

PHILLIPSITE ALTERATION IN HYDROTHERMAL BRINES

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Abstract

Hydrothermal alteration of phillipsite in 3N chloride brines of Li^+ , Na^+ , K^+ , NH_4^+ , Rb^+ , Cs^+ , Mg^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+} , Al^{2+} , Fe^{3+} , La^{3+} , and Nd^{3+} was investigated at 300° C under a confining pressure of 30 MPa. Phillipsite altered to α spodumene in LiCl, to analcime and albite in NaCl, to orthoclase and leucite in KCl, NH_4^+ -phillipsite in NH_4Cl , to $\text{RbAlSi}_2\text{O}_6$ in CsCl, to wairakite in CaCl_2 , to Ba^{2+} -phillipsite in BaCl_2 and Sr-zeolite in SrCl_2 under the slightly acidic to neutral conditions (pH 5-7) resulting at 300° C from these brines. Cation exchange appears to be the initial step in all the above transformations. Phillipsite altered to smectite under moderately acidic conditions (~ pH 4.0) resulting at 300° C from MgCl_2 , LaCl_3 , and NdCl_3 brines. Phillipsite alteration to smectite proceeds with the initial hydrolysis of Mg^{2+} , La^{3+} , and Nd^{3+} cations leading to acidic conditions followed by phillipsite dissolution and recrystallization to smectite. Under the extreme acidic conditions (pH 0.3-0.4) developed by the hydrolysis of Fe^{3+} and Al^{3+} cations, phillipsite altered to pyrophyllite and pyrophyllite plus kaolinite respectively by dissolution of phillipsite and recrystallization.

MATERIALS INDEX: phillipsite, zeolites, smectite, beidellite

Introduction

Naturally occurring and synthetic zeolites have found numerous commercial applications. Natural zeolites are used in radioactive-waste disposal, sewage-effluent treatment, agricultural-waste water treatment, stack-gas cleanup, oil-spill cleanup, oxygen production, coal gasification, natural gas purification, solar energy collection, petroleum production, etc. (1). Synthetic zeolites are widely used as catalysts in the petroleum industry and as cation exchangers in waste water treatment. Among the naturally occurring zeolites, phillipsite was not only found to be an excellent cesium ion sieve but was also found to be amenable for the fixation of cesium (2). Another use foreseen for the naturally occurring zeolites such as phillipsite is their utilization as backfill (or packing material) in a nuclear waste repository (3,4). The chemical and physical stability of the zeolite is an important criterion for use as a backfill under the extreme conditions of a repository environment, i.e., under mild hydrothermal conditions anticipated during the thermal period in a backfilled geological repository (5). If the repository were to be in a geologic formation such as salt, the corrosive conditions of the brine on zeolite backfill also need to be evaluated. The objective of this work was to determine the chemical stability of phillipsite under mild hydrothermal conditions in different salt solutions (brines).

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The interconversions of clays to zeolites and vice versa is important both to technology and to possible performance of either in nuclear waste repositories. Koizumi and his co-workers (6-9) have published several papers in this field.

EXPERIMENTAL

A. Materials

A naturally occurring phillipsite from Pine Valley, Nevada was used in this study. This sample was supplied by Minerals Research, P.O. Box 591, Clarkson, New York as a -200 mesh (<75 μm) powder (reference zeolite, 27154). The quantitative spectrochemical analysis of the as-received phillipsite is given in Table 1.

B. Methods

The untreated phillipsite sample was subjected to X-ray diffraction (XRD) analysis for phase identification. The as-received phillipsite contained a trace amount of erionite as an impurity and was used in all the hydrothermal experiments without any pretreatments. The reactions of phillipsite in hydrothermal brines were carried out as follows: a 100 mg of phillipsite was sealed with 200 μl 3N chloride solutions of Li or Na or K or NH_4 or Rb or Cs or Mg or Ca or Sr or Ba or Al or Fe or La or Nd in gold capsules. The gold capsules were sealed using a cold-welding technique developed by Komarneni *et al.*, (10). The sealed capsules were heated at different temperatures in cold-seal vessels for different durations under a confining pressure of 30 MPa.

