and it is  
oile.  
d as follows:

uartz.  
l calciferous

efined zones  
ent 17,000 ft  
ow 17,000 ft  
stage appears  
non-detrital  
hylosilicates  
fringence are

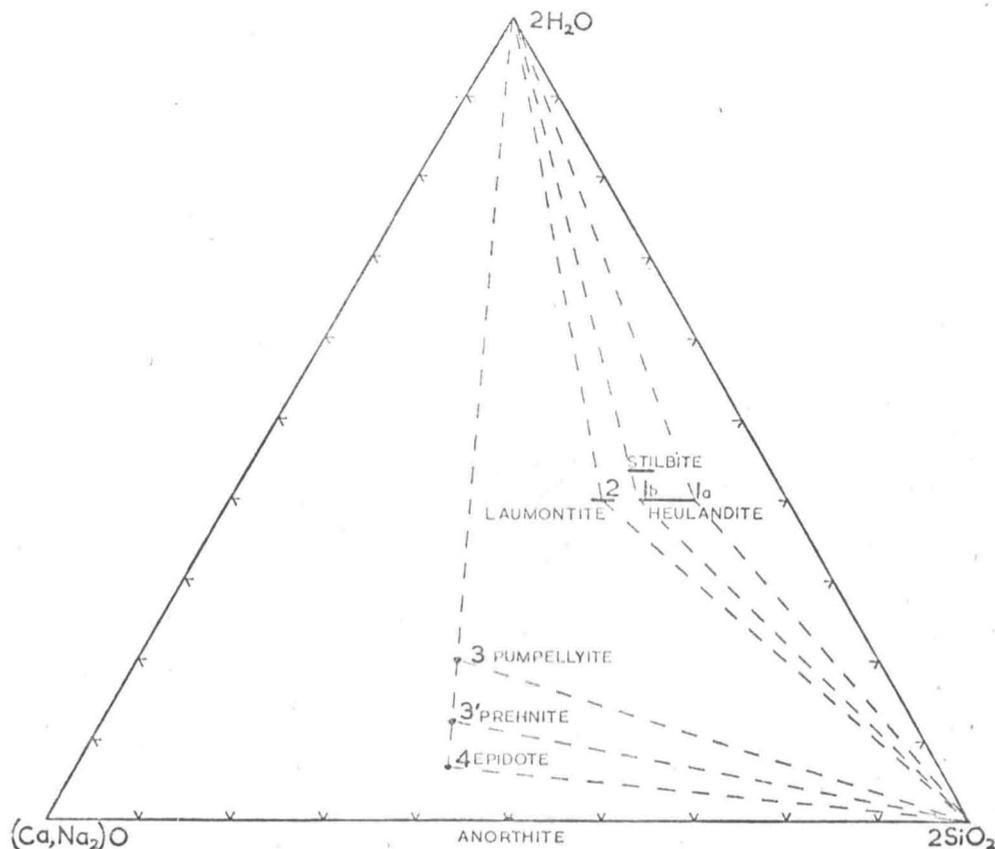
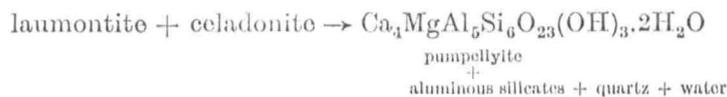


Fig. 3. The sequence of Ca-Al silicates 1, 2, 3, 3', 4 coexisting with quartz and water under regional conditions in southern New Zealand. 1a and 1b are the siliceous and aluminous extremes of the heulandite series.

as clays, micas and chlorites. Using conventional formulae, we have:



inference to  
to be empha-  
epidote is one  
ted in Fig. 3,  
by changes in  
minerals such

Epidote,  $\text{Ca}_2(\text{Al,Fe})_3\text{Si}_3\text{O}_{12}(\text{OH})$ , is characteristic of the greenschist facies of Otago and it may be produced from pumpellyite and prehnite by further dehydration reactions. The final step in the series is the well-known decomposition of epidote in the amphibolite facies, anorthite entering the plagioclase and excess alumina being taken up by such minerals as amphiboles. Dehydration is also involved in the formation of albite from analcime and quartz.



estimated by MAIRWICK (1946) to be 28,000 ft thick. Several hundred thin beds of vitric tuff altered to impure laumontite rock are exposed along the coast. Plagioclase is in part replaced by laumontite and in part is either albitized with sericite inclusions or remains as relict oligoclase or andesine. Subordinate spongy prehnite is not uncommon in laumontitized vitric tuffs, in the groundmass of crystal tuffs and volcanic greywackes, and in tuffaceous siltstones. Calcite-laumontite veins are a feature of crush zones, especially along the bedding planes. Biotite tends to be chloritized, and secondary quartz, calcite, chlorite and sphene occur. Rocks in the heulandite stage were noted but appear to be rare.

### 2.3. *The Otama Igneous Complex and associated Permian sediments*

2.3.1. *Geological setting.* Four miles north-eastwards across the strike from the lowest Triassic beds of the Hokonui Hills, is the Late Paleozoic Otama Intrusive Complex of which about 16 square miles are exposed. It consists dominantly of metagabbros and albite micro-granites, associated with keratophyric and spilitic volcanics, some of which are hornfelsed by the intrusives. Although individual members are not all stratiform in arrangement the mass is roughly concordant with the enclosing sediments and is interpreted by WOOD as having been overturned through an angle of 110°. On its north side, the complex is in steeply dipping thrust-contact with prehnite-bearing greywackes which, as far as is known, grade northwards through progressively more metamorphosed rocks of the Tuapeka Group into the typical schists of Central Otago type.

Permian volcanic greywackes and associated dacitic tuffs immediately south of the complex are partly in the heulandite stage of alteration and partly in the laumontite stage, and it was from this area that HURTON (1949b) first drew attention to the metamorphic significance of laumontite.

2.3.2. *Alteration of the Otama Complex.* At least two types of alteration are represented: contact metamorphic effects produced during the emplacement of successively younger intrusions; and subsequent low-grade alteration of a more regional nature that has affected the igneous complex and sedimentary rocks alike. For example the conversion of keratophyres into plagioclase-hornblende-epidote and plagioclase-hornblende-diopside hornfelses belongs to the first type; albitization of the plagioclase and veining of the same rocks with prehnite and sometimes laumontite belongs to the second type. The later alteration has undoubtedly been promoted by intense crushing almost throughout the complex. This has allowed free access to a vast surface-area of rock, of the water essential for the formation of those minerals diagnostic of zeolite facies conditions, and without which a high-temperature igneous mineral assemblage will be preserved at low temperatures virtually throughout geological time. In both the basic and more acidic rocks calciferous plagioclase is something of a rarity, its place being taken by cloudy albite and/or a variety of other secondary minerals including epidote, pumpellyite, prehnite, laumontite, thomsonite and analcime. Crush-zone laumontite associated with prehnite has already been described (COOMBS, 1952).

The more basic rocks are of particular interest in showing the effects of zeolite facies metamorphism in an environment devoid of free silica. The most typical Ca-Al-silicate in these rocks is thomsonite.

An unusually fresh, basic noritic gabbro, no. 946, from 125 chains NE of Otama Hall, consists of bytownite  $An_{83}$ , augite and hypersthene sometimes mantled with hornblende, minor

iron ore and rare pseudomorphs after olivine. The plagioclase shows minor alteration to feathery wisps and films of thomsonite. Such alteration is more advanced in a slightly crushed anorthositic segregation, no. 950, from the same area, having bytownite  $An_{81}$  as its major primary phase. It is riddled with flecks of thomsonite which are especially abundant near irregular criss-crossing bands of almost pure zeolite, from which innumerable angular embayments extend into the feldspar. Rosette-like clusters of prehnite are often enclosed within the thomsonite and there are also a few threads of an epidote-group mineral, chloritic films and traces of other zeolites. Variable refractive indices such as  $\alpha$  1.527,  $\gamma$  1.538 indicate aluminous members of the thomsonite series (Hey, 1932a, p. 79). To a first approximation, such alteration of calcic bytownite to thomsonite can be regarded as a simple hydration to  $CaAl_2Si_2O_8 \cdot 2.4H_2O$ . In the most crushed rocks plagioclase is completely replaced by thomsonite with nests of prehnite, minor laumontite and tiny veinlets of unidentified fibrous zeolite. There is much relict augite, some hornblende and chloritic material.

Another hypersthene gabbro, 588, from 29 chains downstream from Pyramid Bridge, shows labradorite  $An_{50}$  net-veined and partially replaced by thomsonite, pools and later veins of analcime, minor laumontite and occasional nests of prehnite within the thomsonite. In some associated metagabbros feldspar has been completely destroyed. The earlier analcime is penetrated by needles of thomsonite and is likely to have coexisted in equilibrium with it. The analcime presumably represents excess sodium over that taken up by the thomsonite. Replacement of the albite component of plagioclase by analcime would result in the release of silica. A small amount of this could be taken up by an increase in the Si:Al ratio of the thomsonite and it is tempting to consider that the remaining excess silica has caused the formation of the more silica-rich zeolite, laumontite.

A still less basic differentiate, 1581, an apatite-bearing hornblende hypersthene gabbro from about  $2\frac{1}{2}$  miles NE of Otama Hall has  $An_{36}$  for its plagioclase and shows incipient alteration to laumontite. Another specimen, 1584, which may initially have been rather similar, has had its calciferous plagioclase completely replaced by albite, laumontite and prehnite. These rocks are associated with hornblende and pyroxene andesinites, as well as albitites (e.g. 1587) veined and riddled with laumontite, prehnite, and epidote, suggesting that they were produced by the alteration of andesinites or oligoclases under conditions transitional between the zeolite facies and the greenschist facies. In some cases the prehnite appears to be replacing earlier laumontite.

The Otama albite microgranites, hornblende microgranites and granophyres are remarkable for near-universal signs of cataclasis, for the uniformly purely albitic plagioclase which is usually somewhat cloudy and flecked with sericite, for their liberal sprinkling and veining along crush-bands with prehnite, epidote and in some cases pumpellyite and for the paucity of potash feldspar. Chloritic minerals and secondary sphene are widespread. Zeolitization is rare both in these and in the albite-hornblende-epidote-sphene hornfelses, and except for a late vein of stilbite (9728) and an occurrence of analcime in a mylonite (9683) the only zeolite noted so far in these quartz-bearing rocks is laumontite. In one case (9741) this appears to be in the process of replacement by pumpellyite and prehnite.

The usual mineral assemblage in the unhornfelsed keratophyric and spilitic volcanics is albite-epidote-chlorite-sphene(-quartz). In other cases pumpellyite (9735), or prehnite and pumpellyite (9734), largely take the place of epidote.

Summarizing the above observations on the Otama rocks it may tentatively be concluded:

- (1) At some time subsequent to consolidation, the Complex was subjected to regional cataclasis and alteration under conditions ranging from those of the zeolite to the greenschist facies, quartz-albite-epidote-chlorite-sphene assemblages being typical of the latter.
- (2a) Calciferous plagioclase in the microgranites, hornfelses and spilitic volcanics was replaced by assemblages of albite plus prehnite, pumpellyite

or epidote, together with chlorite and sphene derived from the ferromagnesian.

- (2b) In a few cases in these rocks the prehnite and pumpellyite appear to replace earlier laumontite.
- (3a) In the most basic noritic gabbros thomsonite is the characteristic zeolitic alteration product, and in some cases is itself in process of replacement by prehnite.
- (3b) In the less basic gabbros, thomsonite is accompanied by varying amounts of analcime and laumontite, also sometimes partially replaced by prehnite.
- (4) Laumontite is the only early-metamorphic zeolite recorded from quartz-bearing members, but analcime and stilbite occur in addition in late veinlets and crush-zones.

#### 2.4. Greywackes and associated volcanics of the "Alpine Facies"

2.4.1. *Mid-Canterbury.* The main highway from Christchurch to the west coast of the South Island via Arthurs Pass provides a discontinuous section about 30 miles long from the edge of the Canterbury Plains to Arthurs Pass on the Main Divide. The basement rocks throughout this distance are monotonous, steeply dipping greywackes and associated rocks of WELLMAN'S "Alpine Facies." Their general trend is transverse to the line of section, but their structure remains to be elucidated.

Near the east end of the section, little altered greywackes (15711-15714) containing the annelid *Terebellina mackayi*, of probable Triassic age, are exposed at the upper Kowai River bridge. Detrital grains include unaltered andesine and plentiful biotite which shows incipient bleaching and loss of birefringence, as well as quartz, muscovite, orthoclase, accessory minerals and a variety of rock fragments. Very fine-grained reconstituted chloritic material and calcite are disseminated through the groundmass. Joints are filled with calcite. Boulders (15708-15710) from the Kowai River, which has its source in the Torlesse Range about 5 miles north of the bridge, include prehnite-bearing greywackes, variolitic spilite with veins of quartz-pumpellyite and calcite-prehnite-pumpellyite(-epidote), and radiolarian metachert with pumpellyite-chlorite-quartz(-epidote) veins.

Three miles to the north-west at Porters Pass, the greywackes (15715-15719) are distinctly more altered than at Kowai Bridge although in some cases oligoclase-andesine survives amongst the otherwise albitic detrital plagioclase. Prehnite is a variable but often plentiful constituent, occurring as spongy undulose grains or as better-formed groups of crystals in the groundmass, as inclusions in plagioclase and sometimes even as plates separating the cleavage planes of biotite, which shows marked lowering of birefringence (cf. KOSSOVSKAYA and SHUTOV, 1955). Epidote is not abundant and is in part detrital. The rocks are copiously traversed by quartz-prehnite veins varying from a fraction of a millimetre to two centimetres or more in thickness and apparently controlled by early-formed shatter systems, as is commonly the case in rocks of this metamorphic condition in New Zealand. Several episodes of crushing and recementation of the same vein are often apparent. In some cases a quartz-pumpellyite zone occurs near the walls of the vein, the pumpellyite being an iron-poor, pale-green variety. Porters Pass is on the trace of a major active fault and a younger shatter system has been imposed on the older, some of the younger fractures being filled with laumontite.

Rather similar prehnite-stage greywackes, freely traversed by quartz-prehnite or quartz-prehnite-pumpellyite veins, may be collected at numerous points between Porters Pass, the Waimakariri River and the Main Divide. A particularly instructive specimen (15707) from near the bridge over Craighorn River has the assemblage quartz-albite-prehnite-chlorite-sphene(-epidote) amongst its reconstituted minerals, together with the usual relict detrital minerals, including orthoclase which appears to persist unaltered under prehnite-stage conditions.

The rock is traversed by numerous quartz-prehnite veins which are cut by later fractures cemented by laumontite or lined with dusty analcime, and by still later joints filled with stilbite.

The prehnite from the above rocks appears to be rather uniformly iron-poor. Optical properties of better-crystalline material are  $\alpha$  1.615,  $\beta$  1.624,  $\gamma$  1.644  $\pm$  0.002,  $2V_{\gamma}$  67  $\pm$  2°, dispersion imperceptible; suggesting about 1 per cent  $Fe_2O_3$ .

2.4.2. *Wellington Peninsula.* REED (1957) has described the petrology of the greywackes, argillites, spilites and jasperoids of Wellington Peninsula. He briefly records secondary calcite, laumontite and prehnite as coatings and veins in crush zones and considered them to be the product of shearing (REED, 1957, p. 18). Pumpellyite is recorded from the spilites. The present notes supplement these observations on the basis of an examination of specimens (14951-14974) from the 15,000 ft south-coast section from Houghton Bay to Sinclair Head (BRODIE, 1953). Quartz-prehnite veinlets, with or without calcite, sericite, albite and chlorite are here magnificently developed in tension fractures and shatter-planes in greywackes and to a less extent in argillites throughout the section. The prehnite may be coarse (>1 mm) or fine, spongy or well crystallized. Representative specimens do not vary significantly in their optical properties from those recorded above for Canterbury prehnites. In most cases detrital plagioclase is uniformly albitic and prehnite is often thinly disseminated through the matrix of the rock, but in some cases with sparse film-like veinlets of calcite-prehnite instead of quartz-prehnite, unaltered detrital oligoclase-andesine was observed. At Island Bay, laumontite was observed to replace plagioclase in some cases. In the more altered rocks, biotite shows marked loss of birefringence. Specimens (14975-14979) from Worsler Bay on the west shore of Wellington Harbour were found to be less altered. They lack quartz veins or prehnite, calciferous plagioclase remains and detrital biotite has almost normal colour and birefringence. The range of alteration phenomena on Wellington Peninsula thus closely parallels that in mid-Canterbury.

2.4.3. *Other occurrences.* BROTHERS (1956) showed prehnite to be important both in the matrix and in quartz-prehnite veins in tension fractures of greywackes from North Auckland, and HURTON (1949a) has reported prehnite and minor pumpellyite from greywackes of Kapiti Island.

2.4.4. *Discussion.* Pumpellyite and prehnite, especially the latter, are clearly of key importance in the metamorphic history of vast tracts of WELLMAN'S "Alpine Facies." They are here interpreted as having been derived mainly from the breakdown of detrital calciferous plagioclase and perhaps in part from calcite and clay minerals or earlier zeolites.

The following alteration stages may tentatively be recognized for the lowest grades of metamorphism of the Alpine Facies, three of them being progressive and one retrogressive:

(1) Little visible mineralogical change apart from some loss of birefringence of biotite and the formation of very fine-grained chloritic or clay minerals in the matrix. Zeolites in the matrix are rare.

(2a) Detrital plagioclase partly or completely altered to albite commonly accompanied by prehnite. Associated volcanics (spilites) have mineral assemblages containing albite-calcite-pumpellyite-chlorite, and less characteristically epidote and/or prehnite and sometimes minor quartz.

(2b) Prehnite is concentrated in monomineralic veinlets and prehnite-calcite veins, without much quartz.

(3) Greywackes heavily veined with quartz-prehnite with or without pumpellyite.

(4) Fracture planes produced subsequent to the metamorphic maximum are filled by a sequence of minerals that is one of increasing hydration, namely prehnite, laumontite, stilbite, with analcime also possible before stilbite.

The first stage corresponds in part at least to the zeolite facies of Southland, zeolites being rare largely on account of the scarcity of suitable reacting materials. It is also conceivable that sedimentation was more rapid and the geothermal gradient even less steep in the Alpine Facies than in the Hokonui Facies. This could have caused water to have been expelled and porosity lost by compaction before zeolites could form at an appreciable rate. Stage 2 corresponds directly to the prehnite-pumpellyite stage as defined for Taringatura although osmotic or water-deficient conditions could conceivably cause the formation of prehnite at lower temperatures than in Taringatura (see 4.5, 4.10). The appearance of plentiful vein quartz in stage 3 (zone of quartz-prehnite veins) may well indicate a higher temperature and is not readily compatible with any suggestion of water-deficient conditions. WELLMAN *et al.* (1952) have stressed the importance of "quartz" veins as a metamorphic indicator in New Zealand, and although this is a criterion to be used with great caution, the veins being promoted by shattering or the opening of tension fractures, the abundant incoming of quartz-bearing veins is here accepted as being of potential metamorphic significance, as further discussed on theoretical grounds in a later section.

The sequence of vein fillings noted in stage 4 is a reversal of the trend recorded for progressive metamorphism under increasing load and temperature although with stilbite taking the place of heulandite, and it can be correlated with the filling of fractures under conditions of progressively decreasing load and temperature during denudation. Laumontite in minor faults in chlorite-zone schists at Five Mile Creek, and in joints in greenschists near Shotover Bridge, both near Queenstown, Central Otago, has a similar retrogressive significance. Apart from the possible effects of differing rock pressure and vein-water pressure as discussed later, and in the absence of the incoming of newly heated solutions, the metamorphic significance of a late zeolite- or prehnite-bearing vein is that the rock it cuts has passed through a metamorphic maximum with  $P$ - $T$  conditions at least as severe as those of which the vein mineral assemblage is diagnostic.

#### 2.5. *Later Mesozoic geosynclinal sediments*

Analcime and heulandite in Lower Cretaceous greywackes, in part tuffaceous, collected by D. HAMILTON from the Hurunui Gorge above Ethelton in North Canterbury, veinlets with laumontite and calcite and laumontite replacement of plagioclase in the Cretaceous Taitai sandstone from Motu Falls, Poverty Bay, show that zeolitic alteration also occurs in thick sedimentary sequences of New Zealand younger than those of the main New Zealand Geosyncline.

