EXPERIMENTS ON THE HYDROTHERMAL FORMATION OF CALCIUM ZEOLITES

ULRIKE WIRSCHING

Institut für Technische Geologie, Petrographie, und Mineralogie
Technische Universität Graz, Graz, Austria

Abstract—The crystallization of calcium zeolites was carried out in an open hydrothermal system at 100°–250°C, using reactants that in nature are known to alter to calcium zeolites and 0.1 N $CaCl_2$, 0.01 N $CaCl_2$, and 0.01 N $CaCl_2$ + 0.01 N NaOH (1:1) solutions. The following calcium zeolites were identified by X-ray powder diffraction:

Rhyolitic glass: heulandite, phillipsite, epistilbite, wairakite;
Basaltic glass: phillipsite, scolecite, wairakite, levynite;
Nepheline: thomsonite, wairakite, gismondine;
Oligoclase: heulandite, phillipsite, wairakite.

Factors that influenced the type of zeolite formed were: Si/Al ratio of the starting material, calcium/alkali ratio of the starting material, calcium activity of the reacting solution, presence of an open alteration system, and temperature. The Si/Al ratio of the starting material was of special importance in that zeolites formed with Si/Al ratios similar to or smaller than that of the parent material. The calcium/alkali ratio of the starting material also influenced the kind of the early alteration products in the open system. As alteration progressed, the importance of the starting material decreased. The importance of the calcium activity of the reacting solution and the influence of the open system increased as alteration proceeded. Because of mass transfer during alteration in the open system, the calcium content of the minerals formed increased, while their Si/Al ratio decreased. Temperature was especially effective during prolonged alteration, in that the higher the alteration temperature the smaller was the H_2O content of the alteration product. Initially, H_2O-rich zeolites formed transitorily at higher temperatures.

Key Words—Calcium, Hydrothermal, Open system, Si/Al ratio, Synthesis, Volcanic glass, Zeolite.

INTRODUCTION

Hydrothermally formed zeolites found in nature are usually either calcium or sodium varieties. The most abundant calcium zeolites in such environments are wairakite, scolecite, mesolite, thomsonite, heulandite, stilbite, gismondine, epistilbite, chabazite, levynite, and laumontite. In addition, Ca-rich varieties of phillipsite and clinoptilolite must be considered.

Zeolite occurrences

The parent material of zeolites is commonly volcanic glass (rhyolitic or basaltic), nepheline, or plagioclase feldspar. Although a definite precursor relationship between a given starting material and a particular zeolite cannot yet be established, certain zeolites appear to be more commonly related to one parent material than to others.

Wairakite. Wairakite, $Ca_8[(AlO_2)_{16}(SiO_2)_{32}] \cdot 16H_2O$, has been observed as an alteration product of plagioclase, e.g., at Wairakei, New Zealand, and at Ohaki-Broadlands, New Zealand (Steiner, 1955, 1968; Browne and Ellis, 1970). At Wairakei it is also present in the rhyolitic vitric groundmass (Steiner, 1968). Kristmannsdottir and Tomasson (1978) described wairakite in basaltic vitric rocks of Iceland.

Scolecite. Scolecite, $Ca_8[(AlO_2)_{16}(SiO_2)_{24}] \cdot 24H_2O$, is known primarily from basic volcanic rocks. Sukheswala *et al.* (1974) observed scolecite in the Deccan Traps and believed that vitric material in the rock was important for the formation of this zeolite. Scolecite was also found in basaltic flows and vitric rocks of Iceland (Kristmannsdottir and Tomasson, 1978).

Thomsonite. Thomsonite, $Na_4Ca_8[(AlO_2)_{20}(SiO_2)_{20}] \cdot 24H_2O$, is usually found in amygdules in basaltic rocks. It has also been observed in alkaline igneous rocks. Leyerzapf (1978) described thomsonite from cavities in a nepheline basalt near Darmstadt, Germany, whereas Meixner *et al.* (1956) found thomsonite pseudomorphic after nepheline in a nepheline basanite of Klöch, Styria, Austria.

Clinoptilolite. Clinoptilolite, $Na_6[(AlO_2)_6(SiO_2)_{30}] \cdot 24H_2O$, is found in igneous rocks, mainly in vitric vugs. Wise *et al.* (1969) observed this mineral near Agoura, California, in cavities in a brecciated porphyritic andesite composed of plagioclase and hypersthene set in a glass-rich groundmass. In the Upper Geyser Basin, Yellowstone National Park, Honda and Muffler (1970) found obsidian altered mainly to clinoptilolite.

Heulandite. Heulandite, $Ca_4[(AlO_2)_8(SiO_2)_{28}] \cdot 24H_2O$,

is a common mineral in cavities in basalt and is also found in andesite and diabase (Deer *et al.*, 1963, p. 383). Plagioclase is the most probable parent material.

Laumontite. Laumontite, $Ca_4[(AlO_2)_8(SiO_2)_{16}] \cdot 16H_2O$, is mostly found in plagioclase-containing rocks. Alker (1974) observed the alteration of plagioclase to laumontite in amphibolite and biotite gneiss from the Gleinalm Gallery, Styria, Austria. It has also been found as a large-scale replacement product of vitric tuffs in Southland, New Zealand (Coombs, 1952).

Mesolite. Mesolite, $Na_{16}Ca_{16}[(AlO_2)_{48}(SiO_2)_{72}] \cdot 64H_2O$, usually occurs in basaltic rocks (Deer *et al.*, 1964, p. 375).

Stilbite. Stilbite, $Na_2Ca_4[(AlO_2)_{10}(SiO_2)_{26}] \cdot 32H_2O$, is found in amygdules and in cavities in basalts and many other volcanic rocks (Deer *et al.*, 1964, p. 384; Tröger, 1967, p. 785).

Epistilbite. Epistilbite, $Ca_3[(AlO_2)_5(SiO_2)_{19}] \cdot 12H_2O$, occurs in basaltic and andesitic rocks (Tröger, 1967, p. 784; Galli and Rinaldi, 1974).

Gismondine. Gismondine, $Ca_4[(AlO_2)_8(SiO_2)_8] \cdot 16H_2O$, is a rare zeolite that has been found in basaltic lavas together with thomsonite and phillipsite. Heritsch (1965a) described gismondine in a nephelinite from Stradner Kogel, Styria, Austria.

Levynite. Levynite, $Ca_3[(AlO_2)_6(SiO_2)_{12}] \cdot 18H_2O$, is a typical mineral in vugs and cavities of basaltic rocks (Tröger, 1967, p. 214).

Chabazite. Chabazite, $Ca_2[(AlO_2)_4(SiO_2)_8] \cdot 13H_2O$, commonly occurs in basaltic rocks. Walker (1951) observed it in cavities in the basaltic lavas of Garron Plateau Area, Ireland, together with thomsonite and levynite. Feldspar is the most likely source for these minerals.

