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# ACTIVE ALBITIZATION OF PLAGIOCLASE, GULF COAST TERTIARY

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ABSTRACT. Plagioclase grains in Frio (Oligocene ?) sandstones are being albitized from initial  $Ab_{s0}$ - $Ab_{60}$  compositions to compositions more albitic than  $Ab_{98}$ . The albitization zone occurs between 2500 and 2870 m depth at temperatures varying from 110° to 120°C. Similar albitization trends occur in Wilcox (Eocene) sandstones.

Partially albitized plagioclase grains with dissolution textures are present within the Frio albitization zone. By-products of the albitization reaction include clay minerals (for example, dickite) and nearly pure calcite. Pore fluid compositions within or below the zone are diluted, diagenetically-modified seawater which are either near equilibrium or in the albite stability field for the reaction:

 $\begin{array}{ll} 2\text{SiO}_2 + \frac{1}{2}\text{H}_2\text{O} + \text{H}^+ + \text{Na}^+ + \text{CaAl}_2\text{Si}_2\text{O}_8 = \\ \text{quartz} & \text{anorthite} \\ \text{NaAlSi}_3\text{O}_8 + \frac{1}{2}\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + \text{Ca}^{++} \\ \text{albite} & \text{dickite} \end{array}$ 

The absence of albitization at shallow depths, at apparent thermodynamically favorable pore fluid compositions, combined with SEM studies suggests that grain surface dissolution rates may be a rate-limiting step in the albitization process. The sources of sodium for albitization were mobile pore fluids with minimal flow rates of about 8 pore volumes per million years.

#### INTRODUCTION

Albitization of detrital plagioclase is one of the most important changes that occur in feldspathic sandstones and graywackes. Although this reaction has long been recognized in association with spilitization of basic lavas (for example, Bailey and Grabham, 1909), Coomb's (1954) classic study in New Zealand was the first to recognize its importance during advanced burial of sediments. Today the effects of albitization are recognized in sedimentary rocks throughout the world (for example, Martini, 1968; Dickinson, Ojakangas, and Stewart, 1969; Iijima and Utada, 1972; Surdam, 1973; Merino, 1975; and Garbarini and Carpenter, 1978).

Albitization, as shown below,

andesine (201.7cc)

 $Na^+ + H_4SiO_4 + NaAlSi_3O_8 \cdot CaAl_2Si_2O_8 =$ 

2NaAlSi <sub>3</sub> O <sub>8</sub> + Al <sup>+3</sup> + Ca <sup>++</sup> + 4OH <sup>-</sup>
albite
(200.1cc)

involves replacement of calcic plagioclase<sup>1</sup> by an equal volume of albite <sup>1</sup> Andesine and albite densities assumed to be 2.68 and 2.62 g/cc, respectively.

(Coombs, 1954; Boles and Coombs, 1977). The albite product is very pure (usually greater than 99 mole percent albite), has a low albite structure,<sup>2</sup> and is riddled with minute inclusions. In contrast, most authigenic feldspar cements or overgrowths lack inclusions (Kastner and Siever, 1979). Sodium and silica is supplied from pore fluids and diagenetic reactions; calcium and aluminum by-products are typically consumed by carbonates, clays, and calcic zeolites.

The mass transfer implied in the above reaction suggests that albitization of plagioclase can play a critical role in the mass balance of sodium, silica, calcium, and alumina in these rocks and their pore fluids. For example, Pettijohn, Potter, and Siever (1973) suggest that albitization of plagioclase may be the cause of the high Na<sub>2</sub>O content of many graywackes. Clearly, the albitization reaction is an important diagenetic process, yet surprisingly little is known about the subsurface conditions at which it occurs. It is the purpose of this paper to document such conditions in the modern burial setting of the Gulf Coast Tertiary.

### **REGIONAL SETTING**

The Gulf Coast Tertiary basin is a relatively simple down-warped basin without major regional uplift (Murray, 1960). Hence, present day pressure and temperature conditions within basin sediments are probably at maximum values. Many of the burial diagenetic changes observed in this basin are believed to be in progress today (Burst, 1969; Perry and Hower, 1970; Loucks, Bebout, and Galloway, 1977; Boles, 1978; Boles and Franks, 1979).

