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SYNTHESIS OF ANALCIME FROM NATURAL HEULANDITE AND CLINOPTILOLITE

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ABSTRACT

Analcime has been synthesized from natural heulandite and clinoptilolite at 100°C with solutions of NaOH (0.1M) and Na_2CO_3 (0.1M and 0.01M) in 3-week runs. Both increased pH and Na^+ concentration favor the reaction. The Si/Al ratio of the analcime product is largely a function of the Si/Al ratio of the zeolite reactant. Analogy of the experiments with saline-alkaline lakes and marine environments is discussed.

INTRODUCTION

Numerous occurrences where analcime and heulandite group minerals co-exist in the same suite of sedimentary rocks have been summarized by Hay (1966, p. 21–30). Additional occurrences, both non-marine and marine are recorded at Kaka Point, New Zealand (Coombs, 1965); in the Green River Formation, Wyoming (Goodwin and Surdam, 1967); at Pleistocene Lake Tecopa, California (Sheppard and Gude, 1968); in the Barstow Formation, California (Sheppard and Gude, 1969); at Beardmore Glacier area, Antarctica (Barrett, 1969); in geothermal bore holes, Yellowstone Park, Wyoming (Honda and Muffler, 1970); and in the Wagon Bed Formation, Wyoming (Boles and Surdam, in preparation). At all these localities the host rocks show evidence for the former presence of volcanic glass. Saline or saline-alkaline solutions are inferred to have been present in most cases.

Hay (1966) and Iijima and Hay (1968) point out that in lacustrine environments analcime commonly forms in low-temperature reactions from other zeolites including clinoptilolite. These reactions are implied by the distribution of zeolites as a function of age in saline-lake deposits. Stronger evidence for the clinoptilolite to analcime reaction is found in rocks of the Miocene Barstow Formation, California, where Sheppard and Gude (1969) report analcime pseudomorphs after clinoptilolite.

The largely marine Murihiku Supergroup rocks of the Southland Syncline, New Zealand, contain numerous tuffs altered to analcime or heulandite group minerals (Coombs, 1954; this writer's observation). In the Taringatura-Hokonui area these zeolites are probably in contact at some localities; but due to poor exposures, no beds have been traced laterally which grade from one phase to the other. Furthermore, the coexistence of the two phases in the same thin section is rare. In part of this same suite of rocks exposed on wavecut rock platforms 75 miles to the southeast at Kaka Point, numerous relatively thin tuff beds containing either analcime or heulandite-clinoptilolite are common. Here, Coombs (1965) notes that "units of analcime chert, a few inches or feet thick. pass rapidly both along and across bedding into bentonic or silty heulandite-montmorillonite rocks . . .". Coombs also notes the presence of minor amounts of heulandite co-existing with analcime in some tuffs. In the Murihiku rocks no regular distribution patterns are apparent between tuffs altered to analcime and tuffs altered to heulandite-clinoptilolite, either on the outcrop or on a regional scale.

Analcime has been synthesized (*e.g.* Noll, 1936; Barrer and White, 1952; and Barrer *et al.*, 1959) from highly reactive aluminosilicate gels with excess NaOH at temperatures ranging from 150 to 450°C. Saha (1959) and Coombs *et al.* (1959), have prepared analcime from glasses, and the latter workers have also synthesized analcime at temperatures from 115°C to 275°C using oxide mixes and quartz as reactants. More recently Holler (1970) reported the synthesis of analcime from basaltic glass and nepheline in NaOH solutions (0.01 to 4N) at temperatures of 100, 140, and 180°C with run times of 4 and 7 months. The present writer has sought to establish conditions under which heulandite group minerals might be converted to analcime in natural environments.

SAMPLE MATERIAL AND PREPARATION

The following samples were used in these experiments:

(a) OU 16672; clinoptilolite—altered vitric tuff; Hector, California (Ames *et al.*, 1958).

(b) SM-4-4A; Si-poor clinoptilolite—altered vitric tuff, Barstow Formation, San Bernardino County, California (Sheppard and Gude, 1969).

(c) OU 26043; Si-poor clinoptilolite—altered vitric tuff; Taringatura Hills, Southland, New Zealand.

(d) OU 26042; Si-poor clinoptilolite—altered vitric tuff, Hokonui Hills, Southland, New Zealand.

(e) OU 14989; heulandite in cavities in basalt; Cape Blomidon, Nova Scotia (Coombs *et al.*, 1959).

