[AMERICAN JOURNAL OF SCIENCE, VOL. 259, JUNE 1961, P. 401-409]

American Journal of Science

JUNE 1961

THE ZEOLITE FACIES: AN INTERPRETATION*

E-AN ZEN

U. S. Geological Survey, Silver Spring, Maryland

ABSTRACT. The zeolite facies, formed under conditions intermediate between diagenesis and regional metamorphism, is characterized by mineral assemblages bearing laumontite, heulandite, or analcite, together with quartz. If H_2O and CO_2 are regarded as mobile components, these assemblages, under the same conditions, rule out the following: calcite-kaolinite-quartz, calcite-pyrophyllite-quartz, or albite-quartz; these assemblages are all familiar in sediments, sedimentary rocks, or low-grade regional metamorphic rocks.

The relations among these alternative assemblages are analyzed by means of isothermal, isobaric diagrams using as variables the chemical potentials of the two mobile components, H_2O and CO_2. For a given reaction, it is not only possible to arrange correctly the relative dispositions of the pseudo-univariant lines around pseudo-invariant points, but also to assign numerical values to the slopes of the pseudo-univariant lines on the basis of the stoichiometric coefficients of the two mobile components. Such diagrams show that mineral assemblages of the zeolite facies can be obtained, isothermally and isobarically, by increasing the chemical potential of H_2O relative to that of CO_2. Thus the zeolite facies is not a necessary intermediate step between diagenesis and regional metamorphism.

Fyfe, Turner, and Verhoogen (1958, p. 167) urged the establishment of a new metamorphic facies at the low-grade end of the metamorphic spectrum. This facies is characterized by zeolites such as laumontite, heulandite, and analcite, and is called by these authors the zeolite facies. The petrographic evidence for mineral assemblages of regionally metamorphosed rocks, characterized by zeolite, is based largely upon the detailed study of Coombs (1954) on the altered Triassic sediments of Southland, New Zealand. Recently Coombs, Ellis, Fyfe, and Taylor (1959) supplied more data, both petrographic and experimental, on zeolitic assemblages and their stability ranges; these authors also reviewed the existing data on the occurrences of zeolitic metamorphic rocks. The reality and importance of zeolite-bearing mineral assemblages in regionally metamorphosed rocks seem well documented.

Fyfe, Turner, and Verhoogen (1958, p. 167, 201) state that the zeolite facies occurs under conditions of lower temperature and pressure than the greenschist facies, which is characterized by such mineral assemblages as quartz-albite-muscovite-chlorite. These authors suggest that the zeolite facies occurs between common sediments and the greenschist facies of metamorphism. In view of the rather extensive record of mineral assemblages which do not bear zeolites, in rocks ranging from sediments (Revelle, 1944; Neeb, 1943; Zen, 1959a, 1959b) to sedimentary rocks (Potter and Glass, 1958; Millot, 1950; Ostrom, 1959; Ehlmann, 1958; Robbins and Keller, 1952; Grim, Lamar, and Bradley, 1937; Grim, Bradley, and White, 1957; Lippmann, 1955), however, such a facies is almost certainly not a necessary intermediate stage of rock metamorphism. The writer recently also observed (Zen, 1960) that, in the Champlain Valley-Taconic Range area of western Vermont at least,

---

* Publication authorized by the Director, U. S. Geological Survey.

metamorphic assemblages characteristic of the greenschist facies merge imperceptibly into apparently unmetamorphosed sedimentary rocks without the occurrence of any zeolite.

Clearly two different trends of metamorphic evolution are indicated. To explain the observations, however, it is desirable to consider more independent variables than just temperature and/or total pressure; for although Fyfe, Turner, and Verhoogen (1958, p. 167, 201) and also Coombs and others (1959, p. 54, 60) imply that the zeolite facies is separated from the greenschist facies by differences in temperature and/or total pressure, the definition of a metamorphic facies should depend on the entire set of independent and externally imposed physicochemical variables (Thompson, 1955, p. 66) as reflected in differences in mineral assemblages. Under ordinary conditions, the most significant of the variables besides temperature and total pressure are the externally controlled values of the chemical potentials of mobile components. It is the purpose of this paper to call attention to this fact and also to offer a possible interpretation of the zeolite facies.

As the only general description of rocks belonging to the zeolite facies is for the area in New Zealand, Coombs' descriptions and data will be used extensively.