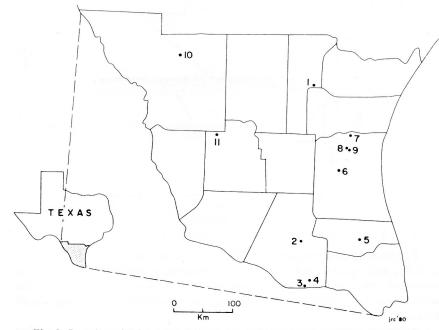
In the Gulf Coast Tertiary, feldspathic sandstones of both the Wilcox (Eocene) and Frio (Oligocene ?) formations appear to be undergoing active albitization. The most convincing evidence is in Frio sandstones, where plagioclase is abundant and compositions as calcic as andesine are present.

## ALBITIZATION IN THE FRIO

The Frio Formation was studied in cores from depths of 1 to about 4.5 km where *in situ* temperatures range from about 50° to 160°C. In this area (fig. 1), Frio standstones consist of approximately equal proportions of feldspar, quartz, and rock fragments (fig. 2; also see Loucks, Debout, and Galloway, 1977). Point count analysis indicates plagioclase is 10 to 20 percent of the rock, K-feldspar is less than 5 percent. Rock fragments are dominantly intermediate to acidic volcanics, and much of the plagioclase in these rocks was apparently derived from this volcanic source. There are no systematic depth changes in *detrital* petrology in these sandstones, hence changes in plagioclase composition with depth do not appear to be related to changes in source area.

<sup>2</sup> Albitized plagioclase separated from a Triassic-age crystal tuff from New Zealand has  $d_{(000)}$  and  $d_{(\overline{2}04)}$  spacings of 2.173 Å and 1.784 Å, respectively, indicating an ordered structure (see Wright, 1968).

Active albitization of plagioclase, Gulf Coast Tertiary



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Fig. 1. Location of Frio and Wilcox core samples with respect to county boundaries in South Texas. Numbers correspond with well numbers in table 1.

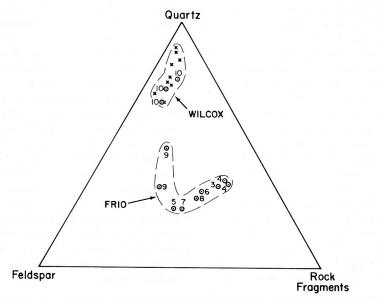


Fig. 2. Modal proportions of quartz-feldspar-rock fragments in Frio and Wilcox sandstones. Three hundred to four hundred counts per thin section. Numbers correspond with well numbers in figure 1. X = well no. 11.

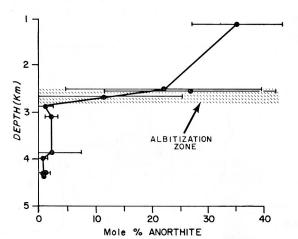


Fig. 3. Average anorthite content in Frio plagioclase grains. Data from table 1.

Plagioclase compositions in Frio sandstones were determined with an ARL microprobe analyzer by simultaneously analyzing for sodium, potassium, and calcium.<sup>3</sup> Each grain was analyzed on the rim and in the core; about 30 grains per thin section were analyzed from ten depth intervals.

Feldspar compositions shown in figure 3 and table 1 indicate that there is a marked transition toward albitic compositions at about 2.5 to 2.8 km burial depth. For example, plagioclase grains in a shallow sample from 2521 m have an average composition of  $Ab_{70.3}An_{26.7}Or_{3.0}(n = 35)$ . In contrast, a sample from 4338 m has an average plagioclase composition of  $Ab_{99.3}An_{0.6}Or_{0.1}(n = 29)$ . Both the anorthite and the orthoclase component show significant decreases from shallow to deep samples. Standard deviations of average plagioclase composition also show significant decreases with increasing burial depth. All these changes are interpreted as active albitization of calcic plagioclase (mainly oligoclase) to nearly pure albite. In summary, albitization occurs mainly in a relatively sharp zone between 2.5 and 2.8 km burial depths. The exact onset of albitization is difficult to define with the present data. The decrease in average anorthite content between 1109 and 2519 (table 1) may be due to differences in detrital compositions rather than to incipient albitization.

A number of *partially* albitized plagioclase grains are present within the inferred albitization zone. The albitic parts of the grain have distinctively lower refractive indices and have inclusions compared with the unaltered parts of the grain. Microprobe analysis of these partially altered grains shows that a "fresh" calcic plagioclase coexists with nearly pure albitic domains within the same grain (table 2 and fig. 4). There is a trend for the altered parts of partially albitized plagioclases to be

<sup>8</sup> Calculations indicate that if silica and aluminum are added to these elements in ideal feldspar proportions, the average total weight percent oxides of 337 analysis is  $101.1 \pm 1.6$ . Thus, these partial analyses are considered to be an accurate measure of the feldspar composition.

more albitic with increasing depth (table 2). The coexistence of fresh compositions with nearly pure albite replacement suggests that once started albitization goes to completion rather quickly within a certain domain of the grain.