#### 2.6. *A prehnite-pumpellyite zone*

The above descriptions show that prehnite-bearing rocks are of regional extent in New Zealand. They appear to grade continuously into chlorite-zone schists, and prehnite-bearing assemblages are also found in the more altered members of the zeolite facies. TURNER and HUTTON (see TURNER, 1948, p. 38) have divided the "chlorite zone" of metamorphism in Southern New Zealand into four *texturally* defined subzones, these being progressively more reconstituted from subzone Chl. 1 to Chl. 4. ROBINSON (1958) shows that pumpellyite occurs freely in semi-schists of subzones Chl. 1 and 2 on the east Otago coast south of Brighton, but

disappears at about Chl. 3 beyond which epidote is the only Ca-Al silicate apart from actinolite. Pumpellyite is now known to be a characteristic Ca-Al silicate of semi-schists of similar metamorphic grade described by MACKIE (1936) from his traverse south of the Waitaki River, although epidote is also present. It is also common, for example, in the lower grade schists of north-west Otago (HUTTON, 1937) in the Kakanui Ranges (TURNER, in WILLIAMSON, 1939; AMIES, 1952) in South Canterbury (AMIES, 1950), and in Upper Palaeozoic spilites, greywackes and tuffs of about Chl. 1 grade from northern Southland (REED, 1950).

Mutually associated minerals in the Alpine Facies greywackes include quartz, albite, prehnite, pumpellyite, chlorite, sphene and detrital orthoclase; and in typical Chl. 2 rocks from East Otago there is some combination of the following: quartz, albite, chlorite, sphene, actinolite, muscovite, stilpnomelane, pumpellyite and epidote. An extremely broad zone can thus be mapped in New Zealand characterized by prehnite and/or pumpellyite. The incoming of actinolite and stilpnomelane in rocks of appropriate composition, the conversion of orthoclase to mica, and the disappearance of prehnite represent possible isogradic markers within the zone. Beyond a zone of transition, zeolites disappear and the rocks are not to be placed in the zeolite facies. We suggest that it may prove convenient to erect a new facies or low-grade subfacies of the greenschist facies to accommodate these rocks but that further field work on their subdivision is desirable before this is done. It will be recalled that MIYASHIRO and BANNO (1958) have recently shown that pumpellyite occurs in the lowest grade schists of the Sanbagawa-Mikabu zone in Japan and that DE ROEVER (1950, 1955) has already suggested that pumpellyite-bearing assemblages belong to a special subfacies, perhaps of the greenschist facies. His further suggestion that it represents a very low-grade equivalent of the glaucophane schist facies is hardly applicable to the New Zealand occurrences in which glaucophane is almost unknown.

### 2.7. *Distribution of the lower metamorphic grades in New Zealand*

As far as is known, all Lower Mesozoic formations of the Hokonui sedimentary facies (Fig. 1) show zeolite facies alteration although, as recorded above, transitions occur to prehnite-pumpellyite assemblages. At least some of the sediments of the Later Mesozoic geosyncline are to be included and probably also some of those of the Alpine sedimentary facies, as well as part of the belt of Late Palaeozoic rocks, including the Otama Igneous Complex, which separates the Lower Mesozoic rocks of Southland from the Otago schists. The remainder of this belt, a corresponding belt to the west of the higher grade schists of Marlborough and almost certainly most of the Alpine Facies rocks belong to a prehnite-pumpellyite zone as described above.

## 3. REVIEW OF OTHER ZEOLITE OCCURRENCES

(D. S. C., A. J. E.)

In the following section, the principal types of zeolite occurrence as reported in the literature will be briefly reviewed to test their bearing on the facies concept and on the conditions of zeolite formation.

3.1. *Zeolites in sedimentary rocks*

3.1.1. *U.S.S.R.* Analcime, "mordenite" and laumontite have been reported as authigenic cements in a wide variety of sediments of Permian to Tertiary age coming from vast areas of Russia and Siberia (e.g. RENGARTEN, 1940, 1945, 1950; BOLDYREVA, 1953; DZOTSENIDZE and SKHIRTLADZE, 1953; BUR'YANOVA, 1954, 1956; VASIL'EV, 1954; KOLBIN and PIMBURGSKAYN, 1955; KOSOVSKAYA and SHUTOV, 1955; VASIL'EV, KOLBIN and KRASNOVA, 1956). According to BUSHINSKY (1950) associated authigenic minerals in Upper Jurassic and Cretaceous clays, sandstones, marls and chalk of the Russian platform include glauconite, opal, chalcedony, quartz, montmorillonite, nontronite, calcite, pyrite or marcasite, hydromica and the phosphates kurskite and francolite.

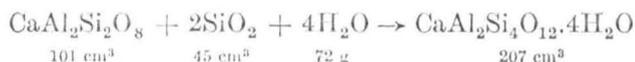
On the basis of its refractive indices and platy habit as figured by BUSHINSKY and in the absence of X-ray data, the present writers believe that much of the "mordenite" of the above authors is likely to be clinoptilolite, the silica-rich variety of heulandite. VASIL'EV (1954) gives a table of crystallographic measurements of crystals isolated from the phosphorites of Kashpur, and shows that they compare closely with those of DANA (1892) for "mordenite." DANA's crystallographic data were obtained from material from Hoodoo Mts., Wyoming, which was subsequently taken by SCHALLER (1932) as his type clinoptilolite, and shown by HEY and BANNISTER (1934) to be silica-rich heulandite. Crystallographically this is quite distinct from true mordenite.

The Russian authors do not appear to have recognized any zoning in the occurrence of the above zeolites; in fact in two cases (RENGARTEN, 1950; KOLBIN and PIMBURGSKAYN, 1955), analcime and laumontite occur together, whereas in southern New Zealand they are characteristic of, though not confined to, two distinct depth zones. Significant to the concept of mineralogical zoning with depth is the work of KOSOVSKAYA and SHUTOV (1955) who recognize a progressive sequence of changes in the alteration of clastic biotite to chlorite at varying depths in more than 5000 m of Permian, Jurassic and Cretaceous sediments of the Verkhojansk geosyncline in north-east Siberia. Laumontite is recorded as occurring as a cement in the Lower Cretaceous members, whereas the cement in the Upper Permian consists of quartz and albite with new-formed limonite and rutile, and in the Lower Permian of quartz and muscovite. Subsequently (1956) the same authors reported authigenic epidote in the same pile of sediments.

3.1.2. *U.S.A.* The work of BRADLEY (1928, 1929), ROSS (1928, 1941) and KELLER (1951, 1952, 1953) on very low temperature sedimentary analcime is well known. HEADY (1952) has detected the mineral in a Colorado oil shale while FOSTER and FEICHT (1946) and ROZENDAL (1957) have found it in coal. Similarly BRAMLETTE and POSNJACK (1933) and KERR and CAMERON (1936) have demonstrated the common occurrence of clinoptilolitic heulandite partly preserving glass shards in bentonites, while GILBERT and McANDREWS (1948) have described authigenic heulandite cement in Miocene sandstone from Santa Cruz Co., California.

Laumontite cements have been reported by GILBERT (1951) from Mendocino Co., California, by KALEY and HANSON (1955) from Miocene feldspathic sandstone at a depth of 11,000 ft in a well in San Joaquin Valley, California, and by HEALD

(1956) from the fluvialite New Haven arkoses of Connecticut. The aggregate maximum thickness of the Triassic of Connecticut is given as rather more than 15,000 ft and the laumontite is reported to occur sporadically in the lower part of the section. Cements of authigenic albite and potash feldspar are abundant throughout the column, although they occur in traces only in the laumontite-bearing rocks. There is minor secondary quartz in the cement and sporadic sericite. HEALD considers that since the laumontite occurs as interstitial fillings, part of its material, as of the secondary albite, must have been introduced. Derivation from the Triassic diabases was suggested. It may be pointed out, however, that the alteration of calcic plagioclase to laumontite involves an equation such as:



Hence, if this type of alteration occurs, some of the laumontite constituents must migrate from an altered plagioclase crystal at least as far as the nearest pore space (cf. ANTUN, 1953, p. 69). Such a cement does not require an outside derivation. Whatever the chemical origin of the laumontite or of the authigenic albite, the assemblage of interstitial minerals, albite, potash feldspar, laumontite and quartz, suggests conditions very similar to those prevailing in the middle and lower parts of the Taringatura section of southern New Zealand as reviewed above.

More recently Ross (1958) has described laumontitized tuffs from wells in Clinch County, Georgia, which are remarkably similar in texture and mineral assemblage to those of Taringatura. The alteration of celadonite to chlorite and its association with saponite are to be noted.

3.1.3. *Australia.* GILL (1957) has recently reported laumontite replacing wood in richly feldspathic Jurassic arkoses from East Gippsland, Victoria, and observations by one of us (D. S. C.) show that the mineral occurs in the groundmass and as a replacement product of plagioclase in the same series of rocks. GILL (personal communication) suggests an original cover of about 3000 ft for the rocks concerned. COOMBS (1958) has shown that glass in Carboniferous volcanic ashes of the Kuttung Series, near Seaham, New South Wales, has been altered to clinoptilolite coexisting with quartz, celadonite and sphene. Joints in the same rocks are coated with stilbite, but sometimes contain laumontite as well.

### 3.2. *Formation of zeolites in active thermal areas*

3.2.1. *Wairakei, North Island, New Zealand.* At Wairakei, a hot-spring and fumarole area in the volcanic region of New Zealand, numerous wells have been drilled to provide steam and hot water for electric power generation. These wells provide an unusual opportunity for studying the mechanism and properties of an active hydrothermal system. From drill cores and cuttings, STEINER (1953, 1955a, b) has demonstrated the following zones of hydrothermal alteration (Fig. 4) caused by the action of steam and hot solutions on a sequence of rhyolite tuffs and breccias interbedded with minor mudstones and claystones. The hot solutions are saturated in silica which precipitates at all levels.

(a) Surface acid leached zone: The characteristic minerals are kaolinite, alunite and opal.



(b) Zone of argillization: Rhyolite glass is changed to montmorillonitic clays. Plagioclase crystals are sometimes unaltered but are sometimes replaced by calcite.

(c) Zone of zeolitization: This is superimposed on the zone of argillization and is subdivided into an upper and a lower zone. In the upper zone the lime-soda zeolite "ptilolite", structurally indistinguishable from mordenite, is characteristic, and fills vesicles in pumice. In some cases it is associated with minor heulandite. Plagioclase phenocrysts are practically unaltered. In the lower zeolite zone wairakite (calcium analcime) replaces andesine and also fills veins and cavities by direct crystallization from solution.

Laumontite has subsequently been found by STEINER (personal communication) in a zone between ptilolite and wairakite at a depth between 500 and 900 ft where temperatures ranging from 195 to 220°C have been measured. It has also been found at greater depth below the wairakite zone in a deep drill-hole where a reversal of the temperature gradient appears to occur.

(d) Feldspathization zone: An upper subzone is characterized by albitization, and a lower one by adularia replacing plagioclase. Secondary sphene (titano-morphite) is scattered through the rocks and in bore no. 11 adularia and sphene are accompanied by prehnite through a short vertical range. Calcite is locally precipitated, and the alteration of plagioclase to calcite and albite was observed.

(e) Zone of hydromica: In this zone, which exists below about 2000 ft, primary plagioclase is replaced by a hydromica as a result of leaching of alkalis by carbon dioxide solutions entering the zone from below.

The concentrations of sodium, potassium and calcium in the waters collected from bores at various depths (ELLIS and WILSON, 1955; ELLIS, 1958) correlate very well with this sequence of alteration. The hot solutions in the deepest zones tapped have a high concentration of potassium, which is progressively lowered by the formation of adularia from the original plagioclase. The concentrations of sodium and calcium are increased correspondingly until in the zone of zeolite formation some of these ions are again precipitated. By this stage the atomic ratios Na/K and Ca/K have increased from about 9 and 0.06 in the hydromica zone, to 20 and 0.15, respectively. The pervading solutions are approximately 0.05 N in sodium chloride, saturated with silica, and their pH is controlled by the bicarbonate-carbon dioxide system. Under pressure deep within the area the waters contain sufficient carbon dioxide to make them slightly acid with respect to pure water at the same temperature, e.g. at 250°C, pH = 5.0 (approx.) and for pure water pH = 5.7 (approx.). At lower pressures towards the surface the carbon dioxide is lost from solution and the waters become slightly alkaline with bicarbonate.

3.2.2. *Other active thermal areas.* The recent recognition of wairakite from The Geysers, California (STEINER, 1958) may be noted.

Some data from drill cores from the Upper Basin, Yellowstone National Park (FENNER, 1936) are included in Table 1. The introduction of potash feldspar in the lower levels is noteworthy, as at Wairakei.

WEED (1900) described a close association of quartz, stilbite, calcite and a little opal in veins from which the Boulder hot springs, Montana, now issue at temperatures up to 73°C. Similarly the Hunters hot springs (WEED, 1904) containing

abundant  $\text{CO}_2$  and some  $\text{H}_2\text{S}$ , issue at  $64^\circ\text{C}$  from a vein-system of gypsum seamed by stilbite. In both cases WEED relates deposition of the stilbite to the present as well as ancestral waters, but WHITE (1955) considers the evidence inconclusive.

SAKURAI and HAYASHI (1952) have described the silica-rich lime zeolite yugawaralite from andesitic tuff which has been much metamorphosed by hot-spring action about 300 miles from the present Yugawara hot spring, Japan. Coexisting minerals are quartz, and minor laumontite, chabazite and mordenite (ptilolite). Epistilbite, heulandite and stilbite are also reported (SAKURAI, 1953).

It is well known that chabazite, christianite (phillipsite), rarer mesotype (natrolite) and possibly other zeolites have been deposited in the wall-work of Roman baths at Plombières and elsewhere (DAUBRÉE, 1879) where hot spring water emerges at a maximum temperature of  $70^\circ\text{C}$ . The zeolites occur both within the pores of old tiles and in the mortar, and are accompanied by opal, chalcedony, plombierite, calcite and apophyllite.

### 3.3. Michigan copper deposits

BRODERICK (1929, 1931; esp. 1929, Figs. 4, 7, 8) has described a crude zoning related to depth in the copper-bearing amygdaloids of Keweenaw Point. Successive zones in downward order are characterized by zeolitization (with laumontite, analcime, natrolite, stilbite, datolite, apophyllite); prehnitization overlapping on to the zeolitization zone and characterized by abundant adularia as well as prehnite; and sericitization and propylitization in which sericite takes the place of adularia, and sulphides and ankerite are introduced. Persistent in all zones are epidote, pumpellyite, calcite, quartz, chlorite and native copper, and late veins and vug-fillings of laumontite, prehnite and datolite. Assemblages typical of the deeper, higher-temperature zones penetrate upwards in the neighbourhood of fissures suggesting invasion by heated solutions. Apart from the presence of such minerals as apophyllite, datolite, copper and sulphides, the zoning is broadly analogous to that of the greywackes and semischists of southern New Zealand, natrolite and thomsonite, which are rarer than laumontite and analcime (BUTLER and BURBANK, 1929), possibly being indicative of local silica-deficient conditions. The vesicles are considered by BUTLER and BURBANK to have been filled after accumulation and tilting of the whole lava sequence and overlying sedimentary formations.

### 3.4. Zeolites in amygdales, joints and other cavities

The larger part of zeolite literature refers to occurrences in amygdales and to fillings of other cavities, especially in igneous rocks. Yet such occurrences are particularly difficult to interpret from a physicochemical point of view. It has been customary for authors to publish paragenetic sequences based largely on textural considerations which are often questionable, and furthermore the sequences have often been pieced together from incomplete series in separate cavities (e.g. NIGGLI *et al.*, 1940, Fig. 242), a procedure of doubtful significance unless composition of the depositing solutions can be equated. An observed sequence of cavity fillings may be a function either of changing composition of the depositing solutions or of changing  $P$ - $T$  conditions, or both.

In the case of amygdale descriptions, there is often an underlying assumption that the zeolites have been deposited from magmatic solutions with falling temperature during initial cooling of a lava flow. It may well be that minor coatings of zeolites on the walls of cavities in some massive flows may have this origin but zeolites are rare or absent in the vesicles of newly cooled lavas. WALKER (1951) has shown convincingly that zeolite deposition in the Garron plateau of Ireland post-dates effusion and cooling of a pile of some forty to fifty flows, in all about 1000 ft thick. It is in a sense metamorphic, as has also been shown for the Keweenaw amygdaloids.

The present writers consider that sequences in cavities may be related to falling temperatures during initial cooling of a thick lava flow or intrusion, to rising temperatures and pressure following burial, to rising temperature resulting from new intrusions of magma or new influxes of hot gases or solutions, or to falling temperature when these conditions are relaxed. Thus MCLINTOCK (1915) has clearly described a consistent sequence epidote-prehnite-scolecite in olivine basalts of Ben More, Mull, which he attributes to increasing hydration with falling temperature in agreement with CORNU's "rule" (1908), followed by a reverse sequence of dehydration culminating in garnet, and promoted by the thermal metamorphic effects of a subsequent intrusion.

Published zeolite sequences often show no obvious consistent trend. Nevertheless in view of the difficulties outlined above, we do not consider that this fact should outweigh the evidence from well-studied hydrothermal and regionally altered areas where with increasing temperatures progressively less hydrous zeolites tend to form.

A general correlation also emerges between the silica content of zeolites and the availability of free silica. Thus descriptions given above, together with observations of many other writers, show that the typical zeolites in veins and joints of quartz-bearing rocks are stilbite, heulandite, laumontite and analcime. Other zeolites in such environments appear to be quantitatively insignificant, although scolecite and chabazite are reported by NIGGLI *et al.* (1940) in "Alpine cleft" localities in quartzose rocks such as gneisses and the Aar granite. The amygdale sequence mordenite, heulandite, chabazite, stilbite, accompanied by quartz, chalcedony or opal reported by MASON and GREENBERG (1953) from southern Brazil is one of increasing hydration in silica-rich zeolites, except for chabazite which is rare and was generally found to occur alone. Observations at Wairakei and Yugawara show that mordenite is typical of active thermal areas where silica activity is particularly high, although it also occurs in tholeiitic basalt amygdaloids.