From the study of Coombs (1954) and Coombs and others (1959), it appears that the phases most typical of the zeolite facies are laumontite, heulandite, and analcite, all found typically with quartz. These phases have the ideal compositions, respectively, of $CaAl_2Si_4O_{12}.4H_2O$, $CaAl_2Si_7O_{18}.6H_2O$, and $NaAlSi_2O_6.H_2O$. This paper discusses only the reactions involving the calcic zeolites, laumontite and heulandite, and will use the above ideal formulas for these minerals. The argument can be easily extended to analcite-bearing assemblages. The use of ideal formulas would not affect the general discussion; modifications necessary for nonstoichiometry of the phases will be briefly considered later.

In many sediments and sedimentary rocks, the assemblage calcite-kaolinite-quartz is known (Zen, 1959a, 1959b; Millot, 1950; Ostrom, 1959; Ehlmann, 1958; Potter and Glass, 1958; Grim, Lamar, and Bradley, 1937; Keller and Ting, 1950; Robbins and Keller, 1952). The assemblage calcite-pyrophyllite-quartz has also been reported from shales of the Mississippian Manning Canyon formation in Utah (Ehlmann, 1958, p. 21, 37, 61). These assemblages are related to the laumontite-quartz and heulandite-quartz assemblages by the following reactions, using ideal formulas for the zeolites given by Coombs and others (1959, p. 61):

$$\begin{array}{l} \text{Calcite} + \text{pyrophyllite} + 3\,H_2O = \text{laumontite} + CO_2 \\ CaCO_3 \quad Al_2Si_4O_{10}(OH)_2 \qquad\qquad CaAl_2Si_4O_{12}.4H_2O \end{array} \tag{1}$$

$$\begin{array}{l} \text{Calcite} + \text{kaolinite} + 2\,\text{quartz} + 2\,H_2O = \text{laumontite} + CO_2 \\ CaCO_3 \quad Al_2Si_2O_5(OH)_4 \quad SiO_2 \qquad\qquad CaAl_2Si_4O_{12}.4H_2O \end{array} \tag{2}$$

$$\begin{array}{l} \text{Calcite} + \text{pyrophyllite} + 3\,\text{quartz} + 5\,H_2O = \text{heulandite} + CO_2 \\ CaCO_3 \quad Al_2Si_4O_{10}(OH)_2 \quad SiO_2 \qquad\qquad CaAl_2Si_7O_{18}.6H_2O \end{array} \tag{3}$$

$$\begin{array}{lllll} \text{Calcite} + \text{kaolinite} + 5\ \text{quartz} + 4\ H_2O & = & \text{heulandite} + CO_2 & & (4) \\ CaCO_3 \quad Al_2Si_2O_5(OH)_4 \quad SiO_2 & & CaAl_2Si_7O_{18}.6H_2O & & \end{array}$$

Of the four reactions, at arbitrary values of T and P, no more than three can be stable, and the fourth one must involve metastable equilibrium as the reactions are not all independent of one another.

All four reactions involve two volatiles, H_2O and CO_2. If these are mobile components, with their chemical potentials externally controlled, then variations in their values may be used in the same manner as variations in temperatures and pressure in defining metamorphic facies through the different mineral assemblages. It is therefore of interest to plot the reactions as functions of these chemical potentials, μ_{H_2O} and μ_{CO_2}, at some arbitrary temperature and pressure, so chosen as to be of interest in our problem. (A plot such as this one can of course be made even where H_2O and CO_2 are not mobile components. However, if these two components are inert, then the values of their chemical potentials are determined by initial concentrations rather than independently variable. Thus they cannot be used to define metamorphic facies.) In this plot, assuming all solid phases to have constant compositions, it is possible to assign numerical values to the slopes of the univariant lines (univariant at fixed temperature and pressure; actually trivariant) as can be easily demonstrated.