Many, but not all, of the partially albitized plagioclase grains have dissolution porosity (fig. 4), whereas more deeply buried, completely albitized plagioclases generally lack macro porosity. This suggests that

## TABLE 1

Electron microprobe analyses of plagioclase in Gulf Coast sandstones. Well numbers refer to figure 1. Each grain analyzed on core and rim.

		Number	Average	e composition	(mole %)	Standard
Well Number		of grains analyzed	Ab (albite)	An (anorthite)	Or (orthoclase)	deviation of An content
		F	RIO SAND	STONES		
1	1109	22	60.3	35.1	4.6	$\pm$ 8.6
2	2519	24	74.5	22.0	3.5	$\pm 18.2$
	2521	35	70.3	26.7	3.0	$\pm 15.9$
3	2675	30	87.3	11.3	1.4	$\pm 14.3$
4	2866	24	98.2	1.1	0.7	$\pm 1.4$
	3104	7	96.7	1.8	1.5	$\pm 0.9$
5	3878	35	97.3	2.1	0.6	$\pm$ 5.5
6	4005	14	99.0	0.5	0.5	$\pm$ 0.2
7	4329	22	98.3	1.0	0.7	$\pm 1.1$
	4335	16	99.2	0.4	0.4	$\pm$ 0.3
	4338	29	99.3	0.6	0.1	$\pm$ 0.8
8	4394	16	99.0	0.6	0.4	$\pm$ 0.5
9	4409	20	99.1	0.5	0.4	$\pm$ 0.4
		WIL	COX SANI	OSTONES		
10	1777	7	93.2	5.4	1.4	$\pm$ 4.1
	1936	3	97.6	2.2	0.2	$\pm 2.4$
11	3260	4	98.7	0.8	0.5	$\pm$ 0.5
	4631	6	99.6	0.3	0.1	$\pm$ 0.5

#### TABLE 2

Electron microprobe analyses of partially albitized Frio plagioclase from the albitization zone (see fig. 3). Each set of "fresh" and "albitic" analyses are from a single grain.

Depth (m)	"Fresh"		Mole % composition		'Albitic"	
	Ab	An	Or	Ab	An	Or
2519	1		1.1			
	50.0	48.1	1.8	96.7	2.5	0.8
2521						
	63.8	32.1	4.1	81.7	16.1	2.4
	64.6	31.2	4.3	97.0	1.9	0.9
	62.8	34.5	2.7	92.0	6.5	1.5
2675						
	63.9	31.3	4.8	98.9	0.6	0.3
	56.8	40.6	2.6	99.5	0.2	0.1
	67.2	28.6	4.2	99.0	0.6	0.2
	71.4	26.2	2.5	99.3	0.3	0.3
	77.0	18.2	4.9	98.9	0.6	0.3
	63.7	31.1	5.2	97.6	1.9	0.3

albitization proceeds by a dissolution-precipitation mechanism rather than by solid-state diffusion. In most cases, the end product of albitization is an equal volume replacement of calcic plagioclase.

A final observation on partially albitized plagioclase within the albitization zone is that in many cases albitization has progressed preferentially along grain fractures and cleavage traces. This suggests that albitization is enhanced by lattice defects or planes of weakness where fluid films can infiltrate the crystal. Apparently, surface dissolution kinetics, as controlled by the character of the grain surface and lattice defects, is critical to the albitization process.

Below the albitization zone plagioclase feldspar exhibits characteristic "dusty" inclusions and have a mean refractive index less than 1.54. In addition, calcite is present within many albitized grains. This calcite is presumably formed by calcium released from the albitization reaction combined with carbonate ion from pore fluids. The calcite is very pure compared with cements in the same rock which show iron and magnesium enrichment, presumably the iron and magnesium being supplied from clay diagenesis reactions (Boles, 1978; Boles and Franks, 1979), and compared with detrital micrite grains which are relatively high in magnesium (fig. 5). Clearly these carbonates have not completely equilibrated with a single pore fluid, but rather the composition of the authigenic carbonates within the rock seems to reflect local equilibration with various pore fluid during several diagenetic events, including albitization of plagioclase.

## ALBITIZATION IN THE WILCOX

Albitization in the Wilcox Formation has been studied on only a preliminary basis in two wells (fig. 1). These Wilcox sandstones are more homogenous in composition, are more quartzose, and less feldspathic and volcanogenic than Frio sandstones. The source area of the Wilcox detritus was mainly acidic plutonics and clastic sedimentary rocks.