The gold capsules were weighted before and after the hydrothermal treatment to check for leaks. The gold capsules devoid of any leaks were opened and the pH of the equilibrium solution was measured. The solid and solution phases were separated by centrifugation and the solid phases were characterized by powder XRD. Powder XRD of untreated and treated phillipsite was carried out with a Phillips X-ray diffractometer using Ni-filtered $\text{CuK}\alpha$ radiation. The solutions were analyzed for various elements such as Si, Al, Fe, Ca, Mg, K, and Na by atomic emission spectroscopy using a SpectraMetrics SpectraSpan III instrument. Two replicates were used for each brine treatment. Various equinormal salt solutions were used in the treatment of phillipsite to compare their acidic behavior under hydrothermal conditions since their hydrolysis rates and hydrolysis constants are different under hydrothermal conditions.

RESULTS AND DISCUSSION

Alteration of Phillipsite in Alkali Cation Brines at 300° C

Under the slightly acidic to neutral pH conditions (Table II) of the alkali cation brines, phillipsite altered mainly to anhydrous alkali aluminosilicate phases such as $\text{LiAlSi}_2\text{O}_6$, KAlSi_3O_8 , KAlSi_2O_6 , $\text{RbAlSi}_2\text{O}_6$, and $\text{CsAlSi}_2\text{O}_6$ (Table II). In the presence of NaCl brine, phillipsite altered to the metastable hydrous analcime $\text{NaAlSi}_2\text{O}_6 \cdot \text{XH}_2\text{O}$ phase which then transformed to the stable albite, $\text{NaAlSi}_3\text{O}_8$ phase (Table II). Phillipsite did not transform to a new phase in the NH_4Cl brine (Table II). However, NH_4 -exchanged phillipsite resulted as indicated by the solution analyses which showed displacement of 75% of Na^+ from the exchange sites of phillipsite (Table II). Alkali cations did not hydrolyze very much under these hydrothermal conditions and hence led to slightly acidic to neutral pH conditions (Table II). These slight acidic to neutral pH conditions did not appear to decompose phillipsite as revealed by the low concentrations of cations such as Si^{4+} , Al^{3+} , and Fe^{3+} in solution but instead led to an initial exchange of Na^+ , K^+ , and Ca^{2+} from phillipsite by the alkali cations of the brines and the subsequent transformation of exchanged phillipsites to the different anhydrous phases (Table II).

Alteration of Phillipsite in Alkaline Earth Cation Brines at 300° C

The solution and solid phase analyses after hydrothermal treatment of phillipsite in various 3N alkaline earth cation brines are presented in Table III. In the presence of the MgCl₂ brine phillipsite altered to smectite, a hydroxylated layer silicate mineral as a result of the acidic conditions (Table III) generated by the hydrolysis of Mg²⁺ under the hydrothermal treatment (4, 11-13). The mechanism of phillipsite and other zeolite alteration in an acidic Mg-rich brine was postulated earlier (4, 12) to be as follows: hydrolysis of Mg²⁺ brine leads to acidic conditions which then lead to the decomposition of phillipsite followed by recrystallization to smectite. Analyses of the capsule fluids clearly show that the exchangeable cations on phillipsite were released into solution and the pH was low. Almost all of the Si and Al were utilized in the formation of smectite. Substantial concentration of Fe³⁺ remained in

TABLE I
Chemical Composition* of Phillipsite from
Pine Valley, Nevada

Oxide	Percent, %
SiO ₂	52.3
Al ₂ O ₃	15.0
TiO ₂	0.17
Fe ₂ O ₃	2.37
MgO	0.28
CaO	0.60
MnO	0.010
BaO	0.01
Na ₂ O	8.00
K ₂ O	2.71
P ₂ O ₅	0.08
Loss on Ignition	17.67
TOTAL	99.20%

*From Komarneni (1985)

solution as a result of low pH (Table III). The alteration of phillipsite to smectite as a function of temperature and the kinetics of this alteration at 300° C are presented below because this smectite may be useful as a catalytic material.