In contrast, the main lime zeolites of the Garron Plateau olivine basalts are chabazite, levyne, thomsonite, natrolite, mesolite and phillipsite (WALKER, 1951), all these tending to be low in silica, and similar assemblages have been reported from many other undersaturated rocks. In considerations of phase equilibria, it is much more important to know the phases which actually coexist with each other than the inferred order of their crystallization. We believe that the grouping of zeolites in Fig. 5 illustrates their general tendency to occur in immediate environments, A supersaturated with respect to quartz, i.e. coexisting with opal,

underlying assumption is with falling temperature that minor coatings of opal have this origin but are rare. WALKER (1951) has shown that on plateau of Ireland and in hydrothermal flows, in all about 1000 ft. have been shown for the

changes may be related to magma flow or intrusion, to changes in temperature resulting from cooling of solutions, or to changes in pressure. As McLINTOCK (1915) has shown, the transition from scolecite in olivine to opal during hydration with water, followed by a reverse reaction, is noted by the thermal

trend. Nevertheless, it is considered that this fact is of regional and locally essentially less hydrous

content of zeolites and opal above, together with other zeolites in veins and with analcime and scolecite. Relatively insignificant, as shown by GILLI *et al.* (1940) in the Aar granite. In the stilbite, accompanied by analcime (EENBERG (1953) from the same zeolites, except for opal. Observations at active thermal areas show that opal occurs in tholeiitic

in olivine basalts are associated with opal (WALKER, 1951), and it has been reported that in some cases of phase equilibria, opal may coexist with each other. It is possible that the grouping of opal occur in immediate association with coexisting with opal,

crystal or silica-rich glass, B saturated, C undersaturated with respect to quartz. Many exceptions which could be inferred from published paragenetic sequences seem to be more apparent than real, although exceptions undoubtedly do exist. In particular chabazite, which is chemically equivalent to

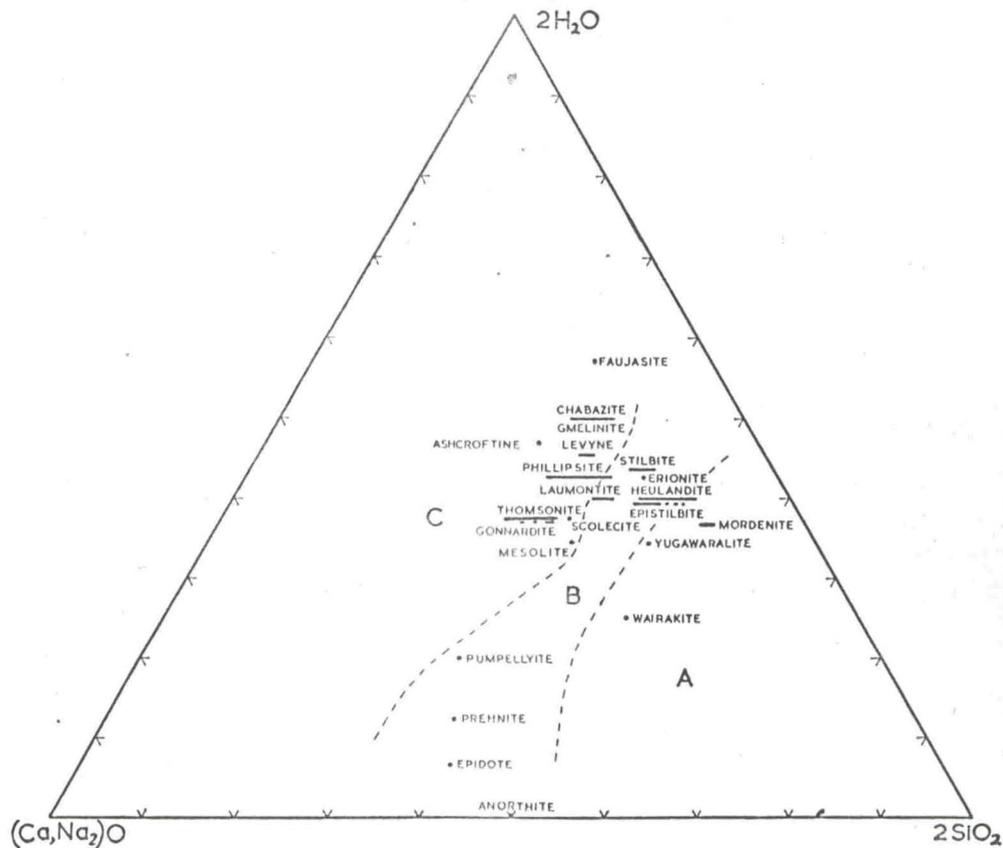


Fig. 5. Composition in molar proportions of lime-rich zeolites (see Appendix 2) and of certain other Ca-Al silicates. For the zeolites and anorthite, (Ca, Na<sub>2</sub>)O is numerically equal to Al<sub>2</sub>O<sub>3</sub>. A. Field of phases favoured by supersaturation in silica. B. Field of phases which can commonly coexist with quartz (erionite coexists with opal). C. Field of phases favoured by a silica-deficient environment.

Stilbite with less silica and to laumontite with additional water, falls in the field of the less siliceous zeolites yet has often been reported in association with quartz (e.g. in the Nova Scotia traps, WALKER and PARSONS (1922) p. 42), although not necessarily in equilibrium with it. Similarly it has been synthesized with quartz (see Table 14).

### 3.6. Groundmass zeolites in igneous rocks, pegmatoids and glasses

It is well known that analcime and other zeolites are common in the groundmass and pegmatoids of basic, alkaline lavas and shallow intrusives. Apart from the fact that they are characteristically silica-poor zeolites, they provide little direct

evidence on zeolite stability. It is known (YODER, 1953) that analcime is stable to about 570°C at 2000 bars in the absence of free silica and may thus form at much higher temperatures than in the presence of quartz (see later). Experimental evidence is inadequate to interpret the occurrence of phillipsite in the mesostasis of apparently fresh basanites (COOMBS in BROWN, 1955, p. 370) but thomsonite appears to break down to anorthite near 300°C (FYFE, 1955) and can be interpreted as either metamorphic, as in the Otama metagabbros, or low-temperature, late stage hydrothermal as in the case of groundmass thomsonite in the Waiholo thermalite (HUTTON, in BENSON, 1942). POVARENENYKH (1954) has discussed how the relative proportions of nepheline, albite and anorthite in feldspathoidal rocks control the proportions of natrolite, analcime and thomsonite in their zeolitic alteration products.

In the later hydrothermal stage in pegmatites of quartzose rocks on the other hand, the typical zeolites are the laumontite-heulandite-stilbite group (e.g. RICHMOND, 1937; WHITEHOUSE, 1937), while HARRIS and BRINDLEY (1954) have described an interesting case of the natural devitrification of a highly siliceous pitchstone glass to mordenite. Similarly HAYASHI and SUDO (1957) have recognized mordenite and opal in the bentonitic hydrothermal alteration products of Japanese rhyolite tuffs. Such examples provide further evidence for the silica-content correlation described above.

### 3.7. Conclusion

Similar recurring assemblages in a variety of environments of widely differing age support the validity of the zeolite facies concept and we consider that it may be extended, in the form of mineral facies rather than of metamorphic facies, to the zone of diagenesis with its heulandite-quartz-montmorillonoid assemblages as well as to the fillings of many veins and amygdales. Nevertheless as stated above low-temperature conditions are probably particularly conducive of non-equilibrium and some of the parageneses, especially those with phases such as mordenite and epistilbite, are probably to be regarded as metastable.

Occurrences in hydrothermal areas, like that of phillipsite in marine sediments (MURRAY and RENARD, 1891; GOLDBERG and ARRHENIUS, 1958), provide some information on actual temperatures and pressures of formation. These data are summarized in Table 1.

## 4. THEORETICAL CONSIDERATIONS ON ZEOLITE STABILITY (A. J. E., W. S. F.)

The broad pattern of progressive regional metamorphism is one of increasing dehydration as the mineral assemblages of low grade rocks pass to the less hydrated high grade assemblages. Coupled with this dehydration is a tendency for phases to increase in density, even more than is implied by dehydration. The general features are consistent with those which would be deduced if the rocks were subjected to increasing temperatures at steadily increasing pressures.

On grounds of entropy, the stable mineral assemblage at low temperatures must be the one with the maximum possible hydration and it will consist largely of clay minerals and zeolites. That such assemblages are commonly developed, at

## The zeolite facies, with comments on the interpretation of hydrothermal syntheses

Table 1. Temperatures of occurrence of some natural zeolites and related minerals (data derived from references given in text)

Mineral	Occurrence	Temperature (T°C)	Depth (m)
Phillipsite	Deep sea sediments	0°	4000-5000
Chabazite, phillipsite, natrolite	Masonry, Roman baths	40-70°	Surface
Clinoptilolite, analcime	Diagenesis	Low	?
Stilbite	Hunters, Boulder Hot Springs	?64°, ?73°	Surface
Clinoptilolite	Yellowstone	125°	19-26
Analcime	Yellowstone	125-155°	26-60
Mordenite	Wairakei	150-230°	73-300
Heulandite	Wairakei	within range of mordenite	
Laumontite	Wairakei	195-220°	150-275
Wairakite	Wairakei	200-250°	180-600
Prehnite	Wairakei	~200°	~100
Albite	Wairakei	160-240°	100-600
Adularia	Wairakei	230-250°	385-650
Zeolite and adularia	Steam Boat Springs*	170°	52

Note: (1) The maximum temperatures recorded for the Wairakei boreholes are 250-260°C.

(2) The appearance of albite and other minerals at abnormally low temperatures and shallow depths in some Wairakei holes suggest that in these cases they may have been deposited under an earlier regime of higher temperatures.

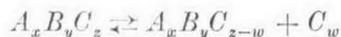
\* See WHITE (1955).

least partially, has been demonstrated in the previous survey. Further, the recurrence of simple assemblages suggests that equilibrium is often approached.

#### 4.1. The importance of silica activity

In the low temperature regional environment where zeolite facies minerals are formed, equilibrium with silica normally implies equilibrium with quartz. But in some of the environments where zeolites are formed on a large scale, less stable modifications of silica, such as opal or cristobalite, may be present. This commonly occurs in active hydrothermal areas and also in shallow sediments where opaline silica may be a cement. A solution which is actively precipitating opaline silica must be supersaturated with respect to quartz, and experimental data indicate that the silica activity could be greater than in equilibrium with quartz by a factor of 10 (ELLIS and FYFE, 1957). Experiments described later suggest that a change of environment from one saturated with cristobalite to one saturated with quartz must change the maximum temperature of stability of a mineral assemblage. Natural zeolite assemblages reported above support this conclusion.

In any reaction of type:



phase  $A_x B_y C_z$  will form over a wider range of conditions if the state of  $C$  is not the stable form at the given pressure and temperature, and if other factors such as nucleation do not interfere. This effect, which is not restricted to silica may be large. Consider, for instance, the reaction:



at equilibrium at 25°C where  $\Delta G = 0$  and the stable silica phase is quartz. As the free energy of vitreous silica is 3 kcal more positive than that of quartz at this temperature (LATIMER, 1952) if silica is added as glass,  $\Delta G$  at 25°C will now become -6000 cal and the field of  $A(\text{SiO}_2)_6$  will be expanded. The silica (or any other component) may be added in an experimental run in an amorphous state and at the end of the run may be recovered partly or entirely as quartz. Nevertheless, phases may have grown while the silica activity was high and may persist in the final products.

Consider the effect this silica activity has on a typical hydrate boundary. Data from synthetic studies indicate that the reaction:



may be at equilibrium around 350°C and 1000 bars. Solubilities (KENNEDY, 1950a) indicate that the free energy of amorphous silica is about 1500 cal/mole above that of quartz. Thus with amorphous silica the above process will have a  $\Delta G$  of +3000 cal. The  $\Delta S$  of dehydration may be of the order of 10-15 cal/water molecule and the equilibrium temperature with respect to amorphous silica may be 100-150°C higher. This is well demonstrated both in direction and magnitude by the data in Table 3.

#### 4.2. Relative importance of silica content and water content

In this paper attention is focused on silica-rich systems. On the basis of entropy it would be expected that the least hydrated phase would also be the high temperature phase. Further, if two assemblages have different amounts of silica bound in silicates it might be anticipated that the assemblage with the greater amount of bound silica would be the more stable. It is a fact that assemblages such as nepheline-quartz, thomsonite-quartz, olivine-quartz are not stable. It might therefore be suggested that the larger silica content of sodium mordenite relative to analcime could conceivably increase its stability and hence make it the higher temperature phase. However, the reaction:



must have a positive entropy change due to the large entropy of free water in the gas or liquid state. This implies that analcime becomes more stable at high temperatures relative to mordenite. Analcime need not be stable at all, but it would be most remarkable if analcime was stable at lower temperatures than mordenite.

The silica-deficient zeolite natrolite ( $\text{Na}_2\text{Al}_2\text{Si}_3\text{O}_{10} \cdot 2\text{H}_2\text{O}$ ) is unlikely to occur with free quartz for although its formula suggests intermediate hydration between mordenite and analcime, on the basis of its Na/H<sub>2</sub>O ratio it is hydrated to the same extent as analcime but has less silica. Natrolite would be expected to occur only in silica-deficient environments.

the state of  $C$  is not the  
of other factors such as  
stricted to silica may be

phase is quartz. As the  
of quartz at this tem-  
will now become  $-6000$   
any other component)  
and at the end of the  
cess, phases may have  
the final products.

hydrate boundary. Data

$- 2H_2O$   
water

itics (KENNEDY, 1950a)  
 $500$  cal/mole above that  
will have a  $\Delta G$  of  $+3000$   
cal/water molecule and  
silica may be  $100-150^\circ C$   
magnitude by the data in

On the basis of entropy  
l also be the high tem-  
amounts of silica bound  
the greater amount of  
at assemblages such as  
not stable. It might  
in mordenite relative to  
ice make it the higher

$2O + 3SiO_2$

opy of free water in the  
ore stable at high tem-  
le at all, but it would be  
atures than mordenite.  
O) is unlikely to occur  
iate hydration between  
is hydrated to the same  
pected to occur only in

The situation with the calcium zeolites is more complex owing to the great number of possible phases. Further, the range of composition of a single phase (e.g. heulandite and its possible polymorph epistilbite) is often considerable (see Appendix 2). In Table 2 some of the possible compositions of calcium end members are listed in order of decreasing water content in relation to anorthite and quartz.

The entropy argument used above would lead one to suggest that the order of

Table 2

Zeolite	Composition
Heulandite (var. clinoptilolite)	An + $8SiO_2$ + $8H_2O$
Chabazite	An + $3.2SiO_2$ + $7.2H_2O$
Mordenite	An + $8SiO_2$ + $7H_2O$
Stilbite	An + $5SiO_2$ + $7H_2O$
Heulandite	An + $5SiO_2$ + $6H_2O$
Chabazite	An + $2SiO_2$ + $6H_2O$
Stilbite	An + $3.2SiO_2$ + $5.6H_2O$
Heulandite	An + $4SiO_2$ + $5.3H_2O$
Epistilbite	An + $4SiO_2$ + $5.3H_2O$
Chabazite	An + $1.3SiO_2$ + $5.3H_2O$
Levyne	An + $2SiO_2$ + $5H_2O$
Heulandite	An + $3.2SiO_2$ + $4.8H_2O$
Yugawaralite	An + $3SiO_2$ + $4H_2O$
Laumontite	An + $2SiO_2$ + $4H_2O$
Gismondine	An + $0SiO_2$ + $4H_2O$
Scolecite	An + $1SiO_2$ + $3H_2O$
Thomsonite	An + $0.8SiO_2$ + $3H_2O$
Thomsonite	An + $0SiO_2$ + $2.4H_2O$
Wairakite	An + $2SiO_2$ + $2H_2O$

stability would be basically controlled by water content. Further, one might anticipate that, given equal water content, the most stable species at any temperature would be that with the most silica. Field data indicate that this latter suggestion is not generally valid; for example yugawaralite should be stable relative to laumontite, but the latter is the common zeolite. Laboratory and field studies suggest that although the silica content of zeolites reflects the silica activity, the silica effect does not override the water effect; with respect to water content (calculated relative to  $(Ca, Na_2)O \cdot Al_2O_3$ , contrast CORNU, 1908), the order of stability is normal.

#### 4.3. Dehydration reactions at high pressures

The experimental boundaries between zeolites and feldspars are normally steep but as they are ill-defined it is a matter of difficulty actually to measure the slope. Changes in slope of zeolite-feldspar boundaries must occur at high pressures owing to the large molar volumes of zeolites. At very high water pressures some zeolites should be dehydrated to anhydrous phases (cf. GRIGGS and KENNEDY, 1956). In

general, successive dehydration boundaries tend to become steeper at low temperatures, a result of the increasing departure of water from ideal behaviour at low temperatures (ELLIS and FYFE, 1957).

The following examples will illustrate such effects. From the data of Appendix 2 the  $\Delta V$ 's of reaction for the following have been calculated at 25°C.

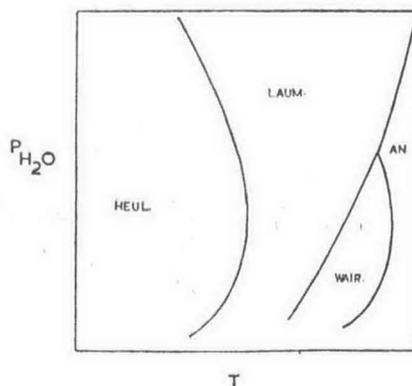
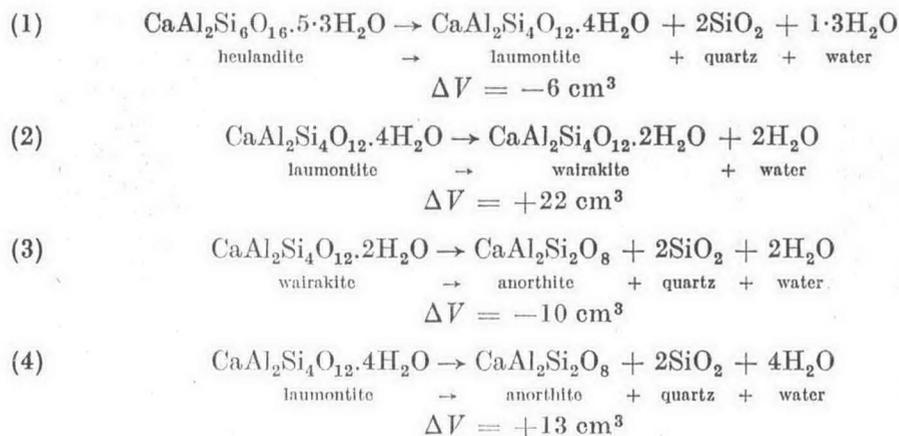


Fig. 6. Possible form of phase relations between heulandite, laumontite, wairakite and anorthite based on volume relations.



These values assume a water density of unity; as equilibrium occurs at low temperatures, the values so calculated could be meaningful at moderate pressure. In a normal dehydration series  $\Delta V$  is positive for each step. This is obviously not the case in the above series and examples of negative boundary slopes and restricted low pressure fields (e.g. wairakite) are to be expected (Fig. 6).

Experimental studies are usually limited at low temperatures to pressures equal to or higher than the vapour pressure of liquid water. As boundaries pass through the two-phase region of water the slopes must change rapidly, but above this region they will be steep over a wide range of pressure.

#### 4.4. Entropy of analcime

FYFE *et al.* (1958) have discussed some general features of entropies of silicates

with emphasis on the limitations of the assumption that entropies of constituent oxides are additive. To the writers' knowledge, the entropy of only one zeolite has been determined, namely analcime for which KING (1955) reports a value of 56.0 cal/deg mole. This entropy is very high compared with the sum of the entropy of the oxides, 44.6 cal/deg mole. However, a large entropy is to be expected since the molar volume of analcime is large. Following the arguments used in FYFE *et al.* (1958) we estimate an entropy of 57.0 cal/deg mole which includes a volume correction and a correction for randomness in the Al-Si arrangement (BEATTIE, 1954). Similarly wairakite would be expected to have a large entropy which is in accord with its ready nucleation and growth (cf. cristobalite). Further, the apparent molar volume of water in analcime is much larger than with most hydrates. The large entropy of analcime leads to some unusual features of its breakdown. At 25°C, the  $\Delta S$  of the reaction: analcime + quartz  $\rightarrow$  albite + water (liquid) is +0.95 cal/deg mole, a value very near zero. For most dehydration reactions removal of one water molecule to give liquid water at 25°C is accompanied by an entropy increase of 7 cal/deg mole (an average of twenty-four cases). The small change noted above indicates the danger of using average figures with zeolites. In fact it could be possible to have negative entropies of dehydration at low temperatures and pressures.

4.5. Osmotic conditions

Data indicate that zeolites will be stable minerals in a low temperature environment or under conditions of moderate depth of burial. In these environments open pores must be common. In hydrothermal areas such as Wairakei, New Zealand, the pressure measured in fissures is often that of the water column and is therefore related to rock pressure in the ratio of water density to rock density. It is thus necessary to consider conditions where the pressure on the solid phases is greater than the pressure in the fluid phase and in particular conditions where  $P_{H_2O} \simeq \frac{1}{3}P_{load}$ . For this to be relevant it is necessary that alteration produces a zeolitized rock which is still porous yet in which the zeolites support the load of overburden. In contrast the zeolites in a cavity in a basalt grow in an environment where clearly  $P = P_{H_2O}$ . At great depths continuous pore systems must become unstable unless some fluid can support them. If the porosity is low and water is being expelled on a large scale by dehydration reactions the most likely conditions are  $P_{H_2O} \simeq P_{load}$ .

For phase changes in hydrate systems where density relations are "normal", if the pressure on the solid phases is greater than the pressure in the gas phase the vapour pressure of the solid will be increased (FYFE *et al.*, 1958). If molar volumes of all phases are known the extent of the effect can be estimated.