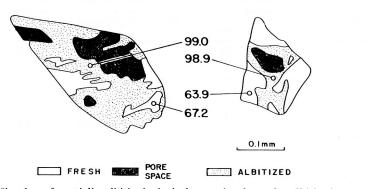


Fig. 4 Sketches of partially albitized plagioclase grains from the albitization zone. Numbers are mole percent albite content (see table 2). Sample from 2675 m.

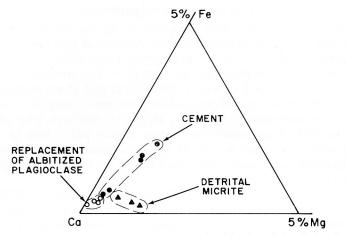


Figure 5. Microprobe analyses (mole percent) of calcite in Frio sandstone from 3878 m depth. Note relatively pure calcium composition of calcite replacing albitized plagioclase.

Microprobe analysis of Wilcox plagioclase shows the same general trend as in Frio sandstones in that samples at and below 3260 m have albitic compositions compared with samples at and above 1936 m (table 1). The fresh Wilcox plagioclases appear more albitic than fresh Frio plagioclase which probably reflects the more acidic source area of the Wilcox samples.

## PRESSURE-TEMPERATURE CONDITIONS OF ALBITIZATION

The zone of active albitization is present in Frio cores from wells 2, 3, and 4 (figs. 1 and 3). The top of the zone is in well 2 at about 2500 m where *in situ* temperatures<sup>4</sup> are 110°C, and fluid pressures are 0.27 kb. The base of the albitization zone occurs in well 4 at about 2800 m. Wells in the immediate vicinity of well 4 have *in situ* temperatures of about 120°C at 2800 m and fluid pressures of 0.54 kb. Total overburden pressures in the Gulf Coast are generally accepted to be about 1.0 psi/ft (Jones, 1969), thus the Frio albitization zone occurs at total pressures of about 0.58 to 0.65 kb.

The Wilcox albitization zone is not as well constrained as in the Frio. In the Wilcox, albitization occurs at depths less than 3660 m. At this depth *in situ* temperatures are about 150°C (Boles and Franks, 1979), fluid pressures are about 0.61 kb, and load pressures are about 0.76 kb.

In summary, the principal zone of albitization in these Gulf Coast Tertiary rocks is between 100° and 150°C, or more likely 110° and 120°C. These temperatures are comparable to estimated albitization temperatures in Miocene oil fields of California based on reconstructed stratigraphic sections (105°C, Merino, 1975) and of Japan (120°C, Iijima and Utada, 1972).

<sup>4</sup> Temperatures based on estimates from shut-in producing well temperatures.

#### FRIO PORE FLUID COMPOSITIONS

Table 3 gives pore fluid compositions of six waters from depths within and below the albitization zone. Analysis B and E are from wells 3 and 4 respectively, as referred to in figure 1 and table 1. Analysis A, D, and F are from wells about 30 km west of well 4. Analysis C is from a well about 50 km north of well 4. Analyses C and D are probably more reliable than the other analyses, and they are more complete and include well-site measurements of alkalinity,  $H_2S$ ,  $NH_3$ , and pH. The pH values shown in table 3 are maximum values. Actual pH values in the subsurface may be as much as 2.0 pH units *less* than shown due mainly to  $CO_2$  degassing as the water enters and moves up the bore hole (Kharaka, personal commun., 1980).

As pointed out by Kharaka, Carothers, and Brown (1978), waters from the Frio of south Texas are Na-C1 type waters with salinities ranging from about 10,000 to 40,000 ppm. They also concluded that these waters represent original conate waters (seawater) modified only by mineral reactions in the sediment and, unlike many other Gulf Coast waters, unaffected by solution of salt from underlying diapirs. The important point to note here is that albitization is occurring in somewhat modified dilute seawater. Clearly, abnormally high salinities or extremely high sodium concentrations are *not* a prerequisite for albitization.

TABLE 3

Pore fluid compositions (mg/L) in the Frio Formation, South Texas. Analysis C and D from Kharaka and others (1978). Analyses A, B, E, F from various petroleum companies. N.A. = not analyzed.