Phillipsite transformed to wairakite which is a Ca-analog of analcime in the presence of CaCl₂ brine as a result of ion exchange (Table III) followed by structural transformation. Solution analyses show that 76% of the Na⁺ and 21% of the K⁺ were displaced by Ca²⁺ during this transformation. As expected, Ca²⁺ did not hydrolyze as severely as Mg²⁺ under these hydrothermal conditions (Table III) and hence smectite did not form in the presence of CaCl₂ brine. In the presence of SrCl₂ brine, phillipsite transformed to Sr-zeolite as a result of cation exchange, i.e., Sr²⁺ for Ca²⁺, Na⁺, and K⁺. Analyses of solutions clearly showed that most of the exchangeable Ca²⁺, Na⁺, and K⁺ from phillipsite were released into solution upon exchange with Sr²⁺ (Table III). Strontium exchange was followed by a structural transformation resulting in a Sr-zeolite. Treatment of phillipsite in BaCl₂ brine lead to Ba²⁺ exchange for Na⁺, Ca²⁺, and K⁺ without further structural transformation. The

TABLE II
Solution and Solid Phase Analyses after
Hydrothermal Treatment* of Phillipsite in
Various 3N Alkali Cation Brines

Oxide	Percent of Oxide Released into Various Brines					
	LiCl	NaCl	KCl	NH ₄ Cl	RbCl	CsCl
SiO ₂	<0.01	0.03	0.01	0.07	0.04	0.04
Al ₂ O ₃	<0.03	0.30	0.02	0.03	0.03	0.21
Fe ₂ O ₃	0.12	0.12	<0.02	0.09	<0.02	0.02
MgO		2.31	1.36		1.01	2.84
CaO	7.93	5.83	12.00	2.91	33.33	64.34
K ₂ O	0.71	72.00		6.49	67.11	34.67
Na ₂ O	17.52		77.51	74.14	70.10	72.11
pH**	6.5	6.6	4.9	7.1	5.1	6.6

Mineralogical analyses of solid phase in order of abundance as determined by XRD:

Spodumene (LiAlSi ₂ O ₆)	Analcime (NaAlSi ₂ O ₆); Trace albite (NaAlSi ₃ O ₈)	Orthoclase (KAlSi ₃ O ₈); Leucite (KAlSi ₂ O ₆)	NH ₄ ⁺ exchanged Phillipsite; NH ₄ -mica	RbAlSi ₂ O ₆	Pollucite (CsAlSi ₂ O ₆)
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*300°C; 30 MPa; 4 weeks

**pH of the capsule fluid after quenching to room temperature

solution and solid phase analyses clearly show that this is only an exchange reaction under the approximately neutral pH conditions. Thus it appears the less hydrated Ba²⁺ ion did not hydrolyze very much under these hydrothermal conditions.

Phillipsite Alteration in 3N MgCl₂ Brine as a Function of Temperature

The solution and solid phase analyses after hydrothermal treatment of phillipsite in 3N MgCl₂ brine at different temperatures are presented in Table IV. The solid phase analyses clearly show that phillipsite did not alter to a new phase at 100° and 200° C indicate that Mg²⁺ did not hydrolyze greatly at these temperatures to dissolve phillipsite and crystallize a new phase. However, Mg²⁺ displaced exchangeable cations, Ca²⁺ and Na⁺ from phillipsite into solution (Table IV). At 300° C, Mg²⁺ hydrolyzed greatly leading to acidic conditions (Table IV). These acidic conditions resulted in the phillipsite dissolution followed by smectite crystallization as has been shown earlier (12).