Phillipsite. Phillipsite, $(K,Na)_5[(AlO_2)_5(SiO_2)_{11}] \cdot 10H_2O$, is a common mineral in cavities of basaltic rocks. It also occurs in alkaline rocks, such as phonolites and nepheline syenite (Tröger, 1967, p. 788).

Formational factors

The hydrothermal formation of calcium zeolites is influenced greatly by the chemical properties of these minerals. The differences in calcium content, Si/Al ratio, and H_2O content suggest that their formation is related to the composition of the starting material, the composition of the reaction solution (which can change continuously in an open system), and temperature. Most of the calcium zeolites have been synthesized (Ames and Sand, 1958; Coombs *et al.*, 1959; Koizumi and Roy, 1960; Hawkins, 1967; Hawkins *et al.*, 1978; Liou, 1970; Goto, 1977); however, artificial starting materials have generally been used, and the experiments were usually conducted in closed systems.

The formation of calcium zeolites from Ca-free minerals, such as nepheline, and in Ca-poor rocks, such as rhyolitic glass, indicates that these reactions need an open system wherein calcium can be added and alkalies can be removed. In addition, the formation of zeolites with a Si/Al ratio different from that of the starting material suggests that mass transport with respect to silicon and aluminum is also necessary.

Through the use of natural starting materials and an open reaction system the present experiments were designed to simulate the natural environment as closely as possible. By varying the above factors the study sought to determine the parameters that influence the hydrothermal formation of calcium zeolites and to investigate the relationship between a given parent material and a particular calcium zeolite product.

EXPERIMENTAL

The following materials were used: (1) rhyolitic glass from Pleistocene Lake Tecopa, Inyo County, California (Sheppard and Gude, 1968); (2) basaltic glass from Steinberg, Styria, Austria (Heritsch and Hüller, 1975); (3) oligoclase (~20% an) from Koralpe, Styria, Austria (Heritsch, 1963, 1965b; Meixner, 1937); and (4) nepheline from Miask, Ilmen Mountain, U.S.S.R. One-half gram of each material was pulverized[1] to less than 5 μm and heated at autogenous pressures in 25 ml of solution that contained either 0.1 N $CaCl_2$, 0.01 N $CaCl_2$ (pH ~ 5), or 0.01 N $CaCl_2$ + 0.01 N NaOH (1:1) (pH ~ 10.5). The experiments were carried out in Teflon-coated stainless steel vessels of ~70-ml capacity. An open system was simulated in the following way: After a certain period of time, the reaction was stopped and the solution was filtered off and renewed. This process was repeated several times. The time between the changes of solution was 8 days at 250° and 200°C, and 20 days at 150° and 100°C.

The minerals were identified by means of X-ray powder diffraction (XRD). Typical XRD patterns of the calcium zeolites formed are given in the following section. Scanning electron micrographs (SEM) were made with a Cambridge Stereoscan Mark 2 A instrument.

RESULTS AND DISCUSSION

The experimental results are listed in Tables 1–4. The calcium zeolites, heulandite, phillipsite, epistilbite, and wairakite, formed from rhyolitic glass under the conditions indicated (Table 1); basaltic glass reacted to form phillipsite, scolecite, wairakite, and levynite (Table 2); oligoclase reacted to form heulandite, phillipsite, and wairakite (Table 3); and nepheline reacted to form thomsonite, wairakite, and gismondine (Table 4).

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[1] Because the experiments were performed on pulverized starting materials, dissolution rates, and thus alteration rates, were probably faster than those that would be expected in nature.

Table 1.   Mineral formation from rhyolitic glass in an open system.[1]

Time (days)	0.1 N CaCl₂			0.01 N CaCl₂			0.01 N CaCl₂ + 0.01 N NaOH
250°C							
8	—			—			—
16	(Mo)			—			Pf
24	Mo,	Ep		(H)			Pf, *H*
32	Mo,	Ep,	H	H			Pf, *H*
40	Mo,	*Ep*,	H	H			Pf, H, *A*
48	Mo,	*Ep*,	H	H			Pf, A/W
56	Mo,	*Ep*,	H	H			Pf, A/W
64	Mo,	*Ep*,	H, (W)	H, (W)			Pf, A/W
72	Mo,	*Ep*,	(H), W	*H*, W, Mo			Pf, A/W
80	Mo,	*Ep*,	W	*H*, *W*, Mo			Pf, A/W
88	Mo,	Ep,	W	H, *W*, Mo			Pf, A/W
96	Mo,	*W*		*W*, Mo			
104	Mo,	*W*		*W*, Mo			
112		*W*		*W*, Mo			
120		*W*,	X	*W*, *X*, Mo			
200°C							
8		—		—			—
16		—		—			—
24		—		(Mo)			—
32		—		(Mo)			(Ph)
40		—		(Mo)			(Ph), (H)
48		—		(Mo)			H
56	(Ph),	(Ep)		(Mo)			H
64	(Ph),	(Ep)		(Mo), (Ep)			H
72	(Ph),	Ep		(Mo), (Ep)			H, (A/W)
80		Ep		Mo, *Ep*			H, (A/W)
88		*Ep*, Mo		Mo, *Ep*			*H*, A/W
96		*Ep*, Mo		Mo, *Ep*			H, A/W
104		*Ep*, Mo		Mo, *Ep*			
112		*Ep*, Mo		Mo, *Ep*			
120				Mo, Ep			
150°C							
20	—			—			—
40	—			—			—
60	—			—			—
80	—			—			—
100	—			—			—
120	—			—			(Ph)
140	—			—			(Ph)
160	—			—			
180	—			(Mo)			Ph, *H*
200	—			(Mo)			H

[1] Change of solution after every 8 days at 250° and 200°C; after every 20 days at 150°C. — = No mineral formation; H = Heulandite; Ep = Epistilbite; W = Wairakite; A = Analcime; Ph = Phillipsite; Pf = Potash feldspar; X = Hexagonal anorthite; Mo = Montmorillonite. Traces of a mineral are marked by ( ). Quantitatively prevailing minerals are in italics.

A comparison of the formation of calcium zeolites from crystalline and vitric starting materials shows that under those conditions minerals (oligoclase and nepheline) were altered to calcium zeolites as quickly and easily as were vitric substances. At low temperatures the alteration of rhyolitic glass was even slower than that of the crystalline minerals investigated. A further result of the experimental investigations is that some calcium zeolites formed preferably from a certain starting material, whereas others depended less on the type of parent material. Epistilbite, levynite, scolecite, thomsonite, and gismondine belong to the first group.

Epistilbite

Epistilbite formed in the experiments from rhyolitic glass only (Table 1). In natural environments epistilbite occurs in basaltic rocks, but there is no definite clue as to which of the basalt components is the parent material. In the experiments epistilbite occurred at higher temperatures, 200°–250°C. The formation of epistilbite required solutions with higher calcium activity and frequent changes of solution. The XRD pattern of the epistilbite product is shown in Figure 1a (formation conditions: T = 250°C; solution = 0.1 N CaCl₂).