Consider the effect on the analcime-albite boundary. In Fig. 7 curve A is our boundary based on synthesis for the experimental conditions that  $P = P_{H_2O}$ . At 1000 atm it passes through  $280^\circ C \pm 10^\circ$ . If at the equilibrium temperature at 1000 atm we add 2000 atm rock load ( $P_{load} = 3P_{H_2O}$ ) then the free energy of the reaction:



becomes

$$2000 \times \Delta V_{solids} \times 0.024 \text{ cal}$$

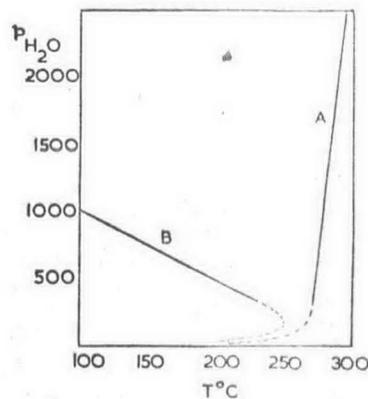


Fig. 7. Equilibrium vapour pressure of the reaction: analcime + quartz = albite + water. Curve A is that suggested by synthesis. Curve B is that estimated for the conditions that  $P_{total} = 3 P_{H_2O}$ . The dotted extensions are schematic and illustrate the behaviour expected at low pressures.

Fig. 8. Diagram illustrating the difference in reaction temperatures in areas where  $P_{total} = P_{H_2O}$  and where  $P_{total} = 3 P_{H_2O}$ . X, Y and Z represent the equilibrium vapour pressures for successive dehydration reactions when  $P_{total} = P_{H_2O}$ , and X', Y', and Z' represent vapour pressures for the same reactions when  $P_{total} = 3 P_{H_2O}$ . A gradient of 30°/km is assumed.

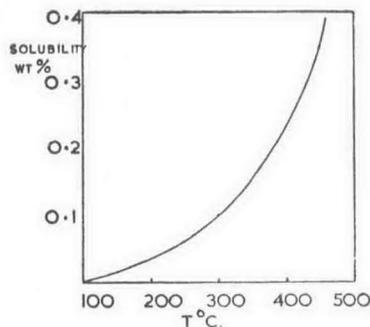
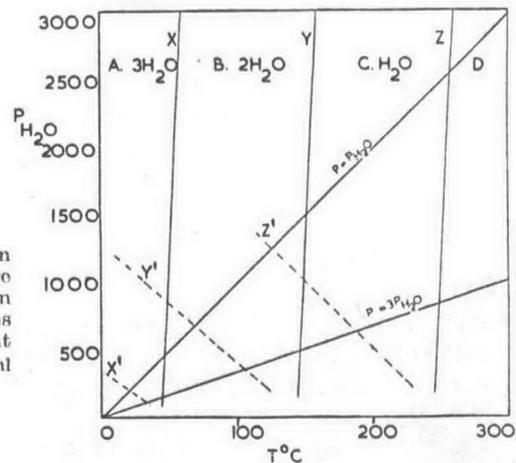


Fig. 9. General form of the 1750 bars solubility curve of quartz in water (after KENNEDY, 1950a).

To regain equilibrium, the temperature must be lowered at constant pressure such that a term  $\Delta T \Delta S$  equals the above  $\Delta P \Delta V$  term. In this region the  $\Delta S$  of the above reaction will be of the order of 5 cal/mole and  $\Delta V_{solids} = 19 \text{ cm}^3$  so the new equilibrium temperature will be 150–200°C below the experimental value. The result is that of curve B (Fig. 7). YODER (1954) has reported failure to produce the expected differential pressure effect with analcime. The subject warrants further investigation (see also HARKER, 1958).

From the above we conclude that at shallow depths the experimental curves will suggest transition temperatures that are too high, the discrepancy being small at very shallow depths but being considerable at depths of more than 1 km. At great depths the free pore condition probably no longer applies so that the experimental results will apply more closely to the natural conditions.

If the rocks are well sealed and a fissure opens we may have in the rock that  $P_{H_2O} = P_{load}$  while in the fissures  $P_{H_2O} \approx \frac{1}{3}P_{load}$ , so that analcime might grow in the rock while albite grows in the fissure. But if the conditions in the rock are osmotic, i.e.  $P_{load} \approx 3P_{H_2O}$ , and a fissure forms and is held open for free growth, then where albite grows in the rock, analcime could grow in the fissure.

The above effects appear to provide a possible explanation for overlapping of zeolite zones at Taringatura. In particular, the relict heulandite assemblages low in the section characteristically occur in non-porous, well cemented beds, where a closer approach to the condition  $P_{load} = P_{H_2O}$  may be expected than in some of the coarser beds which have been converted to laumontite. Variation in composition is another major factor to be considered.

It should be noted that at high temperatures the osmotic correction will be smaller as the entropy of dehydration is larger.

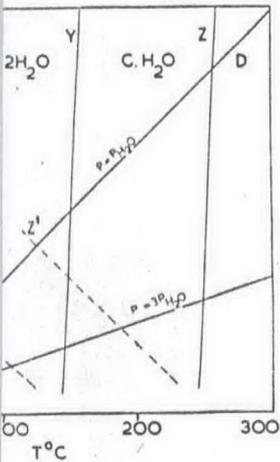
As the apparent molar volume of water in most hydrates is in the range 14–20  $cm^3$ , the high value being typical of low density zeolites, the term  $\Delta V_{solids}$  in most zeolite reactions will be similar to that for the analcime–albite reaction, and the differential pressure effect will be similar in magnitude. Nevertheless the thermal gradient in natural systems operates to restrict the effect. In Fig. 8 an attempt is made to summarize the type of effects anticipated in an environment where  $P_{H_2O} = P_{load}$  (full lines) and where  $P_{H_2O} = \frac{1}{3}P_{load}$  (dashed lines) in an area with a temperature gradient of 30°C/km. The crossing points on the gradient lines are changed by about 10–60°C. If the thermal gradient was less, the adjustment would be larger and conversely. In thermal areas such as Wairakei where gradients may be as large as 200°C/km the osmotic corrections should be small.

#### 4.6. The significance of quartz veins

In New Zealand the appearance of quartz veins on a large scale is typical of rocks near the zeolite–greenschist facies transition and these veins continue into the greenschists. Where they first appear they commonly carry prehnite and/or pumpellyite. In a very broad sense these veins may serve as an indication of the temperatures in the prehnite zone. KENNEDY'S work (1950a) indicates that high pressure solubility isobars have the form shown in Fig. 9. In the region of liquid water, i.e. at temperatures below the critical temperature, pressure has little effect on solubility. Above the critical temperature the isobars steepen rapidly with increasing temperature.

If water is moving out from high temperature areas at a pressure of 2000 bars then between 250 and 350°C 100g of water would deposit about 0.12g of silica. In the range 250–150°C the amount deposited is only 0.04g. It is apparent that the extent of solution and deposition falls off rapidly below the 300°C region. Experimental data (see Figs. 17 and 18) indicate that the incoming of prehnite relative to zeolites should occur at similar temperatures.

of the reaction:  
ter. Curve A is  
B is that esti-  
= 3 P<sub>H<sub>2</sub>O</sub>. The  
d illustrate the  
ressures.



s solubility curve  
EDY, 1950a).

constant pressure such  
ion the  $\Delta S$  of the above  
)  $cm^3$  so the new equi-  
tal value. The result is  
o produce the expected  
rrants further investi-

#### 4.7. pH variation

In natural systems the principal agent responsible for changes in pH must be carbon dioxide; changes in its concentration will affect relative solubilities of silicates and hence the position of phase boundaries. Experiments designed to test this effect will be discussed later. An increase in alkalinity accelerates the formation of quartz from amorphous silica so that variation in silica activity is a complicating factor.

The significance of pH variation on high level occurrences of calcite-laumontite veins and of laumontite replacement of shell material in fossils is a matter for future investigations.

#### 4.8. Water content

The total zeolitization of a feldspathic rock requires a large quantity of water (around 10 per cent) and in many cases this may not be available. Thus in many regions subjected to the  $P$ - $T$  conditions of the zeolite facies alteration may be incipient only. This in no way invalidates the recognition of zeolite facies conditions. Boundaries between hydrates will occur at the same temperatures and pressures as in a system with sufficient water, allowing of course, for possible osmotic conditions. Thus, as far as thermal history is concerned, traces of zeolitization as in some rocks of the Alpine Facies of New Zealand will be just as significant as complete alteration. In the partially altered Taringatura rocks the assemblage heulandite + detrital plagioclase does not represent equilibrium. Nevertheless the heulandite is followed by laumontite, and laumontite by still less hydrous phases. Providing successive dehydration transitions such as heulandite  $\rightarrow$  laumontite are observed with increasing temperature it may be inferred that  $P_{H_2O}$  has been fixed by external conditions, notably depth, and the reasons for persistence of relict plagioclase (or other water-poor phases) are either kinetic or the result of lack of access by water to grain boundaries. Such conditions are not those of true water deficiency. On the other hand some high-level occurrences of laumontite could be due to water deficiency.

#### 4.9. Phase rule relationships

At equilibrium in either the system  $Na_2O \cdot Al_2O_3 - SiO_2 - H_2O$  or  $CaO \cdot Al_2O_3 - SiO_2 - H_2O$  up to two tectosilicates may coexist with an aqueous solution at any arbitrary temperature and pressure and hence there will be only one zeolite in the presence of a silica phase. In the mixed sodium-calcium system three tectosilicates may coexist and two in the presence of quartz. The occurrence of three-phase zeolite assemblages such as thomsonite-laumontite-analcime at Otama, does not therefore necessarily imply disequilibrium. In cases of variable alkali-alumina ratios or under conditions where non-tectosilicates such as garnet, epidote or prehnite may form, yet another phase will be possible.

#### 4.10. Significance of experimental data

If data on stability fields of minerals are to be applied in petrogenetic interpretation, the actual reactions involved in mineral formation need to be known (note the effects of coupled reactions, FYFE *et al.*, 1958). In some cases these appear

changes in pH must be relative solubilities of periments designed to alinity accelerates the n in silica activity is a s of calcite-laumontite fossils is a matter for

arge quantity of water ilable. Thus in many es alteration may be tion of zeolite facies ame temperatures and of course, for possible erved, traces of zeoliti- ill be just as significant a rocks the assemblage im. Nevertheless the ll less hydrous phases. dite → laumontite are that  $P_{H_2O}$  has been ons for persistence of tic or the result of lack not those of true water of laumontite could be

O or  $CaO.Al_2O_3-SiO_2-$  lution at any arbitrary olite in the presence of ee tectosilicates may of three-phase zeolite ma, does not therefore cali-alumina ratios or idote or prehnite may

in petrogenetic inter- on need to be known ome cases these appear

The zeolite facies, with comments on the interpretation of hydrothermal syntheses

to be clear cut, as in the conversion of analcime to pseudomorphs of albite. If calcic heulandite alters to calcic laumontite the interpretation is simple but if sodium is present its distribution between the phases will be important and this factor has not yet been examined experimentally. Similarly the experimental reaction: prehnite → anorthite + wollastonite + vapour does not occur when prehnite breaks down in regional metamorphism and it will certainly not take place under the same P-T conditions.

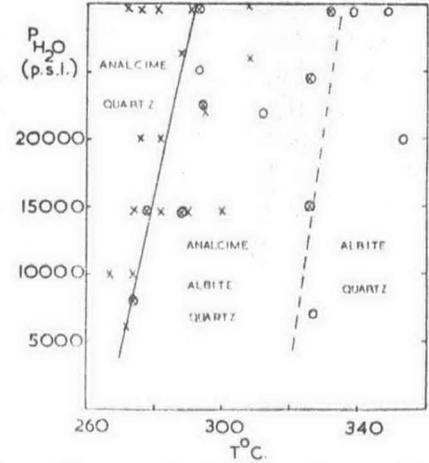


Fig. 10. Results of crystallization of oxide mixes of composition: albite + SiO<sub>2</sub>. The full line represents the lower limit of albite and is considered to be nearer the equilibrium boundary than the upper dashed line which represents the upper limit of analcime. Run times vary from 4 to 340 hr.

5. FIELDS OF SYNTHESIS AND STABILITY OF ZEOLITES AND RELATED PHASES (A. J. E., W. S. F.)

5.1. General

In large part this must be considered a progress report on work which has already occupied about 3 years and a revision of some previous work by one of the writers (FYFE, 1955). The present position is not one of finality; in fact it abounds in problems which are incompletely solved. Experimental data are recorded in Appendix 1.

The majority of experiments reported here involve the crystallization of glasses or oxide mixes. Gels were not used for reasons outlined below. Mixes were made mainly from calcium oxide, sodium hydroxide solution, active chromatographic alumina, and Mallinckrodt A.R. silicic acid. It became clear as work proceeded that these mixes favoured products high in silica, so in later mixes ground quartz was used with little apparent change in the times necessary for reaction. Many experiments were conducted using minerals as starting materials.

A wide range of apparent phase boundaries have been recorded for the same phase using different starting materials. Although in many cases no satisfactory conclusion can be drawn about the true equilibrium boundary, it is certain that if attainment of equilibrium is desired the worst possible starting materials are the most reactive, i.e. gels, mixes and glasses. These are so unstable that a large number

of metastable intermediates may form and persist. However, with less unstable starting materials reaction rates are commonly too slow for recrystallization to be achieved.

It must be stressed that the field of synthesis of a given phase need bear no relation to the field in which this phase is stable. Equilibrium is indicated only if a reaction is reversible or, less decisively, if a number of different starting materials produce the same results. This has not been demonstrated for any of the hydrothermal syntheses described in this paper.

### 5.2. *The system albite-silica-water*

There is a wide field (Fig. 10) in which both analcime and albite appear from compositions within this system containing excess silica, a type of behaviour typical of many of the systems studied. The following conclusions are drawn from the experimental data.

- (1) The apparent upper stability limit of analcime in the presence of quartz, as established by synthesis, is  $280^{\circ}\text{C} \pm 10^{\circ}$  at 1000 bars. The boundary is steep. This is in reasonable agreement with observations of FYFE (1955b), SAND *et al.* (1957), and BARRER and WHITE (1952).
- (2) The fact that analcime alone appears in short runs above  $280^{\circ}\text{C}$  and that albite appears in longer runs (VALPY, 1957) suggests that analcime grows readily in regions where albite is the stable phase, and that the figures in (1) above represent a higher temperature than that for true stability of analcime.
- (3) Preliminary experiments by CAMPBELL (1958) on the solubility of albite in the presence of natural analcime and quartz indicate that the analcime + quartz = albite + water equilibrium temperature is near  $200^{\circ}\text{C}$  at saturated water vapour pressure.
- (4) The possibility of synthetic high silica analcimes suggested by MACKENZIE (1957) is supported by the absence of a silica phase in the recrystallization of albite glass to analcime. Analyses of natural analcimes (Appendix 2) do not indicate a wide variation of composition.
- (5) In experiments using amorphous silica and glasses mordenite appears at temperatures below  $230\text{--}245^{\circ}\text{C}$  at 2000 bars. FYFE (1955b) found that analcime was replaced by mordenite below  $220^{\circ}\text{C}$  at 300 bars.
- (6) When quartz is used in place of amorphous silica analcime, not mordenite, appears at temperatures as low as  $115^{\circ}\text{C}$  (Table 9).
- (7) Lowering the pH by addition of sodium bicarbonate in runs with amorphous silica raises the temperatures at which mordenite appears. This effect can be correlated with the influence of pH on silica activity since high pH increases the rate of formation of quartz.

### 5.3. *The system anorthite-silica-water*

The following main conclusions are drawn from the experimental data (Appendix 1).

- (1) From all starting materials used in experiments in this system wairakite is the highest temperature calcic zeolite to form. The temperature up to which it forms is greatest when amorphous silica is used in the starting materials. A summary of

apparent field boundaries is given in Table 3. The fact that anorthite appears as low as 340°C in the presence of quartz suggests that wairakite is not stable above this temperature. AMES and SAND (1958) and KOIZUMI and ROY (1958) have produced wairakite from reactive materials at higher temperatures.

(2) Calcium mordenite replaces wairakite at lower temperatures when the silica activity is high in the same way as sodium mordenite replaces analcime (Figs. 11

Table 3

Starting materials	Pressure (bars)	Upper limit of wairakite	Lower limit of anorthite
Oxide mixes	335	440°C	440°C
Glass	2000	450°C	420°C
Glass	5000	450°C	450°C
Oxide mix with quartz	w.v.p.	375°C	340°C
Xonotlite + quartz	2000	380°C	360°C
Stilbite	5000	403°C +	not determined
Chabazite	w.v.p.	310°C +	not determined
Laumontite (amorphous) + quartz	2000	380°C +	not determined
Laumontite + quartz	2000	400°C +	not determined
Lawsonite + silica	3000	440°C	440°C
Lawsonite + quartz	2000	400°C +	390°C
Heulandite (amorphous)	2200	410°C	
Heulandite (amorphous)	w.v.p.	370°	370°C
Prehnite + SiO <sub>2</sub> (glass)	2000	440°C	390°C

Table 4

Starting materials.	P (bars)	Lower limit of wairakite (°C)	Upper limit of epistilbite (°C)
Glass	2000	325	360
Glass	5000	not det.	350 +
Oxide mix with quartz	w.v.p.	285	285
Xonotlite + quartz	2000	310	320
Stilbite	5000	ca. 390	ca. 390
Prehnite glass + SiO <sub>2</sub>	5000	(missing)	360

and 18). When the silica activity is reduced by the use of quartz, calcium mordenite does not appear even at 212°C. Its field of synthesis is thus lowered by at least 200°C by reducing silica activity.

(3) With many starting materials epistilbite appears as the common low temperature calcium zeolite. A summary of upper limits of synthesis for epistilbite is given in Table 4. Its ready synthesis contrasts with its comparative rarity in nature.

(4) The naturally important zeolite heulandite appeared as only a minor phase in a few runs. It is doubtful if these represent equilibrium (see A.1.6.8). As heulandite

and epistilbite are chemically similar and may be polymorphs with rather similar structures the nucleation of either phase may inhibit the formation of the other. (5) Laumontite was not synthesized although on the basis of water content it might be expected to form at temperatures intermediate between those of epistilbite and wairakite. This contrasts with its copious occurrence in nature. Our failure to synthesize laumontite (and that of KOIZUMI and ROY, 1958) is a clear indication

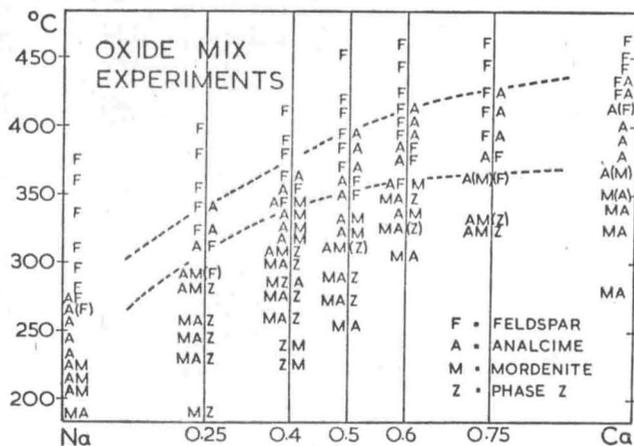


Fig. 11. Phases formed by hydrothermal crystallization of oxide mixes of feldspar compositions. (For pressure data see Appendix I).

of the lack of equilibrium in the synthetic results. On the basis of water content, it is possible that a field of scolecite could occur between laumontite and wairakite. (6) FYFE (1955b) found that in short runs laumontite and heulandite formed readily over a wide range of temperatures from their "amorphous" dehydration products. Longer runs have shown that such materials appear to retain a nucleating memory and tend to form the parent phase over too wide a range. Data in Table 15, however, indicate that laumontite could be stable relative to wairakite near 300°C for, while at 310–323°C only laumontite was observed in the products, above this temperature wairakite was observed in long runs and in one run at 240°C chabazite was observed.

(7) Our suggestion that the true analcime + quartz → albite boundary is near 200°C and the sequence at Taringatura (Fig. 2) indicate that heulandite should also be stable to about 200°C, and laumontite at rather higher temperatures.

#### 5.4. Plagioclase-silica-water compositions

Phases synthesized from compositions within the above system are indicated in Figs. 11 and 12. The lack of a field of synthesis for calcium zeolite + albite, a common assemblage in zeolitized rocks, is strong evidence that equilibrium was not established. It appears that a continuous series of analcimes are formed. Epistilbite was formed only from calcium-rich glasses. Refractive index data suggest that mordenites tend to be calcium-rich and feldspars sodium-rich compared with the starting material. Natural plagioclases and synthetic anorthite produced no zeolites in 60 day runs in the range 250–350°C.

