HYDROTHERMAL SYNTHESIS OF WAIRAKITE AND CALCIUM-MORDENITE

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ABSTRACT

The zeolites wairakite ($CaO \cdot Al_2O_3 \cdot 4SiO_2 \cdot 2H_2O$) and calcium-mordenite ($CaO \cdot Al_2O_3 \cdot 10SiO_2 \cdot 7H_2O$) were synthesized during the course of studies in the system lime-alumina-silica-water. The conditions for hydrothermal synthesis of these zeolites, their hydrothermal stabilities, and x-ray data are reported. The significance of these data is discussed, as it applies to the natural occurrence of wairakite and mordenite at Wairakei.

INTRODUCTION

During the course of studies in the system lime-alumina-silica-water, the zeolites wairakite (calcium-analcime) and calcium mordenite (ptilolite) were synthesized. The conditions necessary for syntheses approximate the natural environment found at the occurrence of these two zeolites at Wairakei, New Zealand.

Steiner (1953) has reported on the hydrothermal alteration at Wairakei. Types of rock being altered include tuffaceous sandstones, breccias, vitric tuffs and ignimbrite with the original composition of a plagioclase thyolite. Steiner divides the hydrothermal alteration at Wairakei into three zones characterized mineralogically by: 1) upper zone-clays of the montmorillonite group, 2) middle zone-zeolites, and 3) lower zone-adularia. Wairakite was reported by Steiner in cores from 600 to 2890 feet, constituting 2 to 15 per cent of the altered rock. The pH in the zeolite zone fluids was reported by him to be alkaline, with temperature and pressure ranges of 200 to 250° C. and 55 to 265 atmospheres.

Steiner (1955) also reported the physical and chemical properties of wairakite. Coombs (1955) has reported x-ray diffraction data on wairakite.

PREVIOUS WORK ON CALCIUM ZEOLITE SYNTHESES

Noll (1936a, b) first attempted to synthesize a calcium-analcime (wairakite). He used hydrated alumina, silica gel, and $Ca(OH)_2$ in solution in the ratio $CaO \cdot Al_2O_3 \cdot 4SiO_2$. This starting material was run at 300° C. and 87 atmospheres for between 15 and 24 hours. Noll stated that the phase formed could not yet be identified. These were the same P-T-time conditions which resulted in his successful synthesis of analcime.

Barrer (1950) attempted to synthesize wairakite by ion-exchange from analcime with limited success.

TABLE 1. CRITICAL HYDROTHERMAL RUNS ON THE CALCIUM COMPOSITIONS

Composition	T° C.	P (atm.)	Time	Phases
$CaO \cdot Al_2O_3 \cdot 10SiO_2$	330	1000	7	no crystallization
	350		5	mordenite
	380		5	mordenite
	395		5	wairakite+cash-I+cristobalite
	420		4	little crystallization
	435		3	little crystallization
	455		4	anorthite+cristobalite
$CaO \cdot Al_2O_3 \cdot 5SiO_2$	305	1000	3	little crystallization
	325		4	wairakite+cash-I+cristobalite
	360		4	wairakite+anorthite
	400		3	wairakite+anorthite
	420		4	anorthite
Ca-mordenite (Nova Scotia)	375	1000	5	mordenite
	385		5	mordenite+wairakite+cristobalite
	400		5	quartz+anorthite

METHODS OF INVESTIGATION

The pressure reactor vessels used were of the "test-tube" type described by Roy, Roy, and Osborn (1950). Runs were made under water pressures of 1000 atmospheres and temperatures from 200° C. to 560° C. The duration of these runs was from one day to one month.

Starting compositions were made by co-precipitating gels and using nitrates and silicic acid with calcination to 600° C. for 20 minutes. Equivalent results were obtained with both types of starting mixtures.

The phases were identified by *x*-ray diffraction analysis.

RESULTS

The critical hydrothermal runs are listed in Table 1.

For comparison, data on the sodium analogues are listed in Table 2. The results on the sodium compositions are in essential agreement with Barrer's work (1948).

TABLE 2. CRITICAL HYDROTHERMAL RUNS ON THE SODIUM MORDENITE COMPOSITION

Composition	T° C.	P	Time (days)	Phases
$Na_2O \cdot Al_2O_3 \cdot 10SiO_2$	180	saturated vapor	3	little crystallization
	200		2	mordenite
	300		1	mordenite
	330		1	albite+quartz