Levynite and scolecite

Levynite and scolecite, silica-poor zeolites, formed only from basaltic glass in the experiments (Table 2). In the natural environment both zeolites occur mainly in basic volcanic rocks, where it is presumed that a vitric component is important for the formation of scolecite. The experiments confirmed their formation from

Table 2. Mineral formation from basaltic glass in an open system.[1]

	Time (days)	0.1 N CaCl₂	0.01 N CaCl₂	0.01 N CaCl₂ + 0.01 N NaOH
	8	(Ph),(A/W)	A	*A*,(M)
	16	W	A	*A*,(M)
	24	W	A/W	*A*,(M)
	32	W	A/W	*A*,(M)
	40	W, (An)	W	*A*,(M), Pl
	48	W, (An)	W	A,(M), Pl
	56	W, (An)	W, (An)	
250°C	64	W, (An)	W, (An)	
	72	W, (An)	W, (An)	
	80	*W*, An	W, (An)	
	88	*W*, An	*W*, An	
	96	*W*, An	*W*, An	
	104	*W*, An	*W*, An	
	112	*W*, An	*W*, An	
	120	*W*, An	*W*, An	
	8	—	(Ph), A	A
	16	Ph	A	A
	24	*Ph*, Sc	A	A
	32	*Ph*, Sc	A	A
	40	*Ph*, Sc	A/W	A, (Sc)
	48	*Ph*, Sc	A/W, Sc	A, (Sc)
	56	Ph, *Sc*	A/W, Sc	A, (Sc)
200°C	64	Ph, *Sc*	A/W, Sc	A, (Sc)
	72	Ph, *Sc*	W, Sc	
	80	(Ph) Sc	W, Sc	
	88	Sc	W, Sc	
	96	Sc	W, Sc	
	104	Sc	W, Sc	
	112	Sc	*W*, Sc	
	120	Sc	W (Sc)	
	128	Sc	W	
	20	Ph	*A*, Ph	Ph
	40	Ph	A, Ph	A, Ph
	60	Ph	A, Ph	A, Ph
	80	Ph	A, Ph	A, Ph
	100	Ph	Ph	*A*, Ph
150°C	120	Ph	Ph	*A*, Ph
	140	Ph	Ph	*A*, Ph
	160	Ph	Ph	*A*, Ph
	180	Ph	Ph	
	200	Ph, (Mo)	Ph	
	220	Ph, (Mo)	Ph	
	20	—	—	—
	40	—	—	—
	60	—	—	—
	80	—	—	—
100°C	100	—	—	—
	120	—	—	—
	140	—	—	—
	160	—	—	—
	180	(Le)	(Le)	
	200	Le	Le	

[1] Change of solution after every 8 days at 250° and 200°C; after every 20 days at 150° and 100°C. — = No mineral formation; Ph = Phillipsite; Sc = Scolecite; Le = Levynite; W = Wairakite; A = Analcime; An = Anorthite; Pl = Plagioclase; Mo = Montmorillonite; M = Mica mineral. Traces of a mineral are marked by ( ). Quantitatively prevailing minerals are in italics.

basaltic glass. Scolecite formed at higher temperatures (200°C) and was the main alteration product when the reaction solution was rich in calcium. However, scolecite was not the first alteration product; it appeared to form partly from earlier formed phillipsite. Figure 1b shows the XRD pattern of the experimentally formed scolecite (formation conditions: T = 200°C; solution = 0.1 N CaCl₂). Figure 2 shows the characteristic prismatic habit of scolecite (Strunz and Weiner, 1978).

As might be expected from its high H₂O content, le-

Table 3. Mineral formation from oligoclase in an open system.[1]

	Time (days)	0.1 N CaCl$_2$	0.01 N CaCl$_2$
250°C	8	(Mo)	Mo
	16	Mo, *H*	Mo
	24	Mo, *H*	Mo
	32	Mo, *H*, (W)	Mo
	40	Mo, *H*, (W)	Mo, (W)
	48	Mo, *H*, (W)	Mo, (W)
	56	Mo, *H*, W	Mo, (W)
	64	Mo, *H*, W	Mo, (W)
	72	Mo, H, W	Mo, (W)
	80	Mo, *W*	Mo, (W)
	88	Mo, *W*	Mo, (W)
	96	Mo (W)	Mo
	104	Mo, An	An
	112	An	An
	120	An	
	128	An	
200°C	8	—	(Mo)
	16	(Mo), Ph	(Mo), (Ph)
	24	(Mo), Ph	(Mo), (Ph)
	32	(Mo), Ph	Mo, *Ph*
	40	(Mo), Ph	Mo, *Ph*
	48	(Mo), Ph	Mo, *Ph*
	56	(Mo), Ph	Mo, *Ph*
	64	Mo, *Ph*	Mo, *Ph*
	72	Mo, *Ph*	Mo, *Ph*
	80	Mo, *Ph*	Mo, *Ph*
	88	Mo, *Ph*	Mo, Ph
	96	Mo, *Ph*	Mo, (Ph)
	104	Mo, *Ph*	Mo
	112	Mo, *Ph*	Mo, (An)
	120	Mo, *Ph*	Mo, (An)
	128	Mo, *Ph*	Mo, (An)
150°C	20	—	—
	40	—	—
	60	(Mo)	(Mo), Ph
	80	(Mo), Ph	(Mo), Ph
	100	(Mo), Ph	(Mo), Ph
	120	(Mo), Ph	Mo, *Ph*
	140	(Mo), Ph	Mo, *Ph*
	160	Mo, *Ph*	Mo, *Ph*
	180	Mo, *Ph*	Mo, Ph
	200	Mo, *Ph*	Mo, Ph
	220	Mo, *Ph*	Mo, Ph
	240	Mo, *Ph*	*Mo*, Ph

[1] Change of solution after every 8 days at 250° and 200°C; after every 20 days at 150°C. — = No mineral formation; H = Heulandite; Ph = Phillipsite; W = Wairakite; An = Anorthite; Mo = Montmorillonite. Traces of a mineral are marked by ( ). Quantitatively prevailing minerals are in italics.

Table 4. Mineral formation from nepheline in an open system.[1]

	Time (days)	0.1 N CaCl$_2$	0.01 N CaCl$_2$
250°C	8	A, Th, X	A, (Th)
	16	(A), X, "Ne"	A, Th, M
	24	X	A, Th, M
	32	X	A, Th, M, "Ne"
	40	X	A, Th, M
	48		A/W, *Th*, X, M
	56		A/W, X, M
	64		W, X, M
	72		X, M
	80		X, M
	88		X, M
	96		X, M
200°C	8	Th	A, Th
	16	Th, "Ne"	A, Th
	24	Th	A, Th
	32	Th	A, Th
	40	Th	A, Th, "Ne"
	48	Th	A, *Th*
	56	Th	(A), Th
	64	*Th*, X	(A), Th
	72	*Th*, X	(A), Th, (M)
	80	*Th*, X	Th, (M)
	88	*Th*, X	Th, (M)
	96	*Th*, X	Th, (M)
	104		Th, (M)
	112		Th, (M)
	120		Th, (M)
150°C	20	Th	A, (Th)
	40	Th, "Ne"	A, Th
	60	Th	A, *Th*
	80	Th	A, *Th*
	100	Th	A, *Th*, "Ne"
	120	Th	Th
	140	Th	Th
	160	Th	Th
	180	Th	Th
	200	Th	Th
	220	Th	Th
	240	Th	Th
100°C	20	(G)	—
	40	G	(G)
	60	G	(G)
	80	G	G
	100	G	G
	120	G	G
	140	G	G
	160	G	G
	180	G, (Ne)	G