In a general reaction $\nu_A\ A + \nu_B\ B + \ldots. = \nu_R\ R + \nu_S\ S + \ldots.$, we have, for each phase γ, the Gibbs-Duhem relation,

$$- S^{\gamma}\, dT + V^{\gamma}\, dP - \sum_{i} (n_i d\mu_i)^{\gamma} = 0$$

where n_i is the total number of moles of component i in phase γ. The expression, at constant temperature and pressure, reduces to

$$\sum_{i} (n_i d\mu_i)^{\gamma} = 0$$

Let us sum all such expressions for the solid phases and all components i for each side of the reaction. Such sums must remain equal to zero, since each phase is in internal equilibrium:

$$\sum_{\gamma}\sum_{i} (n_i d\mu_i)^{\gamma} = 0$$

Along the univariant curve representing the reaction, $\Delta G = 0$; moreover the values of all the μ_i's for each component must be the same in all phases. Therefore we have

$$\sum_{i} n_i^{\text{total}} d\mu_i \Big|_{\text{left side}} = \sum_{i} n_i^{\text{total}} d\mu_i \Big|_{\text{right side}}$$

and

$$\sum_{i} \Delta n_i\ d\mu_i = 0$$

where

$$\Delta n_i = n_i^{\text{right}} - n_i^{\text{left}} .$$

For inert components, $\Delta n_i = 0$ so that we are left with

$$\sum_{i = \text{mobile}} \Delta n_i\ d\mu_i = 0$$

If two mobile components participate in the reaction, we have

$$\Delta n_1 \, d\mu_1 + \Delta n_2 \, d\mu_2 = 0$$

and

$$(\partial\mu_1/\partial\mu_2)_{T,P,\Delta G=0} = -\Delta n_2/\Delta n_1$$

Now these quantities, Δn_1 and Δn_2, are equal to the number of moles of volatiles evolved in our general reaction. If the volatiles appear on opposite sides of the equation, Δn_1 and Δn_2 have different signs; therefore the slopes of the univariant lines are just the inverse of their stoichiometric ratios in the fluid phase for the particular reaction. A similar equation has been given by Korzhinskii (1959, p. 97, 119)[1] by a slightly different method of derivation.

This knowledge, coupled with the condition that a phase assemblage cannot be both stable and metastable in a given divariant field,[2] enables us to draw topologically correct phase diagrams in the $\mu_{H_2O} - \mu_{CO_2}$ projection.

Two possibilities arise. The reaction

$$\text{pyrophyllite} + H_2O = \text{kaolinite} + 2 \text{ quartz} \qquad (5)$$

may occur at a lower value of μ_{H_2O} than the reaction

$$\text{laumontite} + 2 H_2O + 3 \text{ quartz} = \text{heulandite} \qquad (6)$$

or the reverse may be true. Since we have as yet no data to decide which combination occurs in nature, both alternatives are constructed and shown in figure 1A (μ_{H_2O} for reaction 5 lower than for reaction 6) and figure 1B (the converse case). The figures were drawn so that only mineral assemblages including quartz are considered. For assemblages without quartz, the diagrams become much more complex and their construction does not seem justified at this time. With ubiquitous quartz, the system becomes pseudo-binary (in addition to the mobile components CO_2 and H_2O); the possible assemblages can

---

[1] H. P. Eugster pointed out an alternative derivation of this relation (written communication). For a reaction in which all the solids have fixed compositions, and in which one or more of the components are volatiles, we have

$$\ln K = \ln \prod_i a_i^{\nu_i} = \sum_i \nu_i \ln a_i$$

where a_i is the chemical activity and ν_i the stoichiometric coefficient of component i in the reaction, and where the sign of ν_i is determined by the side of the reaction equation in which it occurs. Substituting the relation

$$\mu_i = \mu_i^\circ \, (T, P) + RT \ln a_i$$

and differentiating both sides at constant T and P (thus taking the volatile components to be mobile components), we get

$$0 = \sum_{i=\text{mobile}} \nu_i \, d\mu_i \Big|_{T,P,\Delta G=0}$$

[2] This statement, which is obviously true, implies that angles between stable portions of neighboring lines must be no greater than 180° (Morey and Williamson, 1918, p. 65-66). In addition, in a general case, apart from an ambiguity of clockwise versus counterclockwise progression of univariant curves (Niggli, 1954, p. 408), it also suffices to fix uniquely the relative locations of divariant assemblages. Thus, for example, in a binary system with four phases there are four univariant curves emanating from an invariant point. The stated condition requires that the divariant field in which all four phases are intrinsically stable must contain no metastable extension of univariant curves; the two divariant fields in each of which three phases are stable must each contain the metastable extension of one univariant curve, and the divariant field in which only two phases are stable must contain two metastable extensions of univariant curves.