TABLE 3. LATTICE SPACINGS AND VISUALLY-ESTIMATED RELATIVE INTENSITIES
ON X-RAY DIFFRACTION POWDER PATTERNS

Hydrothermally-synthesized wairakite		Hydrothermally-synthesized calcium-mordenite	
d (Å)	I	d (Å)	I
6.81	4	13.4	3
5.57	9	10.47	1
4.83	4	9.10	8
3.64	3	6.61	8
3.41	10	5.79	1
3.21	2	4.95	1
3.05	1	4.54	5
2.90	8	4.00	6
2.784	1	3.82	6
2.675	4	3.48	10
2.488	5	3.39	4
2.414	3	3.22	9
2.275	1	2.89	2
2.214	3	2.71	1
2.115	1	2.56	3
2.000	1	2.44	1
1.987	3	2.370	1
1.856	2	2.268	1
1.822	1	2.124	1
1.732	4	2.043	1
1.706	1	1.955	1
1.680	1	1.885	2
1.653	1	1.804	1
1.613	1	1.547	1
1.586	2	1.530	1
1.489	1	1.480	1
1.473	1	1.445	1
1.438	1	1.380	1
1.409	3	1.300	1
1.352	3		
1.304	1		
1.279	1		
1.258	2		
1.239	1		
1,217	3		

X-ray diffraction data for the synthetic wairakite and calcium-mor-denite are given in Table 3.

DISCUSSION

Wairakite was not synthesized on composition ($CaO \cdot Al_2O_3 \cdot 4SiO_2$). The compositions $CaO \cdot Al_2O_3 \cdot 5SiO_2$ and $CaO \cdot Al_2O_3 \cdot 10SiO_2$ yielded

wairakite, in the latter case as a decomposition product of calcium mordenite, while $CaO \cdot Al_2O_3 \cdot 4SiO_2$ and $CaO \cdot Al_2O_3 \cdot 6SiO_2$ compositions yielded a new transient phase CASH-I* through the temperature range of wairakite stability. $CaO \cdot Al_2O_3 \cdot 9SiO_2$ and $CaO \cdot Al_2O_3 \cdot 11SiO_2$ compositions did not crystallize through the wairakite stability range with runs up to 6 days in duration. Further, the composition $\frac{1}{2}Na_2O \cdot \frac{1}{2}CaO \cdot Al_2O_3 \cdot 5SiO_2$ yielded a cubic rather than a psuedo-cubic x-ray diffraction pattern, indicating that analcime is the stable phase on this composition. These results support the view of Steiner (1955) and Coombs (1955) who suggested very limited isomorphous substitution between analcime and wairakite due to the structural differences in these two supposed end members.

The presence of limited amounts of sodium would tend to lower the temperature of formation of wairakite, but whether limited isomorphous substitution of Na for Ca would lower the temperature of formation of wairakite a significant amount is hypothetical. The lower limit of formation of wairakite of 315° C. is suspect in any case, although the upper stability limit of about 400° C. probably is accurate to within ±10° C.

The synthesis of mordenite (ptilolite), on the other hand, furnishes a good example of a complete isomorphous series from a pure sodium to pure calcium mordenite. The stability range for the synthesis of sodium mordenite was found to be about 190° to 300° C., essentially the same range as reported by Barrer (2). The calcium mordenite was synthesized from about 340° to 380° C. Intermediate sodium-calcium mordenites were found to have intermediate upper stability limits.

An unusual aspect of this study was the failure to synthesize wairakite on composition ($CaO \cdot Al_2O_3 \cdot 4SiO_2$). Several unsuccessful attempts were made to synthesize wairakite from a $CaO \cdot Al_2O_3 \cdot 4SiO_2$ composition starting material. These included $CaO \cdot Al_2O_3 \cdot 4SiO_2$ plus various amounts of excess $Ca(OH)_2$, variation of the pH from 7 to 12 with the addition of NH_4OH, and the addition of varying amounts of sodium to the $CaO \cdot Al_2O_3 \cdot 4SiO_2$ starting material. The presence of excess silica in amounts greater than 0.5 mole and less than 1.5 moles is required for the synthesis of wairakite from the composition $CaO \cdot Al_2O_3 \cdot 4SiO_2$. Wairakite also was formed as a decomposition product of natural and synthetic mordenite ($CaO \cdot Al_2O_3 \cdot 10SiO_2 \cdot 7H_2O$). All of the natural zeolites studied (mordenite, heulandite and three clinoptilolites) initially decompose either to analcime or wairakite.

Steiner (1953) reports that ptilolite (mordenite) is the predominant mineral of the zeolite alteration zone at Wairakei, New Zealand, with some wairakite and heulandite.

* Follows nomenclature of Rustum Roy (personal communication) who also has noted this phase.

These laboratory phase studies support the premise that excess silica is required for the formation of wairakite. Such an environment exists at Wairakei in the hydrothermally altered rhyolites. It is possible that wairakite is present at Wairakei as a decomposition product of mordenite, rather than as a primary phase.

ACKNOWLEDGMENTS

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