[1] Change of solution after every 8 days at 250° and 200°C; after every 20 days at 150° and 100°C. — = No mineral formation; Th = Thomsonite; G = Gismondine; A = Analcime; W = Wairakite; X = Hexagonal anorthite; M = Mica mineral; "Ne" = Nepheline completely altered. Traces of a mineral are marked by ( ). Quantitatively prevailing minerals are in italics.

vynite formed at low temperatures (100°C) by the reaction of calcium solutions after frequent changes of solution. Its XRD pattern (Figure 1c) shows all of its characteristic peaks (formation conditions: T = 100°C; solution = 0.1 N CaCl$_2$).

Thomsonite and gismondine

Thomsonite and gismondine, SiO$_2$-poor zeolites, were formed by the alteration of nepheline (Table 4).

Thomsonite formed from nepheline at temperatures above 100°C. In the lower temperature range, thomsonite existed even after the complete alteration of nepheline. At higher temperatures, thomsonite altered
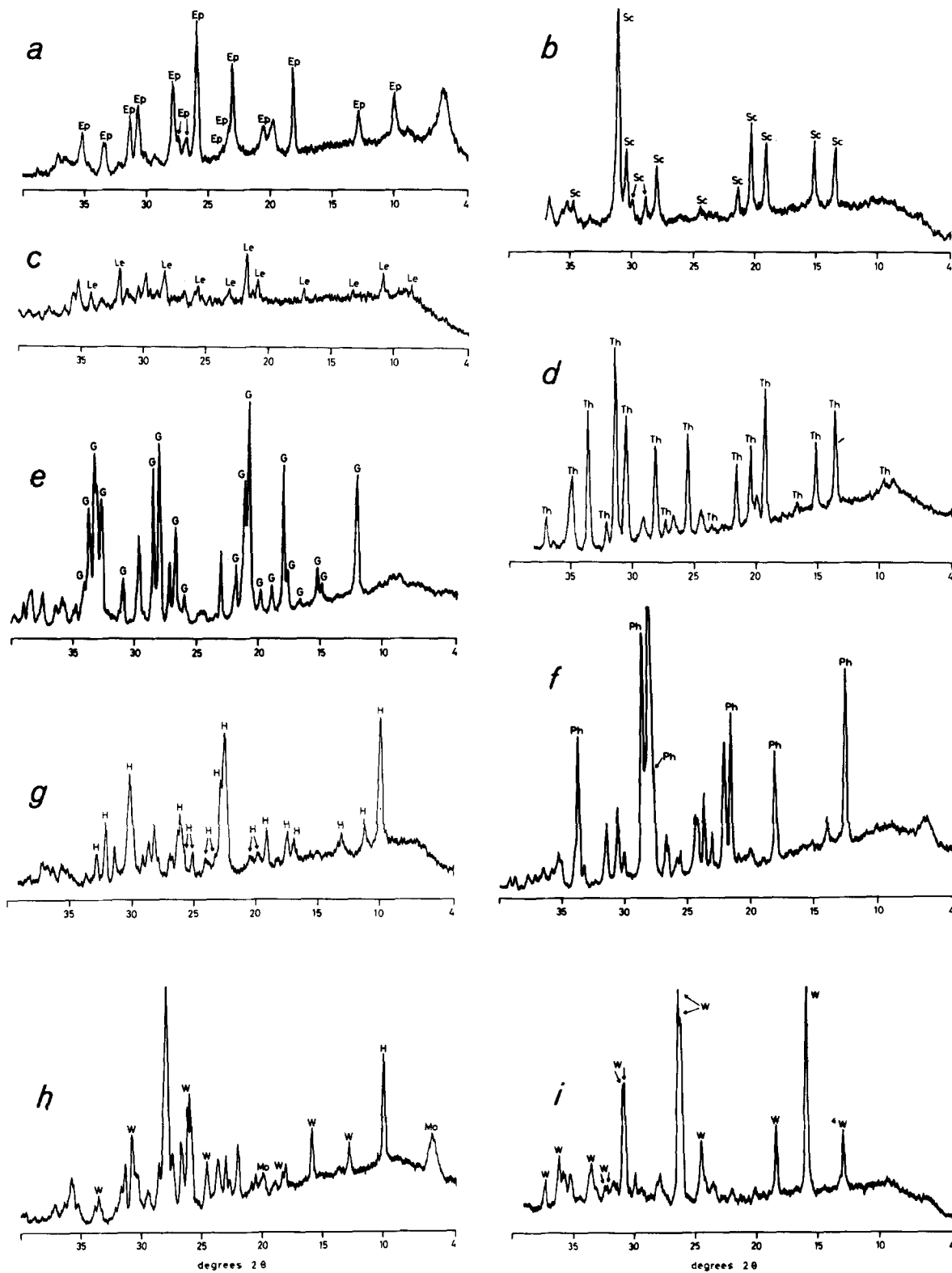
Figure 1.   X-ray powder diffraction patterns of zeolites formed experimentally by hydrothermal alteration in an open system (Cukα radiation). (a) epistilbite, (b) scolecite, (c) levynite, (d) thomsonite, (e) gismondine, (f) phillipsite, (g) nevlandite, (h) oligoclase partly altered to nevlandite, wairakite, and montmorillonite, (i) wairakite.

Figure 2. Scanning electron micrograph of scolecite formed by the experimental hydrothermal alteration of basaltic glass in open system (T = 200°C; solution = 0.1 N CaCl₂).

Figure 3. Scanning electron micrograph of thomsonite formed by the experimental hydrothermal alteration of nepheline in open system (T = 200°C; solution = 0.01 N CaCl₂).

rather quickly to a more Ca-rich and H_2O-poor mineral, depending on the calcium activity of the solution. Figure 1d shows the XRD pattern of thomsonite formed from nepheline (formation conditions: T = 200°C; solution = 0.01 N $CaCl_2$). The SEM (Figure 3) shows the typical prismatic form of thomsonite like that from vugs and amygdules (Leyerzapf, 1978).

Gismondine formed at low temperatures (100°C) only, directly from nepheline. Figure 1e shows the XRD pattern of gismondine (formation conditions: T = 100°C; solution = 0.1 N $CaCl_2$). Figure 4 shows gismondine in its characteristic pseudooctahedral form (Strunz and Weiner, 1978).

Phillipsite, heulandite, and wairakite are calcium zeolites, that formed from different starting materials.