Kinetics of Phillipsite to Smectite Alteration in MgCl₂-Brine at 300° C

The kinetic studies of phillipsite to smectite alteration in MgCl₂ brine at 300° C are shown in Table IV and Figure 1. These results demonstrate that phillipsite alters completely to smectite in a manner of 4 days at 300° C. This smectite was found to be of the deidellite type by XRD after Li⁺ and K⁺ treatments (14) and by solid state nuclear magnetic resonance spectroscopy (results to be published elsewhere). These results show that the naturally occurring phillipsite can be altered hydrothermally to be deidellite which may be useful as a catalytic material.

TABLE III
Solution and Solid Phase Analyses after Hydrothermal Treatment* of Phillipsite in Various 3N Alkaline Earth Cation Brines

Oxide	Percent of oxide released into various brines			
	MgCl ₂	CaCl ₂	SrCl ₂	BaCl ₂
SiO ₂	0.03	0.02	0.02	0.03
Al ₂ O ₃	0.01	0.23	0.08	0.24
Fe ₂ O ₃	10.80	0.06	0.05	0.07
MgO		4.44	3.08	2.84
CaO	60.61		88.11	37.30
K ₂ O	70.22	21.33	45.33	34.67
Na ₂ O	89.30	75.82	80.88	72.11
pH**	4.2	4.9	4.1	6.6

Mineralogical analyses of solid phase in order of abundance as determined by XRD:

Smectite	Wairakite	Sr-Zeolite (PDF #18-1267)	Ba ²⁺ exchanged phillipsite; 3.11 Å un- identified peak
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*300° C; 30 MPa; 4 weeks

**pH of the capsule fluid after quenching to room temperature.

Alteration of Phillipsite in Some Trivalent Cation Brines at 300° C

It is well known that some trivalent cations such as Al³⁺, Fe³⁺ hydrolyze rather readily under non-acidic ambient conditions. The effect of these and other trivalent cations on phillipsite alteration under hydrothermal conditions is presented in Table V. Under the extremely high acidic conditions of Fe³⁺ and Al³⁺ cations, phillipsite altered to pyrophyllite and pyrophyllite plus kaolinite respectively. On the other hand, phillipsite altered to smectite under the moderately acidic conditions generated by either La³⁺ or Nd³⁺ just as in the case of Mg²⁺. The formation of Nd(OH)₂Cl phase (Table V) clearly shows that hydrolysis of these cations occurred under the hydrothermal conditions.

CONCLUSIONS

Phillipsite altered to anhydrous and/or hydrous phases such as feldspars, leucite, analcime, Sr-zeolite, etc. in non-acidic brines, to hydroxylated phases such as smectite in moderately acidic brines and to pyrophyllite and kaolinite in extremely acidic brines under hydrothermal conditions.

TABLE IV
Solution and Solid Phase Analyses after Hydrothermal Treatment* of Phillipsite in
3N MgCl₂ at Different Temperatures and Times

Oxide	100° C		300° C				
	28 days	28 days	1/2 day	1 day	2 days	4 days	28 days
SiO ₂	0.01	0.04	0.04	0.03	0.03	0.03	0.03
Al ₂ O ₃	0.11	0.47	0.02	0.01	0.01	0.29	0.01
Fe ₂ O ₃	0.09	0.10	5.67	6.39	3.74	6.15	10.80
CaO	27.74	41.26	36.36	43.36	40.09	43.82	60.61
K ₂ O	0.89	2.04	5.51	12.18	39.11	61.33	70.22
Na ₂ O	25.44	35.72	50.88	57.96	65.04	74.81	89.30
pH**	6.5	4.8	4.1	4.1	4.0		4.2

Mineralogical analyses of solid phase in order of abundance as determined by XRD:

Phillipsite	Phillipsite	Phillipsite; Smectite	Phillipsite; Smectite	Smectite	Smectite	Smectite
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*30 MPa pressure in all cases