5.5. Synthesis of prehnite

From glass of its own composition there was little difficulty in growing prehnite at pressures above 2000 atm. Below this pressure, a range of metastable phases appears at low temperatures. Prehnite also formed readily from glasses of epidote composition. In runs with glasses high in silica prehnite was much more reluctant

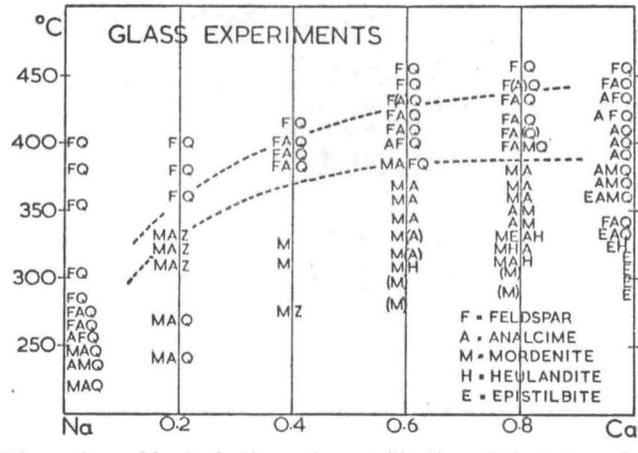


Fig. 12. Phases formed by hydrothermal crystallization of plagioclase plus silica glasses at 2000 bars.

to grow but appeared as a major phase in runs at 5000 bars. The following conclusions emerge. Experiments with three different starting materials (Figs. 13, 14, 15) indicate that prehnite passes to anorthite plus wollastonite at about 450°C at 5000 bars. At temperatures below 300°C (FYFE, 1955) we consider thomsonite to be the stable phase in silica-deficient environments as is also suggested by the thomsonitic alteration of the Otama gabbros. In these earlier experiments although thomsonite and anorthite grew readily, prehnite was most reluctant to form. Data found previously are summarized in Fig. 16. With more siliceous glasses as starting materials prehnite is cut off in the low temperature and pressure regions by the zeolites wairakite and epistilbite.

The recrystallization of epidote glass indicates that prehnite and vesuvianite form readily.

6. CORRELATION OF FIELD AND EXPERIMENTAL DATA  
(W. S. F., D. S. C.)

In active hydrothermal areas such as Wairakei zeolite-forming reactions occur in an area of steep thermal gradient, and solutions moving upwards tend to be supersaturated with silica. At Wairakei the principal zeolites are wairakite and mordenite, phases readily formed in the laboratory by using amorphous silica in the starting materials. However, laboratory data suggest a higher temperature for the metastable transition from mordenite to wairakite than is observed at Wairakei. Three factors may contribute to this lack of temperature correlation. There is evidence that the degree of silica supersaturation at Wairakei is small (ELLIS and WILSON, 1955; ELLIS, 1958) even though amorphous silica is deposited in bores.

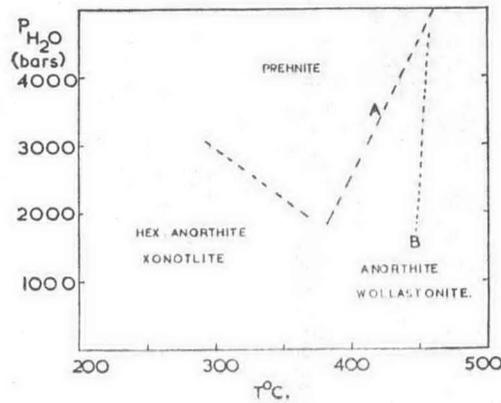


Fig. 13. Phases formed by crystallization of a glass of prehnite composition. Line A represents the upper limit of strong prehnite growth. Small amounts of prehnite persist up to line B. Boundary lines represent limits of major fields and changes in assemblage are transitional.

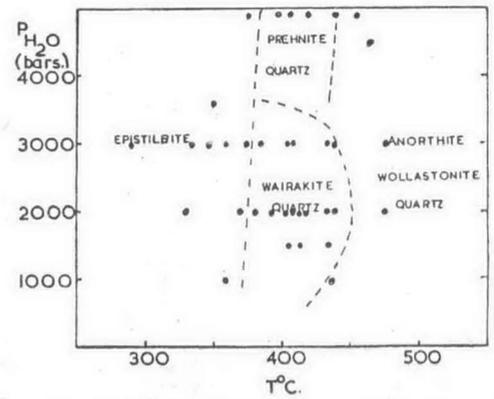


Fig. 14. Phases formed by crystallization of a glass of composition: prehnite + 4 silica.

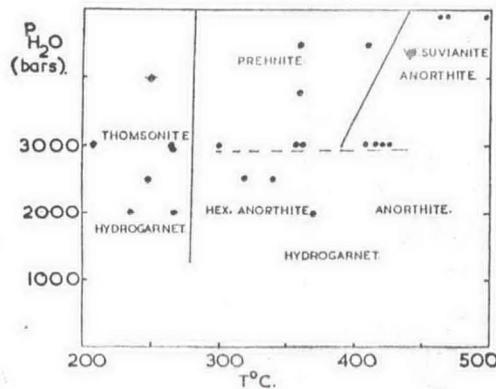


Fig. 15. Phases formed by crystallization of a glass of epidote composition.

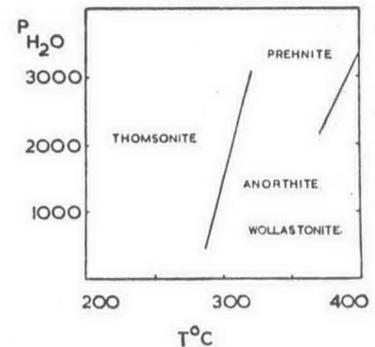


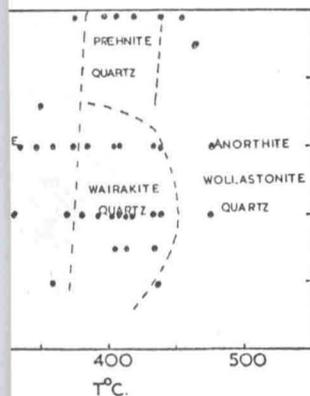
Fig. 16. Phases formed on crystallization of a glass of prehnite composition after FYFE (1955b) (cf. Fig. 13).

This will tend to diminish the field of mordenite with respect to that determined experimentally. Also, the conditions at these shallow depths may be to some extent osmotic as discussed above, and finally it is possible that the thermal gradient has been steeper in the past.

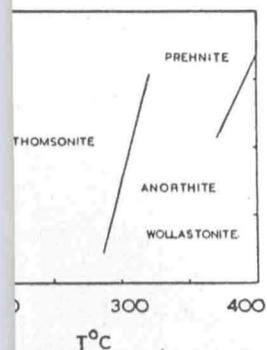
In the large scale regional zeolitization of sediments, a process consequent upon increasing temperature and pressure caused by depth of burial, a different succession of zeolites occurs. Heulandite, analcime and laumontite are dominant. In the Taringatura section described earlier the transition analcime + quartz → albite + water, occurs about half-way down the section. Assuming a thermal gradient no steeper than average it is unlikely that the temperature at this depth could exceed 240°C and a lower value is more likely. Data from Wairakei and Yellowstone are also compatible with an analcime + quartz → albite transition in

the relat  
Stren  
laun  
para  
rene  
laun  
sequ  
conc  
othe  
stab

(1) vary  
zeol  
tion  
(2) at lo  
incl  
the  
laur  
(3) cime  
high  
chlo  
side  
(4) occu  
dyn  
(5) of o  
zeol  
stab  
(6) in o  
of E  
the  
(7) Zeal  
pelly



Phases formed by crystallization of prehnite composition: prehnite + 4 silica.



Phases formed on crystallization of prehnite composition after FE (1955b) (cf. Fig. 13).

respect to that determined by the thermal gradient has

process consequent upon burial, a different succession of minerals may be dominant. In the case of analcime + quartz → albite + quartz. Assuming a thermal gradient of 10°C/cm, data from Wairakei and the albite → quartz transition in

#### The zeolite facies, with comments on the interpretation of hydrothermal syntheses

the range 150–240°C (Table 1), and hence with our suggested figure of 200°C. The relation of the heulandite field to that of analcime has been discussed above (5.3).

There is a suggestion (Table 15) that laumontite may be stable near 300°C. STEINER has reported its formation at 195–220°C at Wairakei. Incoming of laumontite above 200°C and gradual transition to a prehnite assemblage at temperatures around 300°C seems possible and is compatible with its main field occurrences in the New Zealand Geosyncline. Nevertheless, a number of occurrences have been noted (e.g. Jurassic of Hokonui Hills and Victorian arkoses) where laumontite would appear to have been formed at lower temperatures.

Wairakite has so far been described only from active thermal areas. The sequence at Taringatura suggests that zeolitization under regional metamorphic conditions could be terminated at the laumontite stage by the coupling effect of other reactions leading to prehnite. Further, it is possible that wairakite is not stable at high pressure as shown in Fig. 14 and hypothetically in Fig. 6.

#### 7. CONCLUSIONS (W. S. F., D. S. C.)

(1) Recurrent formation of similar, zeolite-bearing mineral assemblages in rocks varying in age from Upper Paleozoic to Tertiary justifies the recognition of a zeolite facies. This facies largely bridges the gap between diagenesis and conventional metamorphism.

(2) As certain zeolites are stable in a silica-deficient environment to temperatures at least as high as 550°C, we propose that the zeolite facies should be defined to include at least all those assemblages produced under physical conditions in which the following are commonly formed: quartz–analcime, quartz–heulandite, quartz–laumontite.

(3) In sedimentary rocks the characteristic minerals include heulandite and analcime with quartz in a low grade stage, and laumontite, albite and quartz in a higher grade stage; together with adularia, celadonite, saponite, montmorillonoids, chlorite, calcite and sphene. In silica-deficient environments thomsonite is considered to represent an equivalent stage of metamorphism.

(4) In well-studied areas, there is a general tendency for less hydrated zeolites to occur at higher temperatures in conformity with experimental results and thermodynamic prediction.

(5) There is a tendency for zeolites to fall into three groups according to their mode of occurrence: silica-poor zeolites favoured by an environment lacking free silica; zeolites which coexist with quartz; and highly siliceous zeolites which may only be stable in solutions supersaturated in silica with reference to quartz.

(6) Where zeolitization is confined to the cements in sediments, or to cavity fillings in other rocks the assemblages of new-formed minerals may be considered in terms of ESKOLA's mineral facies concept. In this respect we are extending the range of the zeolite facies proposed by TURNER for metamorphic assemblages only.

(7) Between the rocks of the zeolite facies and typical greenschist facies in New Zealand, there is a very extensive zone characterized by prehnite and/or pumellyite. There appears to be justification for the erection of a distinct subfacies

of the greenschist facies (or possibly a new facies) to accommodate the rocks concerned.

(8) Extensive laboratory studies on systems related to zeolites have emphasized limitations of synthetic methods of establishing equilibrium phase relations. Change of starting materials has been shown to change apparent phase boundaries by more than 200°C even when run times exceed 30 days.

(9) The determination of phase boundaries by measurement of solubility may provide a sounder approach to the study of some silicate equilibria. Preliminary work on analcime appears promising and suggests that the analcime + quartz → albite + water transition occurs near 200°C at low pressures.

(10) The state of silica in starting materials appears critical where the phases on opposite sides of a phase boundary have different silica contents. The field of high-silica phases such as wairakite and mordenite is extended when the silica activity is higher than that of quartz. Observed effects of silica activity can be correlated with thermodynamic expectations and with natural occurrences. Similar conclusions could be drawn for other components in other systems.

(11) We consider that in quartz-bearing systems sodium and calcium zeolites are not stable above temperatures of about 320°C although they may be synthesized readily at temperatures as high as 450°C.

(12) We consider that the prehnite subfacies, transitional between the zeolite facies and greenschist facies, may come in at temperatures around 300°C ( $\pm 50^\circ$ ) in regions where water and load pressures are approximately equal and at lower temperatures if osmotic conditions occur.

*Acknowledgements*—Appreciation is expressed to all those individuals who have assisted the above project. Included among these are Mr. J. D. CAMPBELL, Dr. M. GAGE, Mr. D. HAMILTON, Dr. H. W. WELLMAN and Dr. A. J. R. WHITE who have discussed some of the problems and portions of the manuscript. Mr. A. STEINER has provided unpublished data on Wairakei and specimens for examination. Other specimens have been provided by Professor S. BONATTI, Mr. E. D. GILL, Mr. D. HAMILTON, Professor B. MASON, Dr. B. NASHAR, Dr. N. E. ODELL, Professor A. PABST, Dr. S. C. ROBINSON, Dr. C. S. ROSS, Dr. K. SAKURAI, Professor L. W. STAPLES, and Dr. G. P. L. WALKER. Dr. D. A. BROWN and Mrs. A. G. COOMBS have assisted with translations. Two chemical analyses by Mr. J. A. RITCHIE were provided by the Dominion Laboratory.

In particular we wish to express our gratitude for University of New Zealand research grants towards field expenses, and for the purchase of apparatus including a Philips X-ray diffractometer which was regularly used for identification of phases in both the experimental and petrographic parts of the work. The experimental work was also greatly assisted by the MELLOR Fund. Valuable technical help was provided by Messrs. G. CLARKSON, L. SEEUWEN, V. TYRRELL and L. WYLIE.

## APPENDIX I

### *Experimental*

(A. J. E., W. S. F., A. M. T.)

#### A1. 1. *Apparatus*

A great number of experiments were conducted in small closed vessels of capacity 2–10 cm<sup>3</sup>. Two features of these should be noted. Firstly they are most satisfactory in the water liquid-vapour range, i.e. at small degrees of filling and temperatures below the critical temperature of water. At supercritical temperatures the density of the fluid was maintained at approximately 0.33 and pressures were calculated from the data of KENNEDY (1950b). Secondly, the initial

commodate the rocks con-

zeolites have emphasized equilibrium phase relations. Apparent phase boundaries

ys. increment of solubility may te equilibria. Preliminary the analcime + quartz →

ures. critical where the phases on ca contents. The field of extended when the silica ts of silica activity can be tural occurrences. Similar ner systems.

n and calcium zeolites are they may be synthesized

ional between the zeolite ures around 300°C ( $\pm 50^\circ$ ) nately equal and at lower

viduals who have assisted the r. M. GAGE, Mr. D. HAMILTON, used some of the problems and ublished data on Wairakei and ded by Professor S. BONATTI, B. NASHAR, Dr. N. E. ODELL, K. SAKURAI, Professor L. W. s. A. G. COOMBS have assisted vere provided by the Dominion

sity of New Zealand research tus including a Philips X-ray uses in both the experimental as also greatly assisted by the s. G. CLARKSON, L. SEEUWEN,

ed vessels of capacity 2–10 cm<sup>3</sup>. tisfatory in the water liquid– below the critical temperature as maintained at approximately (1950b). Secondly, the initial

### The zeolite facies, with comments on the interpretation of hydrothermal syntheses

materials and water must be loaded in the cold bomb and the possibility exists of crystallization during the heating-up period which was normally about 3 hr. However, in runs where the same materials were kept dry during initial heating and were then pumped to pressure at the final temperature, identical results were produced and hence the objection does not appear serious. The other types of vessels used were hot-seal bombs and test-tube bombs 14 in. long with cold seals. All these were pumped to pressure at temperature. Samples were normally enclosed in silver capsules (unsealed) and neither leaching nor corrosion caused concern.

Table 5. X-ray powder pattern of phase Z

<i>d</i> (Å)	I	<i>d</i> (Å)	I	<i>d</i> (Å)	I
9.52	16	3.65	10	2.474	4
8.32	1	3.52	16	2.397	2
7.78	1	3.46	16	2.344	1
6.98	4	3.13	6	2.305	1
5.73	4	3.040	6	2.105	1
4.08	20	2.95	4	1.988	1
3.96	18	2.711	2	1.919	1
3.93	10	2.641	1	1.897	2
3.84	8	2.541	1	1.767	1
				1.705	1

Errors in temperature, involving control, measurement, and allowance for gradients in vessels are within  $\pm 5^\circ\text{C}$  and in most cases  $\pm 3^\circ\text{C}$ . Pressures were measured with Bourdon tube gauges calibrated against a manganin coil gauge and results are believed to be accurate to  $\pm 5$  per cent.

#### A1.2. Notes on phases synthesized

Phases were identified by direct comparison of X-ray diffractometer patterns. The identification of the full assemblage of phases produced was often a matter of great difficulty, and in general the phases reported are those which constitute the major products. The identifications of heulandite and tobermorite are somewhat doubtful. Only three lines of heulandite were not masked by other phases. The patterns of synthetic epistilbite compared closely with epistilbites from Yugawara hot spring, Japan and from Krossanes, Iceland. Hydrogarnets had refractive indices in the range 1.666–1.725 indicating a considerable water content (YODER, 1950).

There is evidence (ELLIS, 1958) from refractive indices that a complete range of synthetic analcimes from sodium to calcium end-members may have been formed. This is not in accord with observations of STEINER (1955) or BARBER (1950). Synthetic wairakite like the natural material (COOMBS, 1955) clearly shows the 200 reflection which is absent in strictly cubic analcime and weak in natural non-cubic analcimes. The 400 reflection, although broadened, was not clearly resolved into a doublet. Oxide mixes yielded the closer approach to the cubic modification. With mordenite also a considerable range of intermediate compositions appeared to have been formed between sodium and calcium end-members. Feldspars all tended towards the high temperature forms (MACKENZIE, 1957).

A crystalline phase of unknown composition, "phase Z" was found up to temperatures of about 330° from both glasses and oxide mixes, but mainly from the latter. It was found only from mixed sodium–calcium compositions, and was present usually as small thin rectangular plates, or sometimes as larger irregular tablets. The birefringence was very weak, extinction straight, and the R.I. ranged from 1.473–5 at composition 0.75 Ab to 1.484–6 at 0.25Ab. The X-ray spacings are given in Table 5.

The following abbreviations are used:

A	analcime	Ph	phillipsite
Ab	albite	Pr	prehnite
An	anorthite	Q	quartz
Ch	chabazite	S	stilbite
C	cristobalite	T	thomsonite
E	epistilbite	W	wairakite
H	heulandite	Wo	wollastonite
Hg	hydrogrossular	Xo	xonotlite
Hx	hexagonal anorthite	Z	phase Z
L	laumontite		
M	mordenite		

A1.3. Experiments using oxide mixes

Over 200 experiments were carried out at s.w.v.p. or at a vapour density of 0.33 in closed bombs on compositions in the plagioclase series. The mixtures were made from calcium oxide, sodium hydroxide, active alumina and silicic acid. The normal run time was 4 weeks, although duplicate runs indicated that products after 2 weeks were probably the same. On the other hand, short runs of 24 hr or less produced different results from those of a month's duration. At the soda-rich end final solutions were always alkaline (pH c. 10).

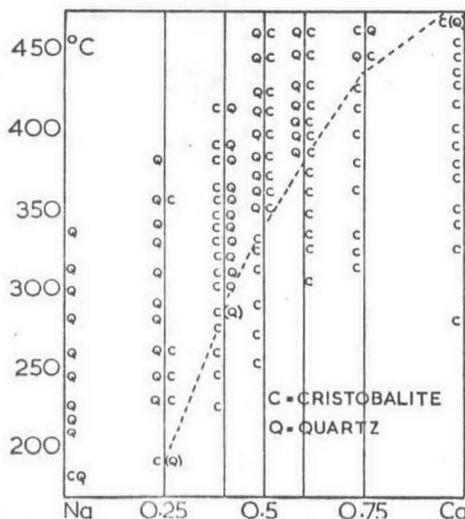


Fig. 17. Variation of silica phases formed during crystallization of oxide mixes of feldspar compositions with excess silica.