The clinoptilolite in samples (a) and (b) appears to be true clinoptilolite as defined by Mason and Sand (1960) and Mumpton (1960). The composition of the clinoptilolite in sample (a) is not known accurately; but on the basis of an analysis published by Ames *et al.* (1958) of a clinoptilolite tuff from the same locality, the Si/Al is estimated to be approximately 5.0. Sample (b) is a portion of the specimen from which clinoptilolite was separated for the analysis published by Sheppard and Gude (1969, p. 14) for which the Si/Al is 4.3. Sample (e) is a portion of the analysed specimen described by Coombs *et al.* (1959, p. 101–102) and is a true heulandite as defined by Mumpton (1960) and Mason and Sand (1960). The Si/Al ratio of this sample is 2.9. Unpublished electron microprobe analyses of samples (c) and (d) show that they are calcium-rich silica-poor clinoptilolite (Si/Al = 4.2–4.3) and calcium-rich silica-poor clinoptilolite (Si/Al = 3.9–4.0), respectively. Terminology for such intermediate members of the group will be discussed elsewhere. The unit cell composition (72 oxygens) of samples (c) and (d) are unusually low in Na^{1+} (.23, .21) but are comparatively high in K^{1+} (1.25, 1.03) and Mg^{2+} (.92, .67).

The zeolitic rocks were pulverized in a TEMA rotary crusher, and the $<45\mu m$ fraction was separated by sieving. The ultrafine portion of the $<45\mu m$ fraction was removed by decanting with water. A relatively pure zeolite concentrate was obtained by repeated centrifuging in a acetone-bromoform mixture ($\rho = 2.23$). The concentrates were examined by X-ray diffractometer, and the only impurity detected was quartz. Inspection of the concentrate in immersion oils revealed a few percent of phyllosilicate minerals. Total impurities were estimated to be <7 percent. The pure crystals of sample (e) were hand ground to less than $45\mu m$.

EXPERIMENTAL PROCEDURE

Except where noted otherwise, 80mg of each mineral concentrate was placed in a polypropylene tube and 15 ml of solution was added. The tubes were capped and sealed by hot air welding and placed in a conventional low-temperature hot air laboratory oven at 100°C ± 3°. At 100°C, the pressure in the tubes was 2 to 3 atm. After heating the samples were filtered, washed, dried, and examined by X-ray diffraction and oil immersion techniques.

RESULTS

Experimental results are summarized in Table 1. The synthetic analcime crystals are euhedral, $<3\ \mu m$ diameter and exhibit a characteristic icositetrahedral habit. In Run 6, the analcime crystals were unusually large, 6 to 20 μm. When NaCl and sample (e) were used as reactants (Runs 8–11) some large subeuhedral icositetrahedra were produced, but the majority of the analcime crystals synthesized were 3–5 μm diameter. All synthetic analcime is isotropic and typical indices of refraction are $n = 1.486 \pm .003$.

The analcime Si/Al ratios shown in Figure 1 were determined by Saha's $\Delta 2\theta$ method (Saha, 1959, 1961) using the displacement of the analcime (639) peak and the calibration curve of Coombs and Whetten (1967). The analcime reflection of the samples examined is somewhat broad. This may be due to small crystallites or may indicate a slight variability in composition.

DISCUSSION OF RESULTS

NaOH solutions. The most complete recrystallization of reactants to analcime was in Runs 1 through 4, and 8 through 11, using 0.1M NaOH solutions. Runs 12 through 16 with progressive dilutions of NaOH failed to yield analcime, even where NaCl was added to maintain the initial Na^+ concentration at approximately 0.1M as in Run 16. The only observable effect of the more dilute NaOH solutions on the reactants is a slight reduction in X-ray diffraction intensities.

The effect of adding NaCl can be seen in comparing Runs 7 and 8. In Run 8, the additional Na^+ in solution from the NaCl evidently favored the crystallization of analcime. From diffractometer intensities, the product of Run 8 is estimated to contain 4–5 times more analcime than the product of Run 7. At first glance the incomplete reaction in Run 7 might appear to be due to the Na-deficient Cape Blomidon heulandite. However, calculations (based on the assumption that all the aluminium in the heulandite is used in the analcime) show that the total Na content of Run 7 is in excess by a factor of 5 or 6 times over that required for complete analcime crystallization.

The two New Zealand samples reacted similarly (Runs 5 and 6) in that only minor analcime was identified in the product of each run. The sluggish reaction of these samples may reflect their low Na content but calculations show that Na is in excess by a factor similar to that given above in Run 7. Alternatively, the relatively high K_2O and MgO contents of these two minerals may hinder the reaction.