Phillipsite

Phillipsite crystallized during the experimental alteration of rhyolitic glass, basaltic glass, and oligoclase at temperatures below 250°C. Previously, Wirsching (1976, 1979) found that phillipsite formed at the same temperatures in experiments with sodium and potassium solutions. From experiments on the hydrothermal stability and interconversion of zeolites, Hoss and Roy (1960) reported that Ca-phillipsite altered to wairakite at 250°C.

The direct experimental formation of phillipsite from a SiO_2-rich starting material, such as rhyolitic glass, is noteworthy (Table 1). A zeolite richer in SiO_2, such as mordenite, clinoptilolite, heulandite, or epistilbite, might be expected depending on the kind and the con-

centration of the reacting solution; however, Hawkins et al. (1978) found that phillipsite grew more quickly than clinoptilolite or mordenite. The early formation of phillipsite can be explained as follows: during the reaction of strongly alkaline solutions with rhyolitic glass, the ratio of aluminum to silicon going into the solution is higher than that of the glass from which these elements were derived (Mariner and Surdam, 1970). The higher Al/Si ratio favors the formation of phillipsite. This theory conforms to the experimental results: in the reaction with $CaCl_2$-solutions (pH ~ 5), a small amount of phillipsite was observed, whereas with 0.01 N NaOH (pH ~ 10.5), a greater amount was observed (Wirsching, 1976). With increasing time of alteration, heulandite, epistilbite, or mordenite were formed depending on the solution composition.

Phillipsite is the predominant alteration product of basaltic glass at 150°C (Table 2). Depending on the calcium activity and the calcium/sodium ratio of the solution, phillipsite formed alone or with analcime. At higher temperatures phillipsite was formed with scolecite during a long time of reaction in calcium-rich solutions. With an increasing number of changes of solution, the ratio of phillipsite to scolecite shifted towards scolecite.

Phillipsite was the main alteration product of oligoclase in calcium solutions at temperatures below 250°C (Table 3), where it formed with montmorillonite. Figure 1f shows the XRD pattern of phillipsite formed by the experimental alteration of oligoclase (formation con-
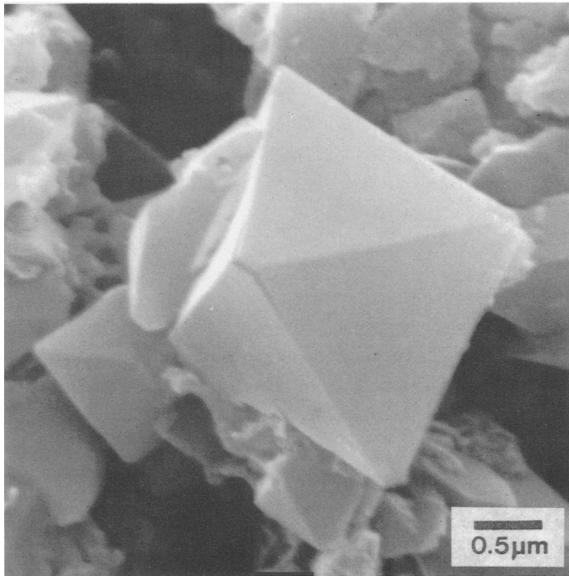
Figure 4. Scanning electron micrograph of gismondine formed by the experimental hydrothermal alteration of nepheline in open system (T = 100°C; solution = 0.1 N CaCl₂).

Figure 5. Scanning electron micrograph of phillipsite formed by the experimental hydrothermal alteration of oligoclase in open system (T = 200°C; solution = 0.1 N CaCl₂).

ditions: T = 200°C; solution = 0.1 N CaCl₂). Figure 5 shows the typical prismatic crystals.

Heulandite

Heulandite formed in the experiments from rhyolitic glass and oligoclase. From rhyolitic glass heulandite formed especially in solutions of low calcium activity (0.01 N CaCl₂; 0.01 N CaCl₂ + 0.01 N NaOH) at temperatures between 150° and 250°C (Table 1). At higher temperatures (250°C) the mineral formed in the first stages of alteration directly from the rhyolitic glass. An increasing number of changes of solution, i.e., the increasing addition of calcium, caused the alteration of heulandite to wairakite, thereby requiring a removal of silicon. Furthermore, one can assume that at 250°C heulandite was only a transitory mineral because of its high H₂O content. At lower temperatures, however, heulandite was not the first alteration product but formed after phillipsite. Thus, zeolite formation does not necessarily start with the mineral having the highest SiO₂ content. Direct alteration of rhyolitic glass to heulandite, however, is possible at later stages of alteration.

Figure 1g shows the XRD pattern of heulandite formed from rhyolitic glass (T = 250°C; solution = 0.01 N CaCl₂). The intensities of the peaks, especially those of the 020 peak at ~9.9°2θ and the 400 peak at ~22.4°2θ, suggested that this mineral is clinoptilolite (cf. Mumpton, 1960). Heating tests, however, showed that it is heulandite: after heating to 500°C for 15 hr and

subsequent cooling to room temperature all the reflections, including the 020 peak at ~9.9°2θ, of the original phase had disappeared, whereas the 020 reflection at ~10.8°2θ of the contracted phase B was observed (Boles, 1972; Alietti, 1972). The intensity of this peak decreased after heating to 550°C (15 hr) and disappeared completely after heating to 600°C (15 hr). Figure 6 shows heulandite formed from rhyolitic glass.

Heulandite crystallized directly from oligoclase by reaction with calcium-rich solutions at high temperatures (250°C) (Table 3). With prolonged reaction it was associated with wairakite and montmorillonite. With frequent changes of solution it altered to wairakite as a result of both the permanent addition of calcium and the high temperature favoring the formation of a Ca-rich and a H₂O-poorer zeolite, wairakite, with increasing time of reaction. Figure 1h shows the XRD pattern of the starting material, oligoclase, partly altered to heulandite, wairakite, and montmorillonite (formation conditions: T = 250°C; solution = 0.1 N CaCl₂). In contrast to the XRD pattern of heulandite formed from rhyolitic glass the 020 peak at ~9.9°2θ is the only main peak in the XRD pattern of this heulandite. This was also confirmed by heating tests (to 500°, 550°, 600°C for 15 hr each) showing the same changes of the XRD pattern as that observed for heulandite formed from rhyolitic glass.