Seven compositions were used corresponding to the following: Ab + 6SiO<sub>2</sub>, 3Ab, An, 24SiO<sub>2</sub>, 3Ab, 2An, 30SiO<sub>2</sub>, Ab, An, 12SiO<sub>2</sub>, 2Ab, 3An, 30SiO<sub>2</sub>, Ab, 3An, 24SiO<sub>2</sub>, An + 6SiO<sub>2</sub>.

The basic results are summarized in Fig. 11. Quartz was always produced in runs from albite composition. The formation of quartz seems to be strongly retarded by the presence of calcium and the time for the appearance of quartz is approximately inversely proportional to the calcium content. It appears possible that a film of calcium silicate may protect the cristobalite which first appears. The data are summarized in Fig. 17. A more detailed study of the crystallization of oxide mixes of the sodium system was carried out by G. W. VALPY (1957). A greater variety of run times was used and mixes were pumped to pressure at the proper temperature. These experiments are significant in indicating that analcime tends to persist above its true stability field and to grow rapidly. The results are summarized in Fig. 10. The position of the boundary at low pressures is very close to that indicated by the data of Fig. 11.

The zeolite facies, with comments on the interpretation of hydrothermal syntheses

A1.4. Experiments with glasses

Experiments were carried out on 130 glass samples having the following compositions and refractive indices:

	Composition	R.I.
A	Ab + 4.25 SiO <sub>2</sub>	1.472
B	0.8Ab + 0.2An + 4.25 SiO <sub>2</sub>	1.484
C	0.6Ab + 0.4An + 4.25 SiO <sub>2</sub>	1.490
D	0.4Ab + 0.6An + 4.25 SiO <sub>2</sub>	1.502
E	0.2Ab + 0.8An + 4.25 SiO <sub>2</sub>	1.508
F	An + 4.25 SiO <sub>2</sub>	1.515

The lower silica content of the glasses is reflected in the lack of free silica in some end products. The crystallization was conducted at 2000 bars for 14 days in each case. Calcium-rich glasses react readily above 300°C, but with increasing soda content the tendency to crystallize falls off. The sodium glass would not crystallize in 2 weeks at 300°C even at a water pressure of 5000 bars. To obtain results from this glass, sodium fluoride was added as a flux ( $\frac{1}{2}$  mole of NaF per mole of NaAlSi<sub>3</sub>O<sub>8</sub>). With calcium members NaF could not be added as insoluble calcium fluoride would form. The crystallization of the soda-rich members was erratic and it appears that small amounts of impurities may have an influence.

Pure calcium glasses did not react rapidly below 275° at 3000 bars but at 5000 bars crystallization was fairly rapid at least down to 212°C. The major results are summarized in Fig. 12. In Table 6 results at 5000 bars are summarized.

Table 6

Glass	T°C	Products
F	212	E
	450	W, An, Q
	460	An, Q
	470	An, Q
D	250	E
	335	M + E
	350	M + E

Some separate experiments (Table 7) were conducted on the crystallization of albite glass at 2000 bars. The glass (R.I. 1.488) was made by melting the very pure albite from Amelia, Virginia. Once more sodium fluoride was added to facilitate crystallization.

Table 7

T(°C)	220	240	255	270	298	310
Products	A	A	A	A	Ab	Ab

The boundary indicated is close to that of VALPY, using oxide mixes, but as found by MACKENZIE (1957) a silica phase was not obtained in sufficient quantities to produce an X-ray pattern. In the presence of fluoride the significance of this observation must be treated with caution as some silica may be held in solution as SiF<sub>6</sub><sup>2-</sup> or sodium silicate.

A1.5. *Mixes with quartz in place of silica*

Results for the pure calcium system (corresponding to anorthite + 8 quartz) are summarized in Table 8. The crystallization was carried out in closed vessels at water vapour pressure or density of 0.33.

Table 8

<i>T</i> (°C)	400	385	375	363	340	330
Products	An	An	An.W	W.An	W(An)	W
	285	265	220			
	E.W	E	E			

The results of a similar series of experiments with the sodium system and quartz are listed in Table 9.

Table 9

<i>T</i> (°C)	335	303	279	267	265	260	160	115
Products	Ab,Q	Ab,Q	A,Ab,Q	A,Q	A,Q	A,Q	A,Q	A,Q

A1.6. *Mixes with sodium carbonate and bicarbonate*

A series of experiments was conducted with mixes of composition  $\text{Na}_2\text{O}$ ,  $\text{Al}_2\text{O}_3$ ,  $18\text{SiO}_2$  where the soda was added as bicarbonate or carbonate. The pH of these solutions is lower than that of mixes using sodium hydroxide. At 250°C the pH of molar  $\text{NaHCO}_3$  is about 9.0 and of an equimolar solution of carbonate-bicarbonate, about 10.8 (ELLIS and FYFE, 1957). The results are summarized in Table 10.

Table 10

Sodium compound	<i>T</i> (°C)	Products
$\text{NaHCO}_3$	255	M.A.C.Q
$\text{NaHCO}_3$	258	A.M.Q
$\text{NaHCO}_3/\text{Na}_2\text{CO}_3$	258	(A.)(M).Q
$\text{NaHCO}_3$	265	A.M.Q
$\text{NaHCO}_3/\text{Na}_2\text{CO}_3$	265	A.Ab.Q
$\text{NaHCO}_3$	262	M.A.C.Q
$\text{NaHCO}_3$	275	M.A.Q
$\text{NaHCO}_3$	280	Ab.Q
$\text{NaHCO}_3/\text{Na}_2\text{CO}_3$	280	Ab.Q

A1.7. *Experiments using minerals as starting materials*

A1.7.1. *Xonotlite*. In a further attempt to reduce the activity of the starting materials the mineral xonotlite was used as a source of calcium and was mixed with quartz and active alumina. The composition used corresponded to calcium mordenite. Results are summarized in Table 11.

Table 11

<i>T</i> (°C)	390	380	380	365	360	320	315	310	265
<i>P</i> (bars)	5000	2000	s.w.v.p	2000	s.w.v.p	s.w.v.p	5000	2000	4000
Products	An.Q	W.An.Q	W.An.Q	W.An.Q	W.An.Q	E.W.Q	W.E.Q	W.E.Q	E.Q

M. TAYLOR

ite + 8 quartz) are summarized  
els at water vapour pressure or

3	340	330
An	W(An)	W

system and quartz are listed in

5	260	160	115
Q	A,Q	A,Q	A,Q

composition Na<sub>2</sub>O, Al<sub>2</sub>O<sub>3</sub>, 18SiO<sub>2</sub>  
of these solutions is lower than  
lar NaHCO<sub>3</sub> is about 9.0 and of  
(ELLIS and FYFE, 1957). The

Products

L.A.C.Q  
L.M.Q  
A.(M).Q  
L.M.Q  
L.Ab.Q  
L.A.C.Q  
L.A.Q  
b.Q  
b.Q

ivity of the starting materials  
mixed with quartz and active  
enite. Results are summarized

320	315	310	265
w.v.p	5000	2000	4000
W.Q	W.E.Q	W.E.Q	E.Q

The zeolite facies, with comments on the interpretation of hydrothermal syntheses

A1.7.2. *Nepheline*. A study was made of the reaction of nepheline from the Haliburton-Bancroft area, Ontario, with natural quartz, Table 12.

Table 12

T(°C)	396	385	380	360	346	338	335	310	250
P (bars)	2000	2000	2000	2000	2000	2000	2000	2000	w.v.p.
Products	Ab.Q	Ab.Q	Ab.Q	Ab.A.Q.	A(Ab)Q	A.Q	A.Q	A.Q	A.Q

A1.7.3. *Stilbite*. A few experiments were conducted on the breakdown of stilbite from an unknown locality (Table 13).

Table 13

T(°C)	315°	350	370	403
P (bars)	s.w.v.p.	5000	5000	5000
Products	S	S (E)	E	W + Q

A1.7.4. *Chabazite*. In Table 14 results are given for the breakdown of chabazite from Richmond, Victoria, a locality that has yielded highly aluminous, alkali-rich specimens such as (Ca<sub>3.3</sub>Na<sub>5.2</sub>K<sub>1.2</sub>)Al<sub>13</sub>Si<sub>23</sub>O<sub>72</sub>·36H<sub>2</sub>O with variable Ca : Na : K ratios, (DOELTER, 1921, pp. 75-77).

Table 14

T(°C)	310	285	255	245	250	240	230	220	180
P	s.w.v.p	s.w.v.p	s.w.v.p	s.w.v.p	s.w.v.p	s.w.v.p	5000	s.w.v:p	s.w.v.p
Products	W	W	W + Ph	W + Ph	W + Ph	W + Ph	Ph + W + C	Ph + W + Ch	Ch

A1.7.5. *Laumontite*. Laumontite, shown by analysis to be almost alkali-free (PABST, personal communication) from Pine Creek Mine, Inyo County, California, with quartz produced wairakite at 400°C, and 380°C, at 2000 bars.

A1.7.6. *Dehydrated laumontite*. When laumontite is heated to 800°C it passes into a state which gives no X-ray pattern (KOIZUMI and KIRIYAMA, 1953). This material was used in a number of 30-day runs (Table 15) which were much longer than those of previous experiments by one of the authors (FYFE, 1955b).

Table 15

P (bars)	s.w.v.p	s.w.v.p	2000	2000	s.w.v.p	s.w.v.p	2000	600
T(°C)	240	310	310	323	330	344	380	380
Products	Ch + Q	L	L + Q	L + Q	W	W.L.(H)	W + Q	(L + W)
Remarks	Q added	100%	Q added	Q added	100%	Houl. doubtful	Q added	3 days

A1.7.7. *Lawsonite*. Lawsonite from Valley Ford, California, with natural quartz gave products indicated in Table 16.

Table 16

P (bars)	2000	2000	2000
T(°C)	400	395	382
Products	An,W,Q	An,W,Q	W,Q

These results may be compared with results on lawsonite and amorphous silica obtained previously by FYFE (1955b) (Fig. 18). Unfortunately the reaction could not be followed to temperatures much lower than the range shown as the rate of reaction is too slow.

A1.7.8. *Dehydrated heulandite*. The amorphous phase formed by heating heulandite

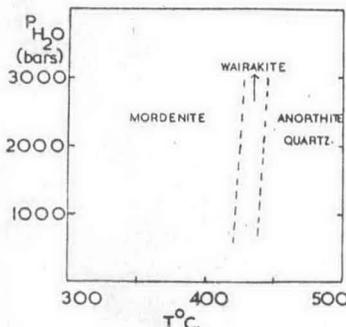


Fig. 18. Phases formed by reaction of lawsonite with amorphous silica.

(Appendix 4) was used in some long runs of more than 30 days. The results (Table 17) differ considerably from those of FYFE (1955b) from short runs on the same material in which 100 per cent crystallization to heulandite was observed. The appearance of wairakite in the long runs implies that it is more stable than heulandite in the range studied.

Table 17

<i>P</i> (bars)	2000	2600	2200	w.v.p	2200
<i>T</i> (°C)	280	340	360	370	410
Products	H + W	H + W	H + W + M	An + (W)	M + W + An
Remarks	Q added				

A1.7.9. *Thomsonite*. Natural thomsonite from Otama, New Zealand, mixed with quartz, produced wairakite in the range 280–316°C at pressures from s.w.v.p. to 4000 bars. The reaction could not be studied at lower temperatures as 30-day runs produced no detectable alteration.

#### A1.8. *Experiments involving glasses of prehnite composition*

The results of crystallization of glass formed by fusing a natural prehnite (Appendix 3) are summarized in Table 18 and in Fig. 13.

A series of thirty-six runs was carried out on a glass formed from the same prehnite as above but with silica added to give a molar ratio of prehnite : silica of 1 : 4. The reluctance of prehnite to form except at high pressures is an indication of metastable crystallization (TAYLOR, 1957). The results are summarized in Fig. 14.

#### A1.9. *Experiments with epidote glass*

A glass was produced by fusion of a deep green epidote (6.2 per cent Fe<sub>2</sub>O<sub>3</sub>) and the results of crystallization (TAYLOR, 1957) of twenty-five samples are summarized in Fig. 15. These results differ from those of EHLERS (1953) who found no field of prehnite or vesuvianite.

## APPENDIX 2

### *Composition and Density of Zeolites* (D. S. C.)

Basic data on composition, density and structure of zeolites are in many cases inadequate for a proper consideration of mutual relationships and stability fields and a tendency remains

M. TAYLOR

and amorphous silica obtained  
ion could not be followed to  
ction is too slow.

formed by heating heulandite

amorphous silica.

The results (Table 17) differ  
same material in which 100 per  
of wairakite in the long runs  
l.

w.v.p	2200
370	410
n + (W)	M + W + An

Zealand, mixed with quartz,  
s.w.v.p. to 4000 bars. The  
runs produced no detectable

natural prehnite (Appendix 3)

om the same prehnite as above  
: 4. The reluctance of prehnite  
rystallization (TAYLOR, 1957).

er cent Fe<sub>2</sub>O<sub>3</sub>) and the results  
ummarized in Fig. 15. These  
prehnite or vesuvianite.

are in many cases inadequate  
fields and a tendency remains

The zeolite facies, with comments on the interpretation of hydrothermal syntheses

Table 18

Temp. (°C)	Pressure (bars)	Time (days)	Products
270	3000	14	Hx(s) Tb(s)
295	2000	10	Hx(s) Pr(s)
300	3000	9	Hx(s) Tb(s)
320	3000	18	Pr(s)
330	2000	1	Pr(s) Hx(s) Xo(s)
338	1000	9	Pr(s) Hx(s)
340	3000	14	Pr(s)
347	1000	8	Hx(s) Xo(s)
350	1700	4	Hx(s) Xo(s)
353	4000	6	Pr(s) An(w)
357	2000	17	Pr(vs)
357	2000	2	Pr(s) An(w) Wo(w)
360	2000	9	Hx(s) An(w) Pr(w)
377	2000	10	Hx(s)
380	2000	1	An(s) Hx(s) Xo(s)
380	3000	10	Pr(s)
386	2000	12	Pr(s) An(s) Wo(s)
400	3000	9	Pr(s) An(s) Wo(s)
400	3000	3	Pr(s)
405	3000	4	An(s) Wo(s)
409	4000	3	Pr(s) An(vw)
415	4000	5	Pr(s) An(s) Wo(s)
415	4000	1	An(s) Wo(s) Pr(w)
425	3000	9	An(s) Wo(s)
425	5000	3	Pr(s)
427	3000	15	An(s) Wo(s) Pr(vw)
430	3000	7	An(s) Wo(s) Pr(w)
440	5000	7	Pr(s) An(s) Wo(s)
442	2000	6	An(s) Wo(s)
445	4000	6	Pr(s) An(s) Wo(s)
448	2000	11	An(s) Wo(s)
450	2000	17	An(s) Wo(s)
450	3000	9	An(s) Wo(s) Pr(w)
453	3860	3	An(s) Wo(s)
455	4000	3	An(s) Wo(s)
455	5000	5	An(s) Wo(s)
457	5000	4	An(s) Wo(s) Pr(w)
469	3000	9	An(s) Wo(s)
475	4500	2	An(s) Wo(s)
490	4000	5	An(s) Wo(s)
490	4000	5	An(s) Wo(s)
492	4000	2	An(s) Wo(s)
516	4700	3	An(s) Wo(s)

for some workers to express compositions in terms of "ideal" formulae which can obscure relationships rather than clarify them. Considerable confidence can be placed in the view that the number of oxygen atoms within the framework of linked (Si,Al) $_4$ O $_4$  tetrahedra is virtually constant for the unit cell of each species. This number must be even, is commonly a multiple of 8, and can be determined unambiguously from reasonably precise chemical, X-ray and density data. Following HEY (1932a) and others, unit cell contents on the basis of this ideal number of structural oxygens have been calculated by the writer for a large number of zeolite analyses. More attention has been given to variations in the Si : Al ratio than to variations in the other cations, as the latter are subject to secondary, base exchange effects and are therefore less fundamental in reflecting conditions of formation. Nevertheless as the various lime zeolites appear to accept such elements as Na, K and Sr into their lattices to varying degrees, the concentration of these latter elements in the environments of formation must influence stability fields. The Mg-bearing species ferrierite and the barium zeolites are not here considered.

It will be found convenient to describe the range of composition of certain zeolites not only in terms of the familiar isomorphous substitutions: (i) NaSi for CaAl; and (ii) Na $_2$  for Ca, or more generally (Na, K) $_2$  for (Ca, Sr, Ba) but also in terms of the substitution: (iii) Al for Si within the tetrahedral framework with additional W group cations (Na, K, Ca $^{1/2}$ ) occupying otherwise vacant lattice sites. This results in a marked variation in the number of W group cations per unit cell and is equivalent to simultaneous operation of the other two types of replacement.

The ranges of composition tentatively accepted for valid species are listed below together with estimates of the specific gravity for some of the compositions listed. Specific gravity is not significantly affected by the substitution of Na $_2$  for Ca (compare analcime and wairakite), but it does vary markedly with the other types of substitution. The values given have been selected, averaged or interpolated from previously published determinations and in some cases are capable of considerable refinement. Only a few leading references have been cited; many others have been considered.

In Fig. 5 compositions of the calciferous zeolites are plotted in molecular proportions on the triangle (Ca, Na $_2$ , K $_2$ )O : 2H $_2$ O : 2SiO $_2$ , the component (Ca, Na $_2$ , K $_2$ )O being numerically equal to Al $_2$ O $_3$  for zeolites and for other true tectosilicates such as anorthite. Horizontal lines therefore represent the range of variation in Si : Al ratios through each series. Prehnite, pumpellyite and epidote have been plotted for comparison and in these the Al $_2$ O $_3$  content is not directly related to the other components. The water content has been plotted arbitrarily at the value which is judged to best reflect the chemical analyses and structural data. In several cases it is open to question. Compositions plotted are based on analyses of apparently good quality of natural zeolites. Laboratory crystallization from highly reactive and unstable starting materials such as glasses is likely to lead to a greater range of metastable compositions than in the case of the natural materials.

*Analcime.* Na $_{17}$ Al $_{17}$ Si $_{31}$ O $_{96}$ .16H $_2$ O to Na $_{14}$ Al $_{14}$ Si $_{34}$ O $_{96}$ .16H $_2$ O, with minor substitution of (K,Ca $_1$ ) for Na; commonly near NaAlSi $_2$ O $_6$ .H $_2$ O;  $Z = 16$  (e.g. HARTWIG, 1928; COOMBS, 1955);  $D = 2.265 \pm 0.01$ . SAITA (1957) has indicated that synthetic analcimes may range from NaAlSi $_3$ O $_8$ . $n$ H $_2$ O, to NaAlSi $_4$ O $_8$ . $m$ H $_2$ O, presumably with  $Z = 12$  and  $Z = 24$  respectively.

*Ashcroftine.* 40(KNaCaAl $_4$ Si $_5$ O $_{18}$ .8H $_2$ O);  $D = 2.61 \pm 0.05$  (HEY and BANNISTER, 1933).

*Chabazite.* (Ca,Na $_2$ ,K $_2$ ) $_5$ Al $_{10}$ Si $_{26}$ O $_{72}$ .36H $_2$ O to (Ca,Na $_2$ ,K $_2$ ) $_{6.75}$ Al $_{13.5}$ Si $_{22.5}$ O $_{72}$ .36H $_2$ O. Alkalis sometimes exceed Ca. STRUNZ (1956) gives (Ca,Na $_2$ )Al $_2$ Si $_4$ O $_{12}$ .6H $_2$ O;  $Z = 6$ ;  $D = 2.082$ .

*Epistilbite.* STRUNZ and TENNYSON (1956) give CaAl $_2$ Si $_6$ O $_{16}$ .5H $_2$ O;  $Z = 3$ . In eight out of fifteen analyses considered by the present writer, there are 15.7 to 16.3 H $_2$ O per unit cell, the others showing rather less. We tentatively accept 16 H $_2$ O per unit cell, which would make epistilbite a true, higher density, polymorph of houlandite with the approximate range (Ca,Na $_2$ ) $_{2.85}$ Al $_{5.7}$ Si $_{18.3}$ O $_{48}$ .16H $_2$ O to (Ca,Na $_2$ ) $_{3.5}$ Al $_7$ Si $_{17}$ O $_{48}$ .16H $_2$ O;  $D$  typically  $2.25 \pm 0.03$ . Ca is dominant over alkalis.