$Ca(OH)_2$ solutions. Analcime (or the calcium analogue) failed to crystallize from 0.05M $Ca(OH)_2$ solutions with or without 0.1M NaCl as in Runs 22 and 21. Diffractometer patterns of the products of these runs indicate an almost complete destruction of clinoptilolite crystallinity. A comparison of Runs 1 and 2 with Run 22 demonstrates that two solutions with similar pH ($\simeq$13) and Na^+ concentration (0.1M) but different Ca concentration can react very differently with respect to clinoptilolite (and presumably heulandite).

Na_2CO_3 solutions. Analcime crystallized from sample (a) clinoptilolite and Na_2CO_3 solutions in Runs 17 and 20, but a substantial amount of clinoptilolite persisted in the products. As with NaOH solutions, the most complete reaction was obtained with the more concentrated Na_2CO_3 solution (Run 17). A comparison of Runs 19 and 20 demonstrates that the addition of 0.1M NaCl favors the crystallization of analcime from a 0.01M Na_2CO_3 solution.

Si/Al ratio of analcime. The Si/Al ratios of the analcime products appear to be determined by the Si/Al ratio of the reactant (see Figure 1) under the conditions of the present experiments. In Runs 1, 2, and 4, about 5 percent quartz was present in the reactants whereas in Run 8 no quartz was present. The addition of quartz in Runs 9 and 10 had essentially no effect on the Si/Al ratio of the analcime product even though quartz is in excess as shown by its presence in the product. These experiments demonstrate that a relatively low-silica analcime may form in the presence of excess quartz (contrast Coombs and Whetten, 1967).

This may be due to non-equilibration between the quartz and alkaline solutions in 21-day run times. Possibly rapid crystallization of analcime

TABLE 1. EXPERIMENTAL RESULTS

Temperature: 100° ± 3°C , Pressure: 2–3 atm.
Solution volume: 15 ml Sample weight: 80 mg
Run time: 21 days

Run	Sample	Solution	pH at 20°C	Product		
				100×I/Io[b]	Synthetic phases	analcime $\Delta 2\theta$[c]
1[a]	(a) clinoptilolite	.1M NaOH	13	0	An	1.90 (2)
2	(a) clinoptilolite	.1M NaOH	13	0	An	1.88 (2)
3	(a) clinoptilolite +.02 gm quartz	.1M NaOH	13	0	An	
4	(b) Si-poor clinoptilolite	.1M NaOH	13	0	An	1.82 (3)
5	(c) Si-poor clinoptilolite	.1M NaOH	13	70	An, P	
6	(d) Si-poor clinoptilolite	.1M NaOH	13	20	An, P	
7	(e) heulandite	.1M NaOH	13	40	An, Z	
8	(e) heulandite	.1M NaOH +.1M NaCl	13	0	An, Z	1.69 (2)
9	(e) heulandite +.02 gm quartz	.1M NaOH +.1M NaCl	13	0	An, Z	1.71 (2)
10	(e) heulandite +.004 gm quartz	.1M NaOH +.1M NaCl	13	0	An, Z	1.70 (5)
11	(e) heulandite +.02 gm silica gel	.1M NaOH +.1M NaCl	13	10	An, Z	1.74 (3)
12	(a) clinoptilolite	.01M NaOH	12 calc	90		
13	(d) Si-poor clinoptilolite	.01M NaOH	12 calc	90		
14	(d) Si-poor clinoptilolite	.01M NaOH	12 calc	90	P	

TABLE 1. (CONTINUED)

Run	Sample	Solution	pH at 20°C	Product		
				100×I/Io[b]	Synthetic phases	analcime Δ2θ[c]
15	(a) clinoptilolite	.001M NaOH	11 calc	80–90		
16	(a) clinoptilolite	.001M NaOH +.1M NaCl	11 calc	80–90		
17	(a) clinoptilolite	.1M Na_2CO_3	11.6–11.7	40	An	
18	(d) Si-poor clinoptilolite	.1M Na_2CO_3	11.6–11.7	60	P	
19	(a) clinoptilolite	.01M Na_2CO_3	11.1	80–90		
20	(a) clinoptilolite	.01M Na_2CO_3 +.1M NaCl	11.1	80–90	An	
21	(a) clinoptilolite	.05M $Ca(OH)_2$	12.9–13.0	10		
22	(a) clinoptilolite	.05 $Ca(OH)_2$ +.1M NaCl	12.9–13.0	10		

[a] 23 day run.

[b] Approximate intensity (percent) of (020) reflection of residual heulandite-clinoptilolite compared with that of starting material.

[c] Each Δ2θ value average of 8 measurements. Variation in brackets.