**pH of the capsule fluid after quenching to room temperature

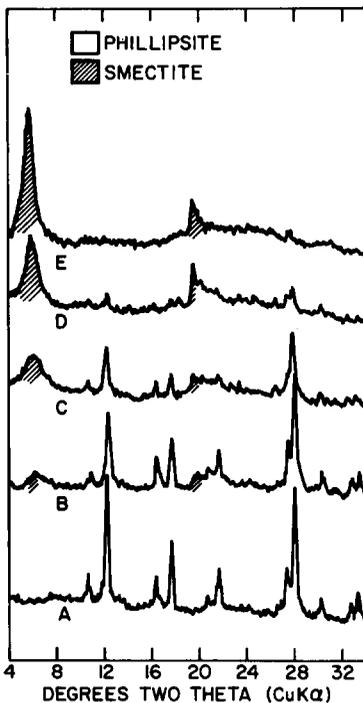


FIG. 1

X-ray diffractograms of phillipsite treated for different periods with 3N MgCl₂ brine at 300°C under a confining pressure of 30 MPa:
 A. untreated phillipsite
 B. treated for 1/2 day
 C. treated for 1 day
 D. treated for 2 days
 E. treated for 4 days

TABLE V
Solution and Solid Phase Analyses after Hydrothermal Treatment* of Phillipsite in Various 3N Trivalent Cation Brines

Oxide	Percent of Oxide Released into Various Brines			
	AlCl ₃	FeCl ₃	LaCl ₃	NdCl ₃
SiO ₂	0.18	0.06	0.02	0.04
Al ₂ O ₃		2.24	0.03	0.13
Fe ₂ O ₃	80.82		20.39	4.64
MgO	108.88+	102.96+		
CaO	90.44	83.92	88.34	83.22
K ₂ O	86.22	77.33	9.87	9.29
Na ₂ O	83.24	83.24	64.03	67.40
pH**	0.4	0.3	3.9	4.2

Mineralogical analyses of solid phase in order of abundance as determined by XRD:

Pyrophyllite; Kaolinite	Pyrophyllite	Smectite	Smectite; Nd(OH) ₂ Cl
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*300°C; 30 MPa; 4 weeks

+>100% represents the uncertainties in chemical analyses of phillipsite as well as the solution

**pH of the capsule fluid after quenching to room temperature

ACKNOWLEDGEMENT

This research was supported by the United States Department of Energy through the Office of Basic Energy Sciences, Division of Materials Research under Grant No. DE-FG02-85ER45204.

REFERENCES

1. F.A. Mumpton in *Natural Zeolites, Occurrence, Properties, Use* (Eds. L.B. Sand and F.A. Mumpton), Pergamon Press, Oxford and New York, pp. 3-27 (1978).
2. S. Komarneni, *Clays Miner.* **33**, 145 (1985).
3. S. Komarneni and R. Roy, *Nucl. Tech.* **56**, 575 (1981).
4. S. Komarneni and D.M. Roy, *Clays Clay Miner.* **31**, 383 (1983).
5. G.J. McCarthy, W.B. White, R. Roy, B.E. Scheetz, S. Komarneni, D.K. Smith, and D.M. Roy, *Nature* **273**, 216 (1978).
6. M. Koizumi and R. Roy, *Am. Mineral.* **44**, 788 (1959).
7. M. Koizumi and R. Roy, *J. Geol.* **68**, 451 (1959).
8. R. Kiriya, M. Koizumi, K. Yamada, and R. Kitagaki, *J. Min. Soc. Japan*, **2**, 347 (1956).
9. R. Kiriya, M. Koizumi, K. Yamada, and R. Kitagaki, *J. Min. Soc. Japan*, **2**, 464 (1956).
10. S. Komarneni, W.P. Freeborn, and C.A. Smith, *Am. Mineral.* **64**, 650 (1979).

11. S. Komarneni, *J. Inorg. Nucl. Chem.* **43**, 2833 (1981).
12. S. Komarneni and E. Breval, *Clay Miner.* **20**, 181 (1985).
13. J.W. Briathwaite and M.A. Molecke, *Nucl. Chem. Waste Management* **1**, 37 (1980).
14. G.W. Brindly and G. Brown, *Crystal Structures of Clay Minerals and their X-ray Identification*, Miner. Society, London, pp. 495 (1980).