Dachiardite is shown by X-ray powder diffraction to be structurally related to epistilbite. It has a higher alkali content with about Si $_{19-19\frac{1}{2}}$  for 48 O.

*Erionite.* (Na $_2$ ,K $_2$ ,Ca,Mg) $_{4.5}$ Al $_9$ Si $_{27}$ O $_{72}$ .27H $_2$ O;  $D$  (calc.) = 2.07 (STAPLES and GARD, 1958).

*Faujasite.* Near (Na $_2$ ,Ca) $_{1.75}$ Al $_{3.5}$ Si $_{8.5}$ O $_{24}$ .16H $_2$ O;  $Z = 16$ ;  $D = 1.92$  (cf. STRUNZ, 1955).

formulae which can obscure n be placed in the view that Al)O<sub>4</sub> tetrahedra is virtually ven, is commonly a multiple precise chemical, X-ray and its on the basis of this ideal for a large number of zeolite : Al ratio than to variations se exchange effects and are Nevertheless as the various ato their lattices to varying omments of formation must the barium zeolites are not

n of certain zeolites not only ; and (ii) Na<sub>2</sub> for Ca, or more tution: (iii) Al for Si within K, Ca<sub>1/2</sub>) occupying otherwise mber of W group cations per er two types of replacement. ies are listed below together ns listed. Specific gravity is are analcime and wairakite), The values given have been minations and in some cases nees have been cited; many

in molecular proportions on Na<sub>2</sub>, K<sub>2</sub>)O being numerically s anorthite. Horizontal lines ough each series. Prehnite, n these the Al<sub>2</sub>O<sub>3</sub> content is as been plotted arbitrarily at d structural data. In several analyses of apparently good ighly reactive and unstable o of metastable compositions

with minor substitution of ERWIG, 1928; COOMBS, 1955); analcimes may range from id Z = 24 respectively. Y and BANNISTER, 1933).  $Ca_{13.5}Si_{22.5}O_{72} \cdot 36H_2O$ . Alkalis <sub>2</sub>O; Z = 6; D = 2.082.  $Ca_{13.5}Si_{22.5}O_{72} \cdot 36H_2O$ ; Z = 3. In eight out 5.7 to 16.3 H<sub>2</sub>O per unit cell, unit cell, which would make with the approximate range ; D typically 2.25 ± 0.03.

aturally related to epistilbite. 97 (STAPLES and GARD, 1958). D = 1.92 (cf. STRUNZ, 1955).

*Gismondine*.  $CaAl_2Si_2O_8 \cdot 4H_2O$ ; Z = 8 (KRAUS, 1939) to  $Ca_{0.92}Al_{1.84}Si_{2.16}O_8 \cdot 4H_2O$  with moderate substitution of (K,Na)<sub>2</sub> for Ca.

*Gmelinite*. According to STRUNZ (1956), polymorphous with Na-rich chabazite, and often containing chabazite in lamellar intergrowth;  $(Na_2,Ca)Al_2Si_4O_{12} \cdot 6H_2O$ ; Z = 4; D = 2.028.

*Gonnardite*. Polymorphous with thomsonite and mostly near  $(Ca,Na_2)_{4.3}Al_{8.6}Si_{11.4}O_{40} \cdot 12H_2O$  (MEIXNER *et al.*, 1956) but can also have higher ratios of Al:Si (MASON, 1957). D = 2.27 ± 0.02.

*Heulandite*. Normally in the range  $(Ca,Na_2)_{4.8}Al_{9.6}Si_{26.4}O_{72} \cdot 24H_2O$ ; D = 2.21 ± 0.03; to  $(Ca,Na_2)_4Al_8Si_{28}O_{72} \cdot 24H_2O$ ; D = 2.18 ± 0.03. There is often appreciable K and/or Sr. In the silica-rich variety clinoptilolite, the composition approaches  $Ca(Na,K)_4Al_6Si_{30}O_{72} \cdot 24H_2O$ ; D = 2.14 ± 0.03.

*Laumontite*.  $Cu_{4.25}Al_{8.5}Si_{15.5}O_{48} \cdot 16H_2O$  to  $Cu_{3.75}Al_{7.5}Si_{16.5}O_{48} \cdot 16H_2O$  with minor replacement of Ca by Na<sub>2</sub>, i.e. near  $CaAl_2Si_4O_{12} \cdot 4H_2O$ ; Z = 4; D = 2.29 ± 0.02 (COOMBS, 1952). Leonhardtite is a partially dehydrated variety with about 14 H<sub>2</sub>O.

*Levyne*. Perhaps  $CaAl_2Si_4O_{12} \cdot 5H_2O$  to  $Ca_{1.1}Al_{2.2}Si_{3.8}O_{12} \cdot 5H_2O$  with moderate replacement of Ca by (Na,K)<sub>2</sub>. STRUNZ (1956) suggests polymorphous and structural relationships with chabazite and gives 6 H<sub>2</sub>O; Z = 9; D = 2.140. The few available analyses appear to indicate 5 H<sub>2</sub>O rather than 6 H<sub>2</sub>O.

*Mesolite*. Essentially  $Na_2Ca_2Al_6Si_9O_{30} \cdot 8H_2O$ ; Z = 8; D = 2.26; minor Na<sub>2</sub> for Ca (HEY, 1933).

*Metascolocite*. Higher temperature polymorph of scolocite (HEY, 1936).

*Mordenite (ptilolite)*.  $(Na_2,K_2,Ca)Al_2Si_{10}O_{24} \cdot 7H_2O$ ; Z = 8 (e.g. WAYMOUTH *et al.*, 1938). with alkalis usually dominant over Ca. D = 2.12 ± 0.03. First-class analyses (as defined by HEY, 1932a) show variations of no more than 0.15 Al and Si. Synthetic mordenites range from pure Ca to pure Na members (BARKER, 1948 and Appendix 1 of this paper).

*Natrolite*.  $Na_2Al_2Si_3O_{10} \cdot 2H_2O$ ; Z = 8; D = 2.24. Up to 1 in 16 Na replaced by K and 1 in 4 Na replaced by Ca<sub>1</sub> (HEY, 1932b).

*Phillipsite*.  $(Ca,K_2)_{2.5}Al_5Si_{11}O_{32} \cdot 12H_2O$  to  $(Ca,K_2)_{3.5}Al_7Si_9O_{32} \cdot 12H_2O$  with Na usually subordinate (cf. WYATT and CHATELAIN, 1938). D = 2.20 ± 0.02 for typical intermediate members of the series.

?*Pseudonatrolite*. Near  $(Ca,Na_2)Al_2Si_6O_{18} \cdot 5H_2O$  (HEY, 1955, p. 162).

*Scolocite*.  $CaAl_2Si_3O_{10} \cdot 3H_2O$ ; Z = 8; D = 2.27 ± 0.02. Minor Na<sub>2</sub> for Ca (HEY, 1936).

*Stilbite*. Approximately  $(Ca,Na_2)_4Al_8Si_{28}O_{72} \cdot 28H_2O$ ; D = 2.15 ± 0.02; to  $(Ca,Na_2)_5Al_{10}Si_{26}O_{72} \cdot 28H_2O$ ; D = 2.18 ± 0.02 (cf. SEKANINA and WYATT, 1936). The average water per unit cell for some two dozen representative analyses is 28.7 H<sub>2</sub>O as against 24.2 for heulandite. The suggestion of STRUNZ and TENNYSON (1956) that a correct formula should show 24 H<sub>2</sub>O as in heulandite and that the two minerals are polymorphs as well as having related (though different) structures, is not therefore accepted.

*Thomsonite*.  $(Ca,Na_2)_{8.4}Al_{16.8}Si_{23.2}O_{80} \cdot 24H_2O$ ; D = 2.30 to  $(Ca,Na_2)_{10.25}Al_{20.5}Si_{19.5}O_{80} \cdot 24H_2O$ ; D = 2.38 (HEY, 1932a).  $CaAl_2Si_2O_8 \cdot 2H_2O$ ; Z = 10; D = 2.37, is a possible synthetic member (GOLDSMITH, 1952).

*Wairakite*.  $CaAl_2Si_4O_{12} \cdot 2H_2O$ ; Z = 8; D = 2.265 (STEINER, 1955; COOMBS, 1955).

*Yugawaralite*. Unit cell contents calculated from the data of SAKURAI and HAYASHI (1952) are approximately  $Ca_{3.84}(Na,K)_{0.34}Al_{7.55}Si_{21.33}O_{58} \cdot 15.3H_2O$ , corresponding roughly to  $4CaAl_2Si_5O_{14} \cdot 4H_2O$ . D = 2.20.

## APPENDIX 3

## Chemical and Physical Data on Heulandite and Prehnite

(A. M. T., D. S. C.)

Chemical analyses and other data on the heulandite and prehnite used in experiments described above are given below.

*Heulandite*

Locality: Cape Blomidon, Nova Scotia. Colourless crystals.

SiO<sub>2</sub> 56.8; Al<sub>2</sub>O<sub>3</sub> 16.6; Fe<sub>2</sub>O<sub>3</sub> tr.; MgO tr.; CaO 5.8; SrO 2.0; Na<sub>2</sub>O 1.6; K<sub>2</sub>O 0.8;

Li<sub>2</sub>O tr.; H<sub>2</sub>O + 110° 12.45; H<sub>2</sub>O - 110° 3.3; TiO<sub>2</sub> n.f.; P<sub>2</sub>O<sub>5</sub> 0.01; MnO n.f., CO<sub>2</sub> n.f.  
Spectrographic analysis: Ag 0.015; Pb 0.015; Sn < 0.01; Ba 0.05. Not detected: V, Cd, As, Be, Zn, W, Mo, Ni, Cr, Co, Bi, Sb, B, La, Yt, Ce. Total: 99.44. J. A. RITCHIE  
*anal.*, s. g. 2.23 ± 0.01.

Structural formula: (Ca<sub>2.9</sub>Sr<sub>0.5</sub>Na<sub>1.5</sub>K<sub>0.5</sub>)Al<sub>9.2</sub>Si<sub>26.8</sub>O<sub>72</sub>·24·8H<sub>2</sub>O in satisfactory agreement with that of HEY and BANNISTER (1934) and Appendix C above.

Refractive indices variable,  $\alpha$  1.500-1.505 ± 0.001,  $\beta$  1.500-1.506 ± 0.001,  $\gamma$  1.506-1.512 ± 0.002.

#### Prehnite

Locality: Prospect Quarry, New South Wales. Large, translucent, very pale green botryoidal masses in cavities in dolerite. Average of comparable analyses by A.M.T. and by J. A. RITCHIE, Dominion Laboratory, Wellington: SiO<sub>2</sub> 43.7; Al<sub>2</sub>O<sub>3</sub> 24.05; Fe<sub>2</sub>O<sub>3</sub> 0.93; FeO 0.03; MgO 0.11; CaO 26.85; Na<sub>2</sub>O 0.04; K<sub>2</sub>O n.f.; Li<sub>2</sub>O n.f.; H<sub>2</sub>O + 110° 4.54; H<sub>2</sub>O - 110° 0.03; TiO<sub>2</sub> tr.; P<sub>2</sub>O<sub>5</sub> 0.02; MnO n.f.; CO<sub>2</sub> n.f.; Spectrographic analysis (Dominion Laboratory): Ag 0.01; Pb 0.04; SnO 0.01; BaO < 0.003. Not detected: V, Cd, etc., as above. Total: 100.36; s. g. 2.93.

Formula on basis of eleven oxygen atoms:

(Ca<sub>1.98</sub>Mg<sub>0.01</sub>Na<sub>0.01</sub>)(Al<sub>1.95</sub>Fe<sub>0.05</sub>)Si<sub>3.01</sub>O<sub>11</sub>·1.04H<sub>2</sub>O in very close agreement with the conventional formula Ca<sub>2</sub>Al<sub>2</sub>Si<sub>3</sub>O<sub>10</sub>(OH)<sub>2</sub>.  $\alpha$  1.615 ± 0.001;  $\beta$  1.624 ± 0.001;  $\gamma$  1.643 ± 0.002;  $\gamma - \alpha$  0.028;  $2V_{\gamma}$  69° ± 2°  $r > v$  strong.

As is common in prehnite from such environments, and in contrast to the prehnite described in Section 2 above from the New Zealand greywackes, basal sections show complex lamellar twinning, and when thick, anomalous interference tints and incomplete extinction.

#### REFERENCES

- AMES L. L. and SAND L. B. (1958) Hydrothermal synthesis of wairakite and calcium-mordenite. *Amer. Min.* **43**, 476-480.
- AMES A. C. (1950) An intrusion of porphyrite near Waihao Forks, South Canterbury. *Trans. Roy. Soc. N.Z.* **78**, 271-279.
- AMES A. C. (1952) Petrological features of the rocks of the Maruwenua district, North Otago. *Trans. Roy. Soc. N.Z.* **79**, 376-385.
- ANTUN P. (1953) Laumontite de Serpont, *Ann. Soc. Géol. Belg.* **77**, 1363-71.
- BANWELL C. J., COOPER E. R., THOMPSON G. E. K. and MCCREE K. J. (1957) Physics of the New Zealand thermal area. *Bull. N.Z. Dep. Sci. Industr. Res.*
- BARBER R. M. (1948) Syntheses and reactions of mordenite. *J. Chem. Soc.* 2158-2163.
- BARBER R. M. (1950) Ion-exchange and ion-sieve processes in crystalline zeolites. *J. Chem. Soc.* 2342-2350.
- BARBER R. M. and WHITE E. A. D. (1952) Synthetic crystalline sodium aluminosilicates. *J. Chem. Soc.* 1561-1571.
- BEATTIE I. R. (1954) The structure of analcite and ion-exchanged forms of analcite. *Acta Cryst.* **7**, 357-359.
- BENSON W. N. (1942) The basic igneous rocks of Eastern Otago and their tectonic environment, Part 3. *Trans. Roy. Soc. N.Z.* **72**, 160-185.
- BOLDYREVA A. M. (1953) Authigenic analcite in Upper Permian sediments of the Chkalova and Aktyubinsk districts. *Mém. soc. russe min.* **82**, 291-297; *Chem. Abstr.* **48**, 5930f.
- BRADLEY W. H. (1928) Zeolite beds in the Green River formation. *Science* **67**, 73-74.
- BRADLEY W. H. (1929) The occurrence and origin of analcite and meerschaum beds in the Green River formation of Utah, Colorado and Wyoming. *U.S. Geol. Surv. Prof. Paper A* **158**, 1-7.
- BRAMLETTE M. N. and POSNJAK E. (1933) Zeolitic alteration of pyroclastics. *Amer. Min.* **18**, 167-171.
- BRODERICK T. M. (1929) Zoning in Michigan copper deposits and its significance. *Econ. Geol.* **24**, 149-162 and 311-326.

The zeolite facies, with comments on the interpretation of hydrothermal syntheses

FLOR

0-01; MnO n.f., CO<sub>2</sub> n.f.  
 a 0-05. Not detected:  
 d: 99-44. J. A. RITCHIE

n satisfactory agreement

1-506 ± 0-001,  $\gamma$  1-506-

ery pale green botryoidal  
 by A.M.T. and by J. A.  
 24-05; Fe<sub>2</sub>O<sub>3</sub> 0-93; FeO  
 + 110° 4-54; H<sub>2</sub>O -110°  
 hic analysis (Dominion  
 detected: V, Cd, etc.,

agreement with the con-  
 0-001;  $\gamma$  1-643 ± 0-002;

ontrast to the prehnite  
 es, basal sections show  
 ice tints and incomplete

s and calcium-mordenite,  
 uth Canterbury. *Trans.*  
 a district, North Otago.  
 -71.  
 J. (1957) Physics of the  
*Soc.* 2158-2163.  
 zeolites. *J. Chem. Soc.*  
 sodium aluminosilicates.  
 s of analcite. *Acta Cryst.*  
 eir tectonic environment,  
 iments of the Chkalova  
*v. Abstr.* 48, 5930f.  
*Science* 67, 73-74.  
 neerschaum beds in the  
*Geol. Surv. Prof. Paper*  
 yroclastics. *Amer. Min.*  
 significance. *Econ. Geol.*

BRODERICK T. M. (1931) Fissure vein and lode relations in Michigan copper deposits. *Econ. Geol.* **26**, 840-856.

BRODIE J. W. (1953) Stratigraphy and structure of the greywackes and argillites on the south coast of Wellington Peninsula. *N.Z. J. Sci. Tech.* B **34**, 205-226.

BROTHERS R. N. (1956) The structure and petrography of greywackes near Auckland, New Zealand. *Trans. Roy. Soc. N.Z.* **83**, 465-482.

BROWN D. A. (1955) The geology of Siberia Hill and Mount Dasher, North Otago. *Trans. Roy. Soc. N.Z.* **83**, 347-372.

BUR'YANOVA E. Z. (1954) Analcime sedimentary rocks from Tuva. *Dokl. Akad. Nauk SSSR* **98**, 261-264.

BUR'YANOVA E. Z. (1956) Authigenic laumontite from Middle Devonian sandstone of Tuva. *Vsesoyuz. Nauch.-Issledovatel. Geol. Inst., Sborn.* **3**, 77-79; *Chem. Abstr.* **51**, 13662c.

BUSHINSKY G. I. (1950) Mordenite in Jurassic, Cretaceous and Paleocene marine sediments. *Dokl. Akad. Nauk SSSR* **73**, 1271-1274.

BUTLER B. S. and BURBANK N. S. (1929) The copper deposits of Michigan. *U.S. Geol. Surv. Prof. Paper* 144.

CAMPBELL A. S. (1958) *The Hydrothermal Crystallization of Amorphous Silica and the Analcime Albite Phase Boundary*. M.Sc. Thesis, Univ. of Otago, New Zealand.

CAMPBELL J. D. (1955) The Oretian Stage of the New Zealand Triassic System. *Trans. Roy. Soc. N.Z.* **82**, 1033-1047.

COOMBS D. S. (1950) The geology of the northern Taringatua hills, Southland. *Trans. Roy. Soc. N.Z.* **78**, 426-448.

COOMBS D. S. (1952) Cell size, optical properties and chemical composition of laumontite and leonhardite. With a note on regional occurrences in New Zealand. *Amer. Min.* **37**, 812-830.

COOMBS D. S. (1954) The nature and alteration of some Triassic sediments from Southland, New Zealand. *Trans. Roy. Soc. N.Z.* **82**, 65-109.

COOMBS D. S. (1955) X-ray observations on wairakite and non-cubic analcime. *Miner. Mag.* **30**, 699-708.

COOMBS D. S. (1958) Zeolitized tuffs from the Kuttung glacial beds near Seaham, New South Wales. *Austr. J. Sci.* **21**, 18-19.

CORNÜ F. (1908) Über die Paragenese der Minerale, namentlich die der Zeolithe. *Österr. Z. Berg-Hüttenw.* **56**, 89-93.

DANA J. D. (1892) *System of Mineralogy* (6th Ed.). Paul, Trench, Trübner, London.

DAUBRIÉE A. (1879) *Études synthétiques de géologie expérimentale*. Paris.

DOELTER C. (1921) *Handbuch der Mineralchemie* Vol. II, Pt. 3. Steinkopf, Dresden and Leipzig.

DZOTSENIDZE G. S. and SKHUTLADZE N. I. (1953) Analcime horizon in the coal-bearing rocks of the Kutais-Gelati district. *Vop. Petrog. Min. Akad. Nauk SSSR* **1**, 301-310; *Chem. Abstr.* **49**, 7461 g.

EHLERS E. G. (1953) An investigation of the stability relations of the Al-Fe members of the epidote group. *J. Geol.* **61**, 231-251.

ELLIS A. J. and FYFE W. S. (1957) Hydrothermal chemistry. *Rev. Pure Appl. Chem.* **7**, 261-316.

ELLIS A. J. (1958) Ph.D. Thesis, University of Otago.

ELLIS A. J. and WILSON S. H. (1955) Unpublished work, Dominion Laboratory, Wellington, New Zealand.

ESKOLA P. (1920) The mineral facies of rocks. *Norsk Geol. Tidsskr.* **6**, 143-194.

ESKOLA P. (1939) *Die Entstehung der Gesteine* (In BARTH T. F. W., CORRENS C. W. and ESKOLA, P.). Springer, Berlin.