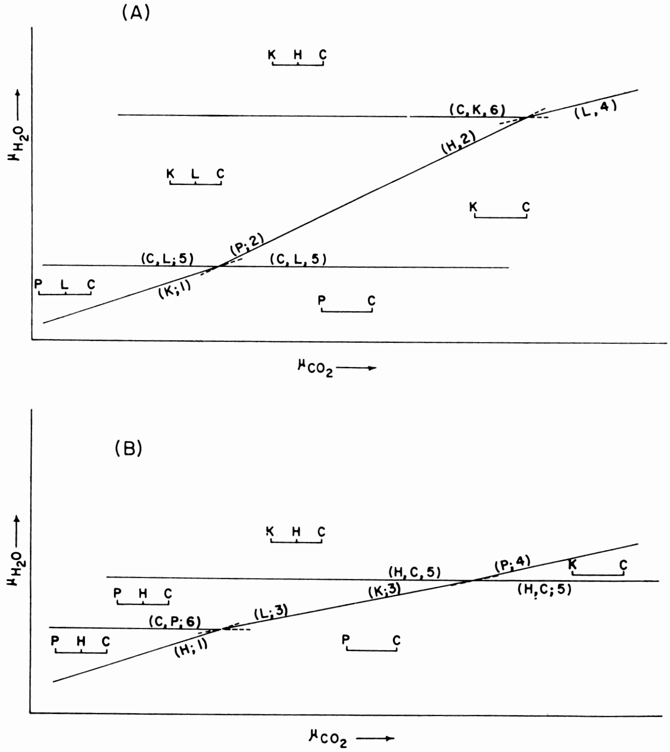

Fig. 1. The system $CaO–Al_2O_3$ in the presence of quartz and at some arbitrary value of temperature and total pressure, as function of the chemical potentials of CO_2 and H_2O. (A) value of μ_{H_2O} assumed to be higher for laumontite breakdown than for pyrophyllite breakdown; (B), the converse case. Abbreviations: K, kaolinite; P, pyrophyllite, H, heulandite; L, laumontite; C, calcite. Symbols in parentheses give the phases absent in each univariant equilibrium; numerals in parentheses give the numbers of the describing equations in the text. Compositional degeneracy is indicated by two symbols appearing together in a parenthesis. Short lines with symbols above give the mineral assemblages in each pseudo-bivariant field, projected from the SiO_2 (quartz) apex to the $CaO–Al_2O_3$ binary boundary (PHC in bottom left field of B should read PLC).

then be shown for each pseudo-bivariant phase field along a single compositional coordinate, the $CaO\text{-}Al_2O_3$ binary, as given in the figures.[3]

For a binary system, an invariant point is a quadruple point from which four univariant lines normally emanate. Of the two invariant points in each of figures 1A and 1B, however, one has only three radiating univariant lines. This is due to the compositional degeneracy of the system in the lime-alumina-silica projection: ignoring H_2O and CO_2, pyrophyllite-kaolinite-quartz, laum-

---

[3] Although montmorillonite is common in the zeolite-bearing rocks described by Coombs (1954) and Coombs and others (1959), this phase is not considered here, because natural montmorillonites generally do not belong to the simple system here considered. Even if it were included in the system, no fundamental revision of our conclusions will result, except that since montmorillonite is a H_2O-rich phase, carbonate-clay mineral assemblages including it will have larger stability fields in the μ-μ plot than those without; correspondingly the sizes of fields of zeolitic assemblages will shrink.

ontite-heulandite-quartz. and calcite-laumontite-pyrophyllite are colinear phases. Where the stable portions of two univariant curves involving these degenerate phases coincide (the situation where the compositions of the nonparticipating phases lie on opposite sides of the line of the degenerate phases), a single curve terminating at the invariant point results; where the stable and metastable portions of the univariant curves coincide (compositions of nonparticipating phases lie on the same side of the line of the degenerate phases), a single curve with continuous slope passes through the invariant point (Morey and Williamson. 1918. p. 69; Morey. 1957. p. 464; for a less mathematical discussion. see Niggli. 1954. p. 413). In figure 1, the fact of degeneracy is manifested by the identity of the missing phases along each univariant line, given in parentheses.