Wairakite

Wairakite formed by the alteration of all starting materials at high temperatures. In the reaction of rhyolitic
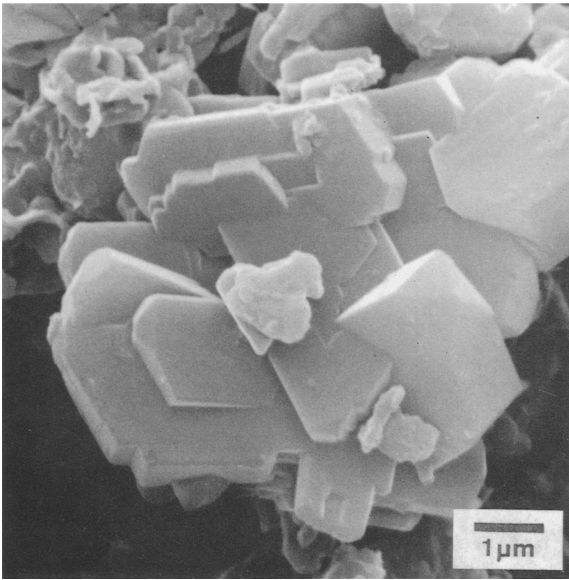
Figure 6. Scanning electron micrograph of heulandite formed by the experimental hydrothermal alteration of rhyolitic glass in open system (T = 250°C; solution = 0.01 N CaCl₂).
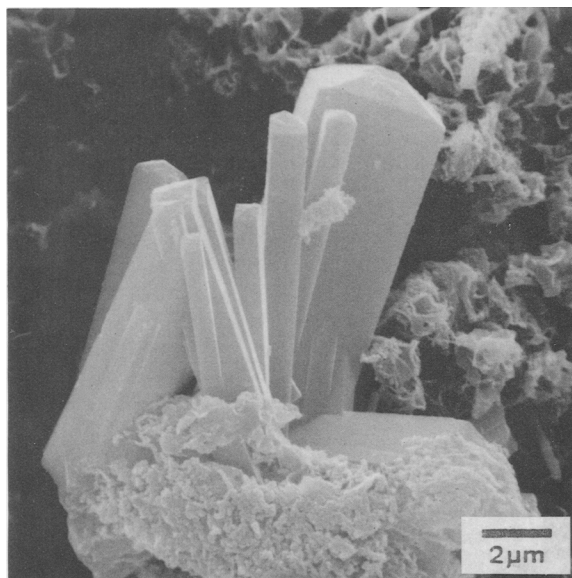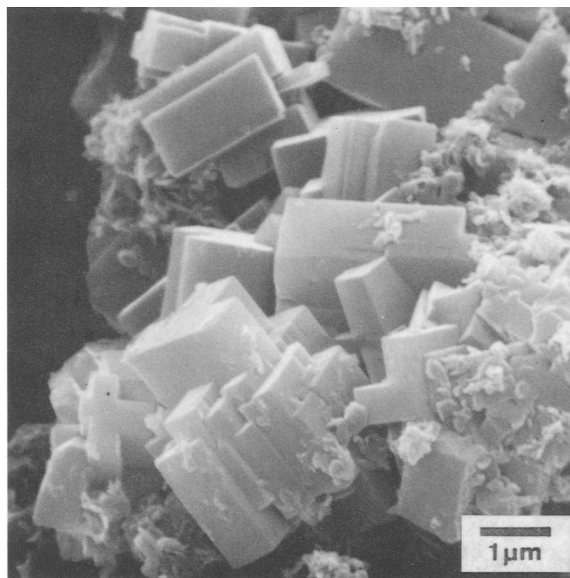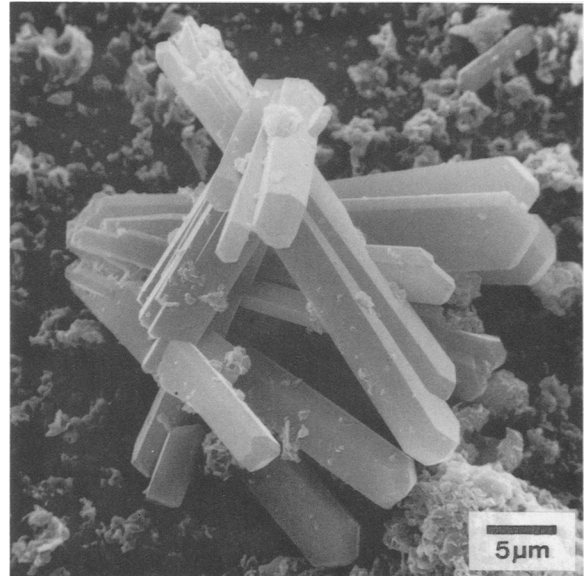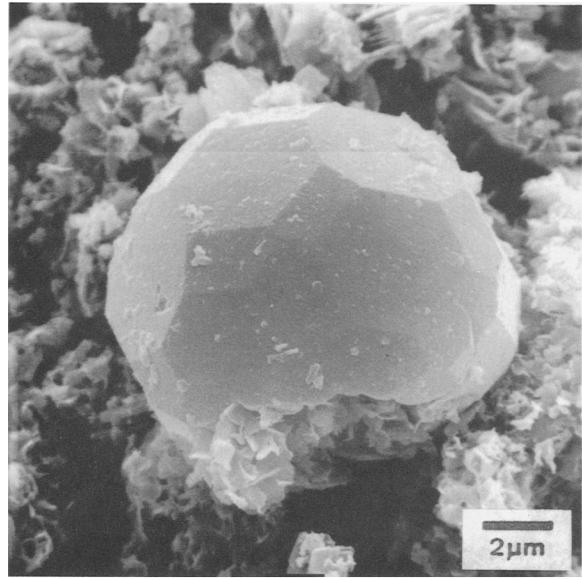

Figure 7. Scanning electron micrograph of wairakite formed by the experimental hydrothermal alteration of basaltic glass in open system (T = 250°C; solution = 0.1 N CaCl₂).

glass with calcium solutions, wairakite formed in advanced stages of alteration only (Table 1), where its formation required not only addition of calcium but also a removal of silicon. Wairakite formed mostly from the early, SiO_2-richer alteration products heulandite and epistilbite. In the Na- and Ca-containing solution, wairakite formed with analcime. The product may be an intermediate mineral of the analcime-wairakite series (Harada *et al.*, 1972). From basaltic glass, wairakite formed only by reaction with pure calcium solutions (Table 2). At high calcium activity it formed directly from the glass; at lower calcium activity analcime formed first and altered to wairakite through the permanent addition of calcium.

Figure 1i shows the XRD pattern of wairakite formed by the direct alteration of basaltic glass with 0.1 N $CaCl_2$ at 250°C. It has the characteristic 200 peak at ~13°2θ, the 400 and 004 peaks at 26.1° and 26.3°2θ, and the 332 and $\bar{3}$31 peak between 30.7° and 30.9°2θ. By this pattern wairakite can clearly be distinguished from analcime (Coombs, 1955). According to Harada *et al.* (1972), the separation of the 400 and 004 peaks is characteristic of monoclinic wairakite. The SEM of wairakite is shown in Figure 7.

Although wairakite formed partly from the earlier formed heulandite, its formation from oligoclase needed a reacting solution with high calcium activity (Table 3). Formation of wairakite by the alteration of nepheline is of minor importance. It was not a direct alteration product but was formed after the complete alteration of nepheline to analcime, thomsonite, and a mica mineral (Table 4). Thus, it can be assumed to have formed mainly from analcime.

Analcime

In addition to the formation of calcium zeolites, analcime was formed in some runs from rhyolitic glass, basaltic glass, and nepheline. The formation of analcime from rhyolitic glass in an open system requires the addition of sodium from the solution. From basaltic glass and nepheline, analcime formed mainly by reaction with Na- and Ca-containing solutions, although it was noted in some runs of the pure calcium solution if the calcium activity was sufficiently small. In the latter case, analcime formed only if enough sodium had entered the solution from the starting material. When the Na/Ca ratio of the active solution became too small because of the addition of calcium and/or the removal of sodium, analcime altered to a calcium zeolite.