FENNER C. N. (1936) Bore-hole investigations in Yellowstone Park. *J. Geol.* **44**, 225-315.

FOSTER W. D. and FEICHT F. L. (1946) Mineralogy of concretions from Pittsburgh coal seam, with special reference to analcite. *Amer. Min.* **31**, 357-364.

FYFE W. S. (1955a) Lower limit of the green-schist facies, *Bull. Geol. Soc. Amer.* **66**, 1649. (Abstract).

FYFE W. S. (1955b) Results obtained by 1955 and contained in FYFE, TURNER and VERHOOGEN (1958).

- FYFE W. S., TURNER F. J. and VERHOOGEN J. (1958) *Metamorphic Reactions and Metamorphic Facies*. Geol. Soc. Amer. Memoir No. 73.
- GILBERT C. M. (1951) Laumontite from Anchor Bay, Mendocino County, California. *Bull. Geol. Soc. Amer.* **62**, 1517.
- GILBERT C. M. and McANDREWS M. G. (1948) Authigenic heulandite in sandstone, Santa Cruz County, California. *J. Sediment. Petrol.* **18**, 91-99.
- GILL E. D. (1957) Fossil wood replaced by laumontite near Cape Paterson, Victoria. *Proc. Roy. Soc. Victoria* **69**, 33-35.
- GOLDBERG E. D. and ARRHENIUS G. O. S. (1958) Chemistry of Pacific pelagic sediments. *Geochim. et Cosmochim. Acta* **13**, 153-212.
- GOLDSMITH J. R. (1952) Synthetic soda-free thomsonite. *Miner. Mag.* **29**, 952-954.
- GRIGGS D. T. and KENNEDY G. C. (1956) A simple apparatus for high pressures and temperatures. *Amer. J. Sci.* **254**, 722-735.
- GUNN B. M. (1956) *The Geology of the Franz Josef-Fox Glacier Region, South Westland*. M.Sc. Thesis, University of Otago.
- HARKER R. I. (1958) The system  $MgO-CO_2-A$  and the effect of inert pressure on certain types of hydrothermal reaction. *Amer. J. Sci.* **256**, 128-138.
- HARRINGTON H. J. (1955) The geology of Naseby district, Central Otago. *N.Z. J. Sci. Tech.* B **36**, 581-599.
- HARRIS P. G. and BRINDLEY G. W. (1954) Mordenite as an alteration product of a pitchstone glass. *Amer. Min.* **39**, 819-824.
- HARTWIG W. (1928) Über die Struktur von Analcim. *Zbl. Miner.* A 380.
- HAYASHI H. and SUDO T. (1957) Zeolite-bearing bentonites. *Mineral J., Japan* **2**, 196-199.
- HEADY H. H. (1952) Differential thermal study of Colorado oil shale. *Amer. Min.* **37**, 804-811.
- HEALD M. T. (1956) Cementation of Triassic arkoses in Connecticut and Massachusetts. *Bull. Geol. Soc. Amer.* **67**, 1133-1154.
- HEY M. H. (1932a) Studies on the zeolites. Part II: Thomsonite (including faroelite) and gonardite. *Miner. Mag.* **23**, 51-125.
- HEY M. H. (1932b) Studies on the zeolites. Part III: Natrolite and metanatroilite. *Miner. Mag.* **23**, 243-289.
- HEY M. H. (1933) Studies on the zeolites. Part V: Mesolite. *Miner. Mag.* **23**, 421-447.
- HEY M. H. (1936) Studies on the zeolites. Part IX: Scolecite and metascolecite. *Miner. Mag.* **24**, 227-253.
- HEY M. H. (1955) *An Index of Mineral Species and Varieties* (2nd Ed.), British Museum, London.
- HEY M. H. and BANNISTER F. A. (1933) Studies on the zeolites. Part IV: Asheroftine (kalthomsonite of S. G. Gordon). *Miner. Mag.* **23**, 305-308.
- HEY M. H. and BANNISTER F. A. (1934) Studies on the zeolites. Part VII: 'Clinoptilolite,' a silica-rich variety of heulandite. *Miner. Mag.* **23**, 556-559.
- HUTTON C. O. (1937) An occurrence of the mineral pumpellyite in the Lake Wakatipu region, western Otago, New Zealand. *Miner. Mag.* **24**, 529-533.
- HUTTON C. O. (1940) Metamorphism in the Lake Wakatipu region, western Otago, New Zealand. *N.Z. Dep. Sci. Industr. Res., Mem.* No. 5.
- HUTTON C. O. (1949a) Notes on the geology of Kapiti Island, Cook Strait, N.Z. Part II: Petrography. *Trans. Roy. Soc. N.Z.* **77**, 465-468.
- HUTTON C. O. (1949b) Occurrence of leonhardite. *Bull. Geol. Soc. Amer.* **60**, 1939-1940. (Abstract).
- KALEY M. E. and HANSON R. F. (1955) Laumontite and leonhardite cement in Miocene sandstone from a well in San Joaquin Valley, California. *Amer. Min.* **40**, 923-925.
- KELLER W. D. (1951) Analcime in the Popo Agie member of the Chugwater formation. *Science* **115**, 241-242.
- KELLER W. D. (1952) Analcime in the Popo Agie member of the Chugwater formation. *J. Sediment. Petrol.* **22**, 70-82.
- KELLER W. D. (1953) Analcime in the Chinle Formation of Utah correlative with the Popo Agie of Wyoming. *J. Sediment. Petrol.* **23**, 10-12.
- KENNEDY G. C. (1950a) A portion of the system silica-water. *Econ. Geol.* **45**, 629-653.

KENNE  
tues  
KERR I  
Calif  
KING E  
Chem  
KOIZUM  
dehy  
KOIZUM  
Geol.  
KOLBIN  
Dokl.  
KOSOV  
durin  
KOSOV  
Moso  
Nauk  
KRAUS  
LATIME  
Solut  
LILLIE  
regio  
LILLIE  
Josef  
MACKE  
MACKIE  
Tran  
McLINT  
arour  
MARWIC  
MASON  
MASON  
Ark.  
MEIXNE  
Mag.  
MIYASH  
256, 9  
MURRA  
MUTCH  
South  
NIGGLI  
Wepf  
POVARE  
SSSR  
REED J  
Trans  
REED J  
Geol.  
RENGAI  
Mém.  
RENGAI  
Paleo  
619-0  
RENGAI  
Cauc

- KENNEDY G. C. (1950b) Pressure-volume-temperature relations in water at elevated temperatures and pressures. *Amer. J. Sci.* **248**, 540-564.
- KERR P. F. and CAMERON E. N. (1936) Fuller's earth of bentonitic origin from Tehachapi, California. *Amer. Min.* **21**, 230-237.
- KING E. G. (1955) Low temperature heat capacity and entropy at 298.16°K of analcite, *J. Amer. Chem. Soc.* **77**, 2192-2193.
- KOIZUMI M. and KIRIYAMA R. (1953) Structural changes of some zeolites due to their thermal dehydrations. *Sci. Rep. Osaka Univ.* No. 2, 67-85.
- KOIZUMI M. and ROY R. (1958) Synthesis and equilibrium stability of the calcium zeolites. *Geol. Soc. Amer. Abstracts of 1958 Meeting*, p. 93.
- KOLBIN M. F. and PIMBURGSKAYN M. I. (1955) Analcime in sediments of Mt. Bogdo-Ola. *Dokl. Akad. Nauk SSSR* **100**, 155-157.
- KOSSOVSKAYA A. G. and SHUTOV V. D. (1955) Changes in the character of fragmental biotite during the process of epigenesis. *Dokl. Akad. Nauk SSSR* **101**, 541-544.
- KOSSOVSKAYA A. G. and SHUTOV V. D. (1956) Epigenic formation of epidote and zoisite in Mesozoic and Upper Paleozoic sediments of the western Verkhoyansk Range. *Dokl. Akad. Nauk SSSR* **108**, 139-141.
- KRAUS O. (1939) Röntgenographische Untersuchungen an Gismondin. *Zbl. Miner.* A 105-109.
- LATIMER W. M. (1952) *The Oxidation States of the Elements and their Potentials in Aqueous Solutions* (2nd Ed.). Prentice-Hall, New York.
- LILLIE A. R., GUNN B. M. and ROBINSON P. (1957) Structural observations in central Alpine region of New Zealand. *Trans. Roy. Soc. N.Z.* **85**, 113-129.
- LILLIE A. R. and MASON B. H. (1955) Geological reconnaissance of district between Franz Josef Glacier and Copland Valley. *Trans. Roy. Soc. N.Z.* **82**, 1123-1128.
- MACKENZIE W. S. (1957) The crystalline modifications of NaAlSi<sub>3</sub>O<sub>8</sub>. *Amer. J. Sci.* **255**, 481-516.
- MACKIE J. B. (1936) A geological traverse from the Waitaki River to Dunstan Peak, Otago. *Trans. Roy. Soc. N.Z.* **66**, 125-142.
- McLINTOCK W. F. P. (1915) On the zeolites and associated minerals from the Tertiary lavas around Bon More, Mull. *Trans. Roy. Soc. Edinb.* **51**, I, 1-33.
- MARWICK J. (1946) The geology of the Te Kuiti Subdivision. *N.Z. Geol. Surv. Bull.* No. 41.
- MASON B. (1957) Gonnardite (ranite) from Langsunds fjord. *Norsk Geol. Tidsskr.* **37**, 435-437.
- MASON B. and GREENBERG S. S. (1953) Zeolites and associated minerals from Southern Brazil. *Ark. Min.* **1**, 519-526.
- MEIXNER H., HEY M. H. and MOSS A. A. (1956) Some new occurrences of gonnardite. *Miner. Mag.* **31**, 265-271.
- MIYASHIRO A. and BANNO S. (1958) Nature of glaucophanitic metamorphism. *Amer. J. Sci.* **256**, 97-110.
- MURRAY J. and RENARD A. F. (1891) Deep sea deposits. *Challenger Rep.* 400-412.
- MUTCH A. R. (1957) Facies and thickness of the Upper Paleozoic and Triassic sediments of Southland. *Trans. Roy. Soc. N.Z.* **84**, 499-511.
- NIGGLI P., KOENIGSBERGER J. and PARKER R. L. (1940) *Die Mineralien der Schweizeralpen*. Wopf, Basel.
- POVARENENYKH A. S. (1954) Problems of the zeolitization of alkaline rocks. *Dokl. Akad. Nauk SSSR* **94**, 761-764.
- REED J. J. (1950) Spilites, serpentinites and associated rocks of the Mossburn district, Southland. *Trans. Roy. Soc. N.Z.* **78**, 106-126.
- REED J. J. (1957) Petrology of the Lower Mesozoic rocks of the Wellington district. *N.Z. Geol. Surv. Bull.* No. 57.
- RENGARTEN N. V. (1940) Authigenic analcime in the Kazanian sandstones of the Kirov region. *Mém. Soc. Russe Min.* Ser. 2., **69**, 50-53.
- RENGARTEN N. V. (1945) A zeolite from the mordenite group in the Upper Cretaceous and Paleocene marine deposits of the eastern slope of the Urals. *Dokl. Akad. Nauk SSSR* **48**, 619-622.
- RENGARTEN N. V. (1950) Laumontite and analcime from Lower Jurassic deposits in northern Caucasus. *Dokl. Akad. Nauk SSSR* **70**, 485-488.

- RICHMOND W. E. (1937) Paragenesis of the minerals from Blueberry Mountain, Woburn, Massachusetts. *Amer. Min.* **22**, 290-300.
- ROBINSON P. (1958) *The Structural and Metamorphic Geology of the Brighton-Taieri Mouth Area, East Otago, New Zealand*. M.Sc. thesis, University of Otago.
- ROEVER W. P. DE (1955) Some remarks concerning the origin of glaucophane in the north Berkeley hills, California. *Amer. J. Sci.* **253**, 240-244.
- ROEVER W. P. DE (1950) Preliminary notes on glaucophane-bearing and other crystalline schists from South East Celebes, and on the origin of glaucophane-bearing rocks. *Koninkl. Ned. Akad. Wet.* **53**, 1455-1465.
- ROSS C. S. (1928) Sedimentary analcite. *Amer. Min.* **13**, 195-197.
- ROSS C. S. (1941) Sedimentary analcite. *Amer. Min.* **26**, 627-629.
- ROSS C. S. (1958) Welded tuff from deep-well cores from Clinch County, Georgia. *Amer. Min.* **43**, 537-545.
- ROZENDAL R. (1957) Analcime in lignite. *Proc. S. Dakota Acad. Sci.* **35**, 39-41; *Chem. Abstr.* **51**, 8590f.
- SAHA P. (1957) Preliminary report on the system albite-nepheline-water. *Bull. Geol. Soc. Amer.* **68**, 1790. (Abstract).
- SAKURAI K. (1953) Studies on zeolites from Yugawara Hot Spring, Kanagawa Pref. Japan, I. *Bull. Nat. Sci. Mus. Tokyo* **32**, 83-98.
- SAKURAI K. and HAYASHI A. (1952) "Yugawaralite", a new zeolite. *Sci. Rep. Yokohama Nat. Univ.*, Sec. II, 69-77.
- SAND L. B., ROY R. and OSBORN E. F. (1957) Stability relations of some minerals in the  $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$  system. *Econ. Geol.* **52**, 169-179.
- SCHALLER W. T. (1932) The mordenite-ptylolite group; clinoptilolite, a new species. *Amer. Min.* **17**, 128-134.
- SEKANINA J. and WYART J. (1936) Sur la stilbite. *Bull. Soc. Franc. Min.* **59**, 377-383.
- SPEEDEN I. G. (1956) *The Geology of the Callins District, South-East Otago*. M.Sc. Thesis, University of Otago.
- STAPLES L. W. and GARD J. A. (1958) The fibrous zeolite orionite: its occurrence, unit cell and possible structure. *Min. Soc. Notice* No. 102 (Abstract).
- STEINER A. (1953) Hydrothermal rock alteration at Wairakei, New Zealand. *Econ. Geol.* **48**, 1-13.
- STEINER A. (1955a) Hydrothermal rock alteration. *Dep. Sci. Industr. Res. Bull. N.Z.* **117**, 21-26.
- STEINER A. (1955b) Wairakite, the calcium analogue of analcime, a new zeolite mineral. *Miner. Mag.* **30**, 691-698.
- STEINER A. (1958) Occurrence of wairakite at The Geysers, California. *Amer. Min.* **43**, 781.
- STRUNZ H. (1955) Zur Kristallechemie des wasserreichsten Zeolithes Faujasit. *Naturwissenschaften* **42**, 485-486.
- STRUNZ H. (1956) Die Zeolithe Gmelinit, Chabasit, Levyn (Phakolith, Horschelit, Seebachit, Offretit). *Neus. Jb. Miner., Mh.* **11**, 250-259.
- STRUNZ H. and TENNYSON C. (1956) "Polymorphie" in der Gruppe der Blätterzeolithe (Hollandit-Stilbit-Epistilbit; Brewsterit). *Neus. Jb. Miner., Mh.* 1-9.
- TURNER F. J. (1933) The metamorphic and intrusive rocks of southern Westland. *Trans. N.Z. Inst.* **63**, 178-284.
- TURNER F. J. (1938) Progressive regional metamorphism in southern New Zealand. *Geol. Mag.* **75**, 160-174.
- TURNER F. J. (1948) Mineralogical and structural evolution of the metamorphic rocks. *Geol. Soc. Amer. Mem.* **30**.
- VALPY G. W. (1957) *Phase Relations of Some Sodium-Aluminium Silicates*. M.Sc. Thesis, University of Otago, New Zealand.
- VASIL'EV V. S. (1954) Mordenite in Mesozoic and Cenozoic sediments of the lower Volga Basin and western Kazakhstan. *Dokl. Akad. Nauk SSSR* **95**, 149-151.
- VASIL'EV V. S., KOLBIN M. F. and KRASNOVA V. N. (1956) Zeolites in the Mesozoic and Cenozoic sediments of the Penza area. *Dokl. Akad. Nauk SSSR* **111**, 410-412.

WALK  
dist  
Min  
WALK  
Geol  
WAYM  
(ptil  
WEED  
Surr  
WEED  
Bull  
WELL  
Gonc  
WELL  
Bull  
WELL  
Upp  
N.Z  
WITE  
Vol.  
WHITE  
Min  
WILL  
Bull  
WOOD  
Seve  
WOOD  
WYAR  
Fran  
YODER  
YODER

TAYLOR

The zeolite facies, with comments on the interpretation of hydrothermal syntheses

berry Mountain, Woburn,  
the Brighton-Taieri Mouth  
glauco-phane in the north  
ring and other crystalline  
ne-bearing rocks. *Koninkl.*  
nty, Georgia. *Amer. Min.*  
*i.* **35**, 39-41; *Chem. Abstr.*  
ter. *Bull. Geol. Soc. Amer.*  
Kanagawa Pref. Japan. *I.*  
lite. *Sci. Rep. Yokohama*  
s of some minerals in the  
ite, a new species. *Amer.*  
*Min.* **59**, 377-383.  
o. M.Sc. Thesis, University  
: its occurrence, unit cell  
ew Zealand. *Econ. Geol.*  
*Industr. Res. Bull. N.Z.*  
e, a new zeolite mineral.  
nia. *Amer. Min.* **43**, 781.  
es Faujasit. *Naturwissen-*  
ith, Herschelit, Seebachit,  
ruppe der Blätterzeolithe  
-9.  
athern Westland. *Trans.*  
New Zealand. *Geol. Mag.*  
metamorphic rocks. *Geol.*  
tes. M.Sc. Thesis, Univer-  
s of the lower Volga Basin  
the Mesozoic and Cenozoic  
2.

- WALKER G. P. L. (1951) The amygdale minerals in the Tertiary lavas of Ireland. I. The distribution of chabazite habits and zeolites in the Garron plateau area, County Antrim. *Miner. Mag.* **29**, 773-791.
- WALKER T. C. and PARSONS A. L. (1922) The zeolites of Nova Scotia. *Univ. Toronto Stud. Geol. Ser. No. 14*, 13-73.
- WAYMOUTH C., THORNELY P. C. and TAYLOR W. H. (1938) An X-ray examination of mordenite (ptilolite). *Miner. Mag.* **25**, 212-216.
- WEED W. H. (1900) Mineral vein formation at Boulder hot springs, Montana. *U.S. Geol. Surv., Twenty-first Ann. Rept. Pt. 2*, 233-255.
- WEED W. H. (1904) Economic value of hot springs and hot-spring deposits. *U.S. Geol. Surv. Bull.* **260**, 598-604.
- WELLMAN H. W. (1952) The Permian-Jurassic stratified rocks. *Symposium sur les séries de Gondwana, Proc. 19<sup>e</sup> Congrès Géol. Int., Alger.* 13-24.
- WELLMAN H. W. (1956) Structural outline of New Zealand. *Dep. Sci. Industr. Res. Bull. N.Z.* **121**.
- WELLMAN H. W., GRINDLEY G. W. and MUNDEN F. W. (1952) The Alpine schists and the Upper Triassic of Harpers Pass (sheet S52), South Island, New Zealand. *Trans. Roy. Soc. N.Z.* **80**, 213-227.
- WHITE D. E. (1955) Thermal springs and epithermal ore deposits. *Econ. Geol. Fiftieth Anniv.* Vol. 99-154.
- WHITEHOUSE M. J. (1937) The deuteric mineral sequence in the Enogerra granite, Queensland. *Miner. Mag.* **24**, 538-546.
- WILLIAMSON J. W. (1939) The geology of the Naseby Subdivision. *N.Z. Geol. Surv. Bull. No. 39*.
- WOOD B. L. (1953) Paleozoic and Mesozoic stratigraphy and structure in Southland *Rep. Seventh Pacific Science Congress, Christchurch, N.Z.* 106-114
- WOOD B. L. (1956) The geology of the Gore Subdivision, *N.Z. Geol. Surv. Bull. No. 53*.
- WYART J. and CHATELAIN P. (1938) Etude cristallographique de la christianite. *Bull. Soc. Franç. Min.* **61**, 121-126.
- YODER H. S. (1950) Stability relations of grossularite. *J. Geol.* **58**, 221-253.
- YODER H. S. (1954) *Carnegie Institution of Washington Year Book.* No. 53, 121-122.