The slopes of the lines will be affected by changing contents of zeolitic water with changing values of μ_{H_2O} This certainly happens; unfortunately we cannot as yet evaluate this effect quantitatively. It is clear, however, that for reactions involving both CO_2 and H_2O, rising values of μ_{H_2O} will cause the slopes to flatten due to increasing amounts of zeolitic water. either continuously or in discrete steps if the zeolitic water changes in discrete amounts as does the water of montmorillonite (Bradley. Grim. and Clark. 1937). For the reaction going from laumontite to heulandite (reaction 6), the effect will be to shift the horizontal univariant line up and down the μ_{H_2O} coordinate. The general appearance of figure 1. however, will not be affected. except in so far as new pseudo-invariant points involving first-order transitions of different hydrates of the zeolites must be added.

Natural laumontite. but even more so natural heulandite (Coombs and others. 1959. p. 101), show compositional variabilities other than in their H_2O content. For example, sodium could substitute for calcium with concomitant substitution of silicon for aluminum. On the $\mu_{H_2O} - \mu_{CO_2}$ plot, reaction (6) therefore should be represented by a band. rather than a line. If, however, a sodic phase such as analcite or albite occurs (Coombs, 1954. p. 84. 86, 87. 90), the chemical potential of sodium is buffered and the band again reduces to a line[4] in the particular projection of the multicomponent system.

The mineral assemblage calcite-kaolinite-quartz has been well documented, both in modern sediments and sedimentary rocks of all ages. in references already cited. The assemblage calcite-pyrophyllite-quartz is reported by Ehlmann (1958). The assemblage laumontite-calcite-quartz is reported by Coombs and others (1959. p. 63). and also by W. S. White of the U. S. Geological Survey (1960. oral communication) from the amygdules in basalt of the Michigan copper deposits. The assemblage calcite-heulandite-quartz is reported by Coombs (1954. p. 86). The writer can find no data on calcic zeolite-kaolinite or calcic zeolite-pyrophyllite assemblages. Coombs (1954. p. 81) reports kaolinite in the altered Triassic rocks of New Zealand, but not specifically associated with zeolite. W. S. White (1960, oral communication) also finds

---

[4] Similarly for the reaction

$$\text{analcite} + \text{quartz} = \text{albite} + H_2O$$

if the analcite is nonstoichiometric but contains potassium, the presence of a potassic feldspar will remove the difficulty of graphical representation.

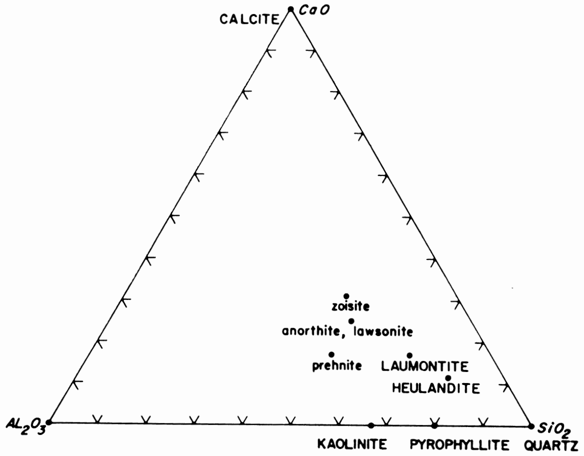

Fig. 2. The $CaO–Al_2O_3–SiO_2$ projection of the chemical compositions of minerals pertinent to the present discussion, calculated in terms of the formula ratios (for laumontite and heulandite, the compositions given in the text are used). Note that in this projection the following phases are compositionally degenerate: quartz-heulandite-laumontite; quartz-pyrophyllite-kaolinite; calcite-laumontite-pyrophyllite; calcite-zoisite-anorthite-lawsonite-kaolinite.

laumontite and kaolinite in the same general sequence of strata in Michigan, but so far these have not been found together. Pyrophyllite-clinozoisite-quartz (Stuckey. 1926; Zen, 1961) has been found, but this association clearly shows (fig. 2) that conditions of metamorphism were such that heulandite and laumontite were intrinsically unstable. It thus appears impossible at the moment to choose between figures 1A and 1B on petrographic evidence. As laumontite has not been synthesized so far (Coombs and others, 1959, p. 88), and the kaolinite-pyrophyllite transition has not been established, laboratory data are of no help here.[5]

The above discussion assumes the validity of the suggestion by Coombs and others (1959, p. 60) that such phases as prehnite and zoisite do not overlap heulandite and laumontite in their stability ranges. Figure 2 shows that prehnite-bearing assemblages and the zeolites are mutually exclusive where, for instance, the assemblage prehnite-calcite-quartz is stable. However, the stability range of prehnite alone is wider than that of prehnite-bearing assemblages. It is thus quite conceivable that such assemblages as laumontite-prehnite-quartz or even heulandite-prehnite-quartz are stable under certain conditions. Such assemblages would exclude heulandite-kaolinite, heulandite-pyrophyllite, laumontite-kaolinite, and laumontite-pyrophyllite assemblages under the same conditions, and would explain why these are not found. It is hoped that petrographic data may soon be available to settle this question.