In addition to zeolites, feldspars, including potash feldspar, anorthite, and hexagonal anorthite, were formed at high temperatures.

Potash feldspar

Potassium-rich alkali feldspar formed by the hydrothermal alteration of rhyolitic glass at 250°C in accordance with a natural occurrence at Wairakei, New Zealand (Steiner, 1970). Its formation depended on the K/Na ratio as well as the K/Ca ratio of the active solution. Because in these experiments the starting material was

the only source of potassium, K-feldspar formed only if the reacting solution was relatively poor in sodium and calcium. The K/Na and K/Ca ratios decreased with increasing number of changes of solution. Furthermore the SiO_2 activity of the solution was highest at the beginning of alteration. With advancing alteration the SiO_2 activity decreased, as can be seen from the formation of minerals which were increasing poor in SiO_2. Therefore, potash feldspar was only observed at the beginning of alteration as a direct alteration product of rhyolitic glass (Table 1).

Hexagonal anorthite

In contrast to potash feldspar, hexagonal anorthite did not form directly from the rhyolitic glass; rather, it formed from the earlier formed zeolites by the addition of calcium and the removal of silicon (Table 1). Formation of hexagonal anorthite from nepheline (Table 4) depended on the calcium activity of the reacting solution and on the temperature. It formed either directly from nepheline (0.1 N $CaCl_2$, 250°C) or from the earlier formed thomsonite (0.1 N $CaCl_2$, 200°C; 0.01 N $CaCl_2$, 250°C).

Anorthite

Anorthite was formed from earlier wairakite (Table 2) as an alteration product of basaltic glass on reaction with calcium solution. Much less mass transfer was needed to change the Si/Al ratio of the basaltic glass to that of anorthite than in the case of rhyolitic glass. Therefore, anorthite formed from basaltic glass at an earlier stage of alteration than did hexagonal anorthite from rhyolitic glass. The formation of plagioclase feldspar was observed in the reaction of basaltic glass with Na- and Ca-containing solution. The final product of the alteration of oligoclase with calcium solutions at 250°C was anorthite (Table 3).

Montmorillonite

Montmorillonite formed by the alteration of rhyolitic glass only in pure $CaCl_2$ solution. A relatively large amount of montmorillonite was observed at an alteration temperature of 200°C at the end of the experimental runs. At lower temperature only a small amount was found (Table 1). Montmorillonite was an important alteration product of oligoclase (Table 3) along with zeolites at low temperatures, and at the end of the experiments it represented about 30% by weight of the products.

Comparison with natural zeolite assemblages

From the above results it seems that the experimental formation of calcium zeolites corresponds well with their natural occurrence insofar as the parent material of natural zeolites is known. The experimental formation of epistilbite from rhyolitic glass is contrary to natural occurrences where it generally forms in basaltic rocks.

Variation of pH during alteration

During the alteration of rhyolitic glass and oligoclase with 0.1 N and 0.01 N $CaCl_2$ (pH ~ 5), no change in pH took place. During reaction of nepheline with 0.1 N $CaCl_2$, pH remained nearly constant as well. When 0.01 N $CaCl_2$ reacted with nepheline, between 150° and 250°C, the alkalies from the nepheline caused the pH to rise to about 9–10. When nepheline was completely altered, the pH dropped abruptly to 6–7. At an alteration temperature of 100°C, the pH rose only to 6–7, probably because of the slow reaction. After a few changes of solution the pH maintained a value of ~5 despite the presence of nepheline.

During the alteration of basaltic glass with 0.1 N $CaCl_2$, the pH remained nearly constant. With 0.01 N $CaCl_2$ the pH was between 7 and 10 during the first changes of solution, but soon reached values of ~6 and finally ~5. During the reaction of 0.01 N $CaCl_2$ + 0.01 N NaOH (1:1), pH ~ 10.5, with rhyolitic glass the pH values were between 6 and 7 at 250°C and between 6 and 8 at 200° and 150°C. During the reaction of this solution with basaltic glass the pH dropped less: at 250°C the pH was ~9 after the first reaction. After further changes of solution, values of about 7 were reached; at 200°, 150°, and 100°C the pH dropped from ~10 to 8.5–9. These results show that the formation of zeolites does not necessarily require a high pH as long as the calcium activity or alkali activity is high in the active solution.

CONCLUSIONS

A comparison of the mineral formation from the different starting materials by alteration in an open system gives the following results:

(1) The composition of the starting material, especially the Si/Al ratio, determined the type of zeolite formed with respect to the Si/Al (cf. Boles, 1977). This parameter was most important during the first stages of alteration. Usually an alteration product formed with a Si/Al ratio similar to or less than that of the starting material. As alteration proceeded, the minerals being formed became poorer in SiO_2, suggesting that desilification took place with continued reaction.

The formation of analcime (which has twice the Si/Al ratio of nepheline) during the initial alteration of nepheline was an exception that required the removal of aluminum. The Si/Al ratios of all other sodium zeolites are equal to or greater than that of analcime, with the exception of natrolite which did not form in this special system. Previous experiments showed that natrolite forms at low temperatures in a sodium-rich environment (Wirsching, 1979).

The formation of phillipsite from rhyolitic glass be-

fore the formation of silica-richer zeolites was another exception that can be explained by the greater formation rate of phillipsite. The alkali/calcium ratio of the starting material may also have influenced the reaction product during the early stages of alteration if the reacting solution had a low concentration of these cations.

(2) Alteration in open system with Ca-rich reactant solutions led to products increasingly rich in calcium. At the beginning of alteration both the Na/Ca ratio of the starting material and the calcium activity of the reactant solution determined whether a pure alkali mineral or a pure calcium mineral formed or whether a mineral containing alkalies as well as calcium was the results. With advancing alteration the influence of the composition of the reacting solution became predominant. When calcium was added continually, pure alkali minerals and alkali-calcium-containing minerals were replaced by calcium minerals. During the last stage of alteration the mineral with the highest possible calcium content was formed, i.e., anorthite or hexagonal anorthite at higher temperature.

(3) The successions of the calcium minerals characterized by an increase in calcium and, simultaneously, by a decrease in SiO_2 suggest that the kind of calcium zeolites being formed depends strongly on the presence of an open system, i.e., on the possibility of addition and/or removal of material. The large variation in Si/Al ratio of the minerals formed during the alteration in an open system means that the minerals formed in an advanced state give no clue as to their parent materials. A particular calcium zeolite may form from very different starting materials. Furthermore it is difficult to ascertain the state of alteration from the particular mineral being formed because it may form at very different stages depending on the composition of the starting material and the composition of the solution.

(4) The H_2O content of the alteration products increased with decreasing temperature in accordance with natural occurrences (Coombs *et al.*, 1959). At the beginning of alteration at high temperatures, H_2O-rich zeolites occurred transitorily.