An = analcime
P = phillipsite
Z = unidentified zeolite:
peaks at 9.5, 5.07 and 4.36 Å,
all with approximately equal intensities.

total amount estimated
to be <15% in all
cases.

may take place from the dissolving zeolite precursors (*i.e.*, clinoptilolite, heulandite) before appreciable amounts of Si from the quartz have gone into solution. The resulting Si/Al ratio of the analcime would then reflect the Si/Al ratio of the zeolite precursor rather than the presence or absence of quartz.

This hypothesis was tested further in Run 11 by using silica gel, a more soluble form of silica than quartz. The resulting analcime is slightly more siliceous than that from quartz-bearing solutions (Run 9 and 10). How-

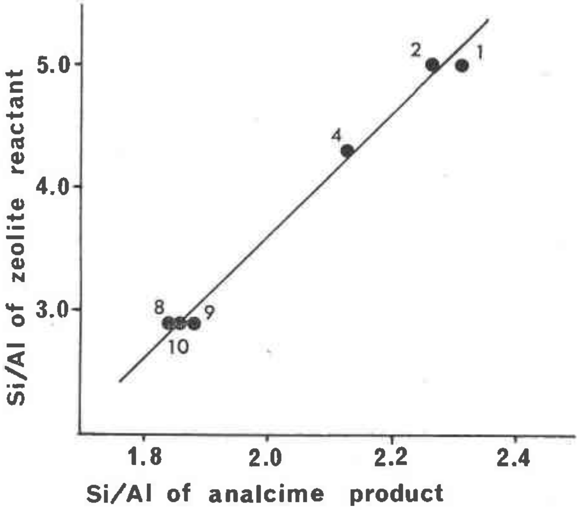

FIG. 1. Correlation between Si/Al ratios of heulandite-clinoptilolite reactants and of the associated analcime product. The numbered dots correspond to the experimental runs listed in Table 1

ever, even with the addition of .02g silica gel the Si/Al ratio of analcime crystallizing from (e) heulandite is still less than the Si/Al value of analcime crystallizing from (a) and (b) clinoptilolites. Possibly the solubility rate of Al^{3+} may be an important control in the reaction.

CONCLUSIONS FROM EXPERIMENTS

1. Higher molar concentrations of NaOH and Na_2CO_3 enhance the crystallization of analcime from clinoptilolite (and presumably from heulandite). Increased pH also appears to favor the crystallization of analcime from clinoptilolite when Na concentration is fixed (compare Run 2 and 16).

2. Na_2CO_3 solutions form analcime more readily than NaOH solutions of similar pH and Na^+ concentrations (compare runs 16 and 20). $Ca(OH)_2$ solutions with similar pH and Na^+ concentration as NaOH solutions do not form analcime whereas analcime readily forms in the NaOH solutions (compare Run 2 and Run 22). The above suggests that in experimental systems, the type of solution creating the alkalinity is important in the clinoptilolite to analcime reaction.

3. The formation of analcime is favored by a large excess of Na^+ under these experimental conditions (compare Run 7 and 8).

4. The failure of Run 5 to yield appreciable analcime indicates that the

initial phase is important in the reaction; the unusual composition of samples (c) and (d) contrasted with samples (a), (b), and (e) may be responsible for their failure to react more completely.

5. The Si/Al ratio of the synthetic analcime closely reflects the Si/Al ratio of the zeolite precursor in these experiments, irrespective of the presence or absence of quartz.

SILICA SOLUBILITY AND ACTIVITY IN ALKALINE SOLUTIONS

The increased solubility of silica in alkaline solutions is well known experimentally and also has been documented in natural alkaline brines (Jones, *et al.*, 1967). Increased silica solubility should imply increased silica activity in solution. In these present experiments a less siliceous phase (analcime) is favored with respect to a more siliceous phase (clinoptilolite) in solutions of higher pH, Na^+ concentration being maintained relatively constant.

The question may be asked: "Why do less siliceous phases crystallize from alkaline solutions when silica solubility is increased in these solutions?" Coombs, *et al.*, (1959) and Campbell and Fyfe (1960) suggest from experimental work that the OH^- ion catalyzes the crystallization of quartz from amorphous silica. The former workers explain the increased stability field of a less siliceous phase in alkaline solutions by the lowering of silica activity as a result of quartz crystallization. The experiments of this paper do not support the above proposed mechanism as an explanation of why silica-poor phases are favored in alkaline solutions. No authigenic quartz was detected in the products of any runs; and in Runs 7 and 8 where no initial quartz was present, analcime formed readily. It is clear from these experiments that analcime will crystallize from clinoptilolite-heulandite in alkaline solutions without the early formation of quartz.