Notwithstanding these gaps in our knowledge, it appears that at constant temperature and pressure, it is possible to obtain, for a system isochemical

---

[5] See, however, the following paper which appeared after this manuscript went off to the press: Carr, R. M., and Fyfe, W. S., 1960, Synthesis fields of some aluminum silicates, Geochim. et Cosmochim. Acta, v. 21, p. 99-109.

with respect to the inert components, both mineral assemblages characteristic of the zeolite facies and of the greenschist facies, depending on the relative values of μ and $\mu_{H_2OCO_2}$. At high values of μ_{H_2O} and low values of μ_{CO_2}, the zeolite facies prevails; however many sediments and sedimentary rocks evidently did not recrystallize under these conditions. Relative values of μ_{CO_2} are commonly high enough so that the alternative assemblages, calcite-kaolinite-quartz or calcite-pyrophyllite-quartz, obtain. Similarly, many rocks show diagenetic development of albite-quartz, albite-muscovite-potassic feldspar-quartz, and possibly also albite-muscovite-kaolinite-quartz (Zen, 1960, p. 152). Such assemblages rule out the zeolitic analcite-quartz assemblage under the same conditions.

Rising temperature and total pressure may or may not favor the nonzeolitic assemblages, depending on which independent variables are held constant. Thus, consider the changes in total Gibbs Free Energy for reactions (1) through (4), proceeding to the right:

$$(\partial \Delta G/\partial T)_{P,\mu} = -\Delta S_s$$

$$(\partial \Delta G/\partial T)_{P,a} = -\Delta S_s + \nu_{H_2O}[S^\circ - R\ln a]_{H_2O} - \nu_{CO_2}[S^\circ - R\ln a]_{CO_2}$$

$$(\partial \Delta G/\partial P)_{T,\mu} = \Delta V_s$$

$$(\partial \Delta G/\partial P)_{T,a} = \Delta V_s + \nu_{CO_2} V^\circ_{CO_2} - \nu_{H_2O} V^\circ_{H_2O}$$

The subscript "s" denotes solid phases, and the symbols μ and a in the subscripts apply to all mobile components. Activity is so defined that the standard state is the pure component in its stable state at the particular temperature and total pressure. If the mobile components behave ideally, the right-hand sides of expressions 2 and 4 above simply reduce to the total entropy and volume changes, respectively. In any case, the departure from ideality is probably small, and ideal-mixture approximations remain useful.[6]

The expressions 1, 2, and 4 cannot be evaluated even as to sign, because of insufficient data. In particular, entropies of the zeolites are needed to evaluate expression 1. In addition, we need to know the state of aggregation of the mobile components in order to evaluate the second and fourth expressions. Expression 3 is the only one for which quantitative data are available. Using a density of about 2.3 for laumontite and 2.2 for heulandite (Coombs and others, 1959, p. 101), the volume changes for reactions (1) through (4) to the right are, respectively, + 42 ml, + 24 ml, + 83 ml, and + 65 ml.

Under the conditions stipulated in expression 3 above, therefore, an increase in total pressure will favor the nonzeolitic assemblages. In general, however, it is unsafe to conclude that temperature and pressure increases favor the nonzeolitic assemblages unless the conditions and processes have been carefully investigated. On the other hand, our preceding discussions do show that at constant temperature and total pressure, changes in the chemical potentials of the mobile components, H_2O and CO_2, could account for the different trends of metamorphism.

---

[6] I am indebted to J. B. Thompson for calling my attention to the need of discrimination between these two sets of conditions in this discussion.

ACKNOWLEDGMENTS

I would like to thank D. S. Coombs, K. A. W. Crook, H. P. Eugster, W. S. Fyfe, J. B. Thompson Jr., and P. Toulmin III, for reading the manuscript and suggesting many improvements. Discussions with these people have deepened my appreciation of the problems related to the zeolite facies and taught me to show greater respect both for thermodynamics and for rocks.