(5) Concerning the importance of the principal variables (Si/Al ratio and alkali/calcium ratio of the starting material, calcium activity of the reacting solution, open alteration system, temperature), each is equally important in determining the reaction product in the early stages of alteration. As alteration progressed, the influence of starting material composition decreased. The calcium activity of the reactant solution and the influence of the open system, on the other hand, became increasingly important as alteration proceeded. The effect of temperature increased with increasing time of alteration. Also, H_2O-rich transitory minerals altered to minerals with a H_2O content more closely in accord with temperature.

The great variety of the calcium zeolites which show chemical or structural similarity to each other suggests, however, that there are further factors, in addition to those discussed, which determine paragenesis.

ACKNOWLEDGMENTS

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Резюме—Кристаллизация кольциевых цеолитов проводилась в открытой гидрогермической системе в диапазоне температур 100–250°C. Использовались реакционные растворы 0,1 N $CaCl_2$, 0,01 N $CaCl_2$, и 0,01 N $CaCl_2$ + 0,01 N NaOH (1:1) и исходные материалы, о которых известно, что в природе они могут видоизмениться в кальциевые цеолиты. Путем рентгеновской порошковой дифракции следующие кальциевые цеолиты были идентифицированы как продукты реакции:

Реолитовое стекло: гейландит, филлипсит, эпистильчит, вайракит;

Базальтовое стекло: филлипсит, сколецит, вайракит, левин;

Непалин: томсонит, вайракит, гисмондин;

Олигоклаз: гейландит, филлипсит, вайракит.

Следующие факторы влияют на тип формированного цеолита: соотнощение Si/Al и соотнощение кальций/щелочь исходного материала; кальциевая активность реакционных растворов и температура. Соотношение Si/Al исходного материала является особенно значительным. На первых этапах видоизменения, оно влияет на тип формирующегося цеолита; если возможно формирующийся цеолит имеет соотношение Si/Al похожее или меньшее, чем его величина в исходном материале. В открытой системе соотношение кальций/щелочь исходного материала влияет также на тип начальных продуктов реакции. Во время процесса значение исходного материала уменьшается, а значение активности кальция в растворе и влияние открытой системы увеличиваются. Вследствие возиожности переноса массы во время реакции В открытой системе, содержание кальция в формированных минералах возрастает, в то время как соотошение Si/Al уменьшается. Влияние температуры особенно проявляется при длительном времени реакции. Чем выше температура реакции, тем меньше содержание H_2O в продуктах реакции. В начальной фазе формирования минералов, H_2O-богатые цеолиты могут создавать быстропеременные формы при повышенных температурах. [Е.С.]

Resümee—Experimente zur Bildung von Calcium-Zeolithen wurden in einem offenen hydrothermalen System im Temperaturbereich 100°–250°C durchgeführt, wobei Ausgangssubstanzen verwendet wurden, die auch in der Natur die Umwandlung in Calcium-Zeolithe zeigen. Die einwirkenden Lösungen waren 0,1 N $CaCl_2$, 0,01 N $CaCl_2$, und 0,01 N $CaCl_2$ + 0,01 N NaOH (1:1).

Folgende Calcium-Zeolithe wurden mittels Röntgenpulverdiffraktometrie identifiziert:

Rhyolith-Glas: Heulandit, Phillipsit, Epistilbit, Wairakit;
Basalt-Glas: Phillipsit, Skolezit, Wairakit, Levynit;
Nephelin: Thomsonit, Wairakit, Gismondin;
Oligoklas: Heulandit, Phillipsit, Wairakit.

Die Faktoren, die bestimmen, welcher Zeolith gebildet wird, waren: das Si/Al-Verhältnis und Calcium/Alkali-Verhältnis des Ausgangsmaterials, die Calcium-Aktivität der einwirkenden Lösung, das offene System und die Temperatur. Das Si/Al-Verhältnis des Ausgangsmaterials war von besonderer Bedeutung, da sich Zeolithe bildeten, die ein ähnliches oder kleineres Si/Al-Verhältnis als das Ausgangsmaterial hatten. Das Calcium/Alkali-Verhältnis der Ausgangssubstanz hatte ebenfalls einen Einfluß auf die ersten Umwandlungsprodukte bei einer Umwandlung im offenen System. Mit fortschreitender Umwandlung nahm der Einfluß des Ausgangsmaterials ab, die Calcium-Aktivität der einwirkenden Lösung und der Einfluß des offenen Systems nahm dagegen an Bedeutung zu. Aufgrund des Stofftransportes während einer Umwandlung im offenen System nahm der Calcium-Gehalt der gebildeten Minerale zu, während ihr Si/Al-Verhältnis abnahm. Die Temperatur wirkte sich vor allem bei langen Umwandlungszeiten aus, wobei der H_2O-Gehalt der Umwandlungsprodukte umso kleiner war je höher die Umwandlungstemperatur war. Zu Beginn der Umwandlung können sich H_2O-reiche Zeolithe als Übergangsphasen bei höheren Temperaturen bilden.

Résumé—La cristallisation de zéolites de calcium a été entreprise dans un système hydrothermal ouvert à 100°–250°C utilisant au départ des matériaux que l'on sait sont altérés à de telles phases dans la nature et dans des solutions de réaction 0,1 N $CaCl_2$, 0,01 N $CaCl_2$, et 0,01 N $CaCl_2$ + 0,01 N NaOH (1:1).

Les zéolites de calcium suivantes ont été identifiées par diffraction poudrée aux rayons-X comme produits de reaction:

Verre rhyolitique: neulandite, phillipsite, epistilbite, wairakite;
Verre basaltique: phillipsite, scolectite, wairakite, levynite;
Nepheline: thomsonite, wairakite, gismondine;
Oligoclase: heulandite, phillipsite, wairakite.

Les facteurs qui influencent le type de zéolites qui est formé sont: la proportion Si/Al du matériel de départ; la proportion calcium/alkalin du matériel de départ; l'activité du calcium de la solution réagissante; et la température. La proportion Si/Al du matériel est d'importance particulière. Dans les premiers stages d'altération, elle influence le type de zéolites qui est formé: si possible, une zéolite est formée qui a une proportion Si/Al semblable à, ou moindre que celle du matériel parent. La proportion calcium/alkalin du matériel de départ influence aussi le genre de premiers produits d'altération dans le système ouvert. Pendant l'altération, l'importance du matériel de départ décroît. Avec l'avancement de l'altération l'importance de l'activité du calcium de la solution réagissante croît. A cause de la possibilité de transfert en masse pendant l'altération dans le système ouvert, le contenu en calcium des minéraux formés croît, tandis que leur proportion Si/Al decroît. L'influence de la température produit surtout son effet pendant des durées plus longues d'altération. Plus la température d'altération est élevée, moins est la teneur en H_2O du produit d'altération. Au début de la formation du minéral, des zéolites riches en H_2O peuvent se former de façon transitoire à de plus hautes températures. [D.J.]