Some studies in natural environments indicate that quartz is more commonly associated with analcime than with heulandite-clinoptilolite (Coombs, 1954 and this writer's observation in Murihiku Group rocks of Southland Syncline, New Zealand; Sheppard and Gude, 1969; Muffler, 1970). This quartz does not necessarily represent an early crystallization product but may in fact be the silica excess from a heulandite-clinoptilolite to analcime reaction.

An alternative explanation for the formation of less siliceous phases in alkaline solutions is given by Mariner and Surdam (1970). These workers show that when rhyolitic glass dissolves in alkaline solutions the concentration of both silica and alumina increases with increasing pH. Because alumina concentration increases at a faster rate than silica concentration,

Table 2. Comparison Of Experimental Solutions With Natural Saline And Saline-Alkaline Waters

Environment	Na^{1+}(ppm)	$HCO_3^{1-}+CO_3^{2-}$ (ppm)	pH at S.T.P.	Reference
experimental - .1M Na_2CO_3	4,600	6,000	11.6-11.7	This paper
experimental - .01M Na_2CO_3+.1M NaCl	2,760	600	11.1	This paper
saline alkaline lakes	2,360- 132,000	1,730- 133,000	9.4-11.0	Hay (1966); Jones et. al., (1967)
sea water	10,556	140	8.0-8.4	Krauskopf (1967)

the net effect is a decrease in Si/Al ratio of the solution with increasing pH. Therefore, the resultant phase to crystallize from the solution has a lower Si/Al ratio than the initial dissolving phase.

ANALOGY OF EXPERIMENTS WITH NATURAL ENVIRONMENTS

A comparison between the experimental Na_2CO_3 solutions and some natural waters is shown in Table 2.

Saline-alkaline lakes. The Na^+ concentration of the experimental Na_2CO_3 solutions are within the range of Na^+ concentrations found in modern saline-alkaline lakes. The higher Na concentrations found in some of these lakes should make them even more favorable for a clinoptilolite to analcime reaction than the experimental solutions.

Although the saline-alkaline lake waters of Table 2 represent some of most extreme alkalinities encountered in modern environments, the experimental solutions are slightly more alkaline. Equilibration of the experimental Na_2CO_3 solutions with atmospheric CO_2 would lower the pH. The experimental Na_2CO_3 solutions are thought to approximate solutions encountered in modern saline-alkaline environments, and these fluids are thought to be responsible for at least some of the analcime associated with clinoptilolite in rocks.

The experiments show that the Si/Al ratio of the analcime may reflect the Si/Al ratio of the zeolite precursor. Sheppard and Gude (1969, p. 29) record a similar correlation from studies of zeolitic tuffs in the Miocene Barstow Formation which was deposited in a saline-alkaline lake. Sheppard and Gude report that analcime associated with clinoptilolite has a higher Si/Al ratio than analcime associated with phillipsite, the latter being a relatively silica-poor zeolite. Field and petrographic evidence showed that both the clinoptilolite and phillipsite had altered to analcime.

Marine environment. Is a clinoptilolite-heulandite to analcime reaction to be expected in a marine environment? In modern marine sediments clinoptilolite is widespread; analcime is very rare. However, in the largely marine Triassic rocks of the Murihiku Supergroup, Southland, New Zealand, both clinoptilolite-heulandite and analcime occur in altered tuffs, locally in the same bed (Coombs, 1954 and 1965; this writer's observations).

Although Table 2 shows that sea water contains excess Na^+ to favor a clinoptilolite-heulandite to analcime reaction, the narrow range of only moderate alkalinity (8.0–8.4) in natural sea water would not appear to favor the reaction at the sediment-water interface. However, progressively buried connate water trapped in sediments might become more alkaline than 8.4 as a result of removal of atmospheric CO_2. This writer obtained some natural sea water ($pH = 8.38–8.40$); and after circulating CO_2-free air through the water for a short time, a pH of 9.25–9.30 was measured. This demonstrates that natural sea water from which CO_2 has been removed can approach the alkalinities favorable for the reaction. Therefore, post-depositional events in a marine succession of sediments might favor the crystallization of analcime from a clinoptilolite-heulandite precursor.

The clinoptilolite-heulandite to analcime reaction has probably taken place at 20–30°C in most of the saline-alkaline lake environments. It is not known whether this inferred reaction in the Murihiku rocks took place when burial was shallow or deep. However, the Murihiku rocks have been buried to depths of about 2 to 10 kilometers where temperatures of the order of 100°C must have prevailed as in the experiments here described.

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