REFERENCES

Bradley, W. F., Grim, R. E., and Clark, G. L., 1937, A study of the behavior of montmorillonite upon wetting: Zeitschr. Kristallographie, v. 97, p. 216-222.

Coombs, D. S., 1954, The nature and alteration of some Triassic sediments from Southland, New Zealand: Royal Soc. New Zealand Trans., v. 82, p. 65-109.

Coombs, D. S., Ellis, A. J., Fyfe, W. S., and Taylor, A. M., 1959, The zeolite facies, with comments on the interpretation of hydrothermal synthesis: Geochim. et Cosmochim. Acta, v. 17, p. 53-107.

Ehlmann, A. J., 1958, Pyrophyllite in shales of north-central Utah: Utah Univ. Bull. 94, 105 p.

Fyfe, W. S., Turner, F. J., and Verhoogen, J., 1958, Metamorphic reactions and metamorphic facies: Geol. Soc. America Mem. 73, 259 p.

Grim, R. E., Bradley, W. F., and White, W. A., 1957, Petrology of the Paleozoic shales of Illinois: Illinois State Geol. Survey Rept. Inv. 203, 35 p.

Grim, R. E., Lamar, J. E., and Bradley, W. F., 1937, The clay minerals in Illinois limestones and dolomites: Jour. Geology, v. 45, p. 829-843.

Keller, W. D., and Ting, C. P., 1950, The petrology of a specimen of the Perry Farm shale: Jour. Sed. Petrology, v. 20, p. 123-132.

Korzhinskii, D. S., 1959, Physicochemical basis of the analysis of the paragenesis of minerals: [English translation], New York, Consultants Bureau, Inc., 142 p.

Lippmann, F., 1955, Ton, Geoden und Minerale des Barrême von Hoheneggelsen: Geol. Rundschau, v. 43, p. 475-503.

Millot, G., 1950, Relations entre la constitution et la genèse des roches sédimentaires-argilleuses: Thesis, Univ. Nancy, Fac. Sciences, 352 p.

Morey, G. W., 1957, The system water–nepheline–albite: a theoretical discussion: Am. Jour. Sci., v. 255, p. 461-480.

Morey, G. W., and Williamson, E. D., 1918, Pressure-temperature curves in univariant systems: Am. Chem. Soc. Jour., v. 40, p. 59-84.

Neeb, G. A., 1943, *in* Kuenen, Ph. H., and Neeb, G. A., The Snellius-Expedition in the eastern part of the Netherlands East-Indies 1929-1930, v. 5, Geological results, sec. 2, The composition and distribution of the samples: Leiden, E. J. Brill, p. 55-268.

Niggli, P., 1954, Rocks and mineral deposits (R. L. Parker, translator): San Francisco, W. H. Freeman and Company, 559 p.

Ostrom, M. E., 1959, Clay mineralogy of some carbonate rocks of Illinois: Thesis, University of Illinois, 167 p.

Potter, P. E., and Glass, H. D., 1958, Petrology and sedimentation of the Pennsylvanian sediments in southern Illinois: a vertical profile: Illinois State Geol. Survey Rept. Inv. 204, 59 p.

Revelle, R. R., 1944, Marine bottom samples collected in the Pacific ocean by the Carnegie on its seventh cruise: Carnegie Inst. Washington Pub. 556, pt. 1, 180 p.

Robbins, C., and Keller, W. D., 1952, Clay and other noncarbonate minerals in some limestones: Jour. Sed. Petrology, v. 22, p. 146-152.

Stuckey, J. L., 1926, Chloritoid from the Deep River region, North Carolina: Am. Mineralogist, v. 11, p. 186-188.

Thompson, J. B., Jr., 1955, The thermodynamic basis for the mineral facies concept: Am. Jour. Sci., v. 253, p. 65-103.

Zen, E., 1959a, Clay mineral-carbonate relations in sedimentary rocks: Am. Jour. Sci., v. 257, p. 29-43.

———— 1959b, Mineralogy and petrography of marine bottom sediment samples off the coast of Peru and Chile: Jour. Sed. Petrology, v. 29, p. 513-539.

———— 1960, Metamorphism of Lower Paleozoic rocks in the vicinity of the Taconic Range in west-central Vermont: Am. Mineralogist, v. 45, p. 129-175.

———— 1961, Mineralogy and petrology of the system Al_2O_3–SiO_2–H_2O in some pyrophyllite deposits of North Carolina: Am. Mineralogist, v. 46, p. 52-66.