		-	-			
	Α	В	C*	D*	E	F
	Swallow	Z.S. Ector	La Blanca	Kelley	Gas Unit	J.W.
Well Name	No 4	#1	#12	A-1	#15 South	Morin
Field Sample	Donna	North Cano	La Blanca	Pharr	Weslaco	Donna
depth (m)	2395	2672-2699	2903	3018	3086-3118	3170
Temp (°Ć)**	* 110	110	148	127	125	135
Na <sup>+</sup>	5711	4627	2680	9420	3191	6725
K+	N.A.	197	46	240	N.A.	N.A.
$Mg^{++}$	36	44	3.3	18	20	30
Ca <sup>++</sup>	2128	992	150	4225	800	110
Sr <sup>++</sup>	N.A.	N.A.	9.6	256	N.A.	N.A.
Ba++	N.A.	N.A.	1.5	27	N.A.	N.A.
Cl-	12,375	8830	3950	22,000	5780	9865
Br-	N.A.	N.A.	15	78	N.A.	N.A.
I—	N.A.	N.A.	16	22	N.A.	N.A.
В	N.A.	N.A.	117	105	N.A.	N.A.
$NH_3$	N.A.	N.A.	4.2	21.5	N.A.	N.A.
HCO <sub>3</sub>	293	332	400	114	527	1129
SO4	175	410	57	7	420	175
Si0 <sub>2</sub>	N.A.	N.A.	88	90	N.A.	N.A.
pН	6.3	7.2	7.3	6.8	7.3	6.4
TDS	20,968	15,432	7500	36,600	10,738	18,250

\* Additional elements present in amounts less than 10 ppm are Li, Rb, Cs. Fe, F, H<sub>2</sub>S.

\*\* Estimated at sample depth.

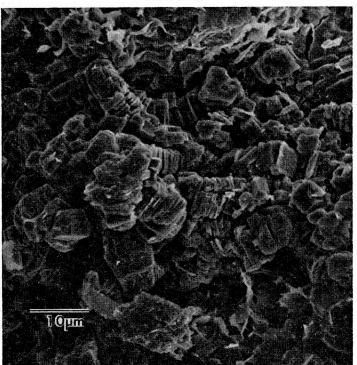
### FRIO ALBITIZATION REACTION

The albitization reaction in Frio sandstones is one in which calcic plagioclase is converted to albite. This reaction releases aluminum and calcium which, in Frio sandstones, is consumed by formation of clay minerals and sometimes calcite (also see Garbarini and Carpenter, 1978). Authigenic kaolinite (variety dickite) is known to form at depths about equivalent to the albitization zone described here in south Texas (Lindquist, 1977) and has been found in many rocks of this study (pl. 1). The albitization reaction is a ready explanation for the occurrence of this clay. Authigenic chlorite and illite also occur within the albitization zone, and in some cases one or more of these clays may form in place of kaolinite. Pore fluid composition (that is, pH,  $a_{K^+}$ ,  $a_{Mg^{++}}$ ,  $a_{Fe^{++}}$ ,  $a_{H_4SiO_4}$ ) is probably the controlling factor in determining which clays will form from the albitization reaction.

In summary, the Frio albitization reaction is similar to:

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PLATE 1



Authigenic kaolinite in Frio sandstone, 2590 m depth, Hidalgo County, Texas. SEM photo. Clay has probably formed as a by-product of the albitization reaction.

The equilibrium boundary for this reaction can be evaluated at various temperatures and pressures as a function of pH and log  $a_{Ca}^{++}/a_{Na}^{++}$ using the methods shown by Garrels and Christ (1965). The free energy of formation of the phases (other than water) were calculated at temperatures above 25°C from the expression  $\Delta G_f = \Delta H - T\Delta S$ . Where  $\Delta G_f$ is the free energy of the phase at temperature T (in °K), 1 atm pressure, and  $\Delta H$  and  $\Delta S$  are the enthalpy and entropy of formation of the phase, respectively at 298° K, 1 atm pressure. Enthalpy and entropy values at 298° K were taken from Robie, Hemingway, and Fisher (1978). It should be noted that entropy values given by Robie, Hemingway, and Fisher are entropies of formation from the elements and thus must be corrected (generally by subtracting entropies of the elements) in order to be used with their cited enthalpy values. The assumption that  $\Delta G_{T} = \Delta H_{298}$  –  $T\Delta S_{\scriptscriptstyle 298}$  assumes that the heat capacity of the phase is constant as a function of temperature. This is a reasonable assumption for solid phases and presumably for ions for the narrow temperature range being considered here. Free energy values for water at various temperatures and pressures were taken directly from Fisher and Zen (1971).

After calculating the  $\Delta G$  for the reaction at temperature T (that is,  $\Delta G_T$ ), the equilibrium constant K for the reaction was calculated from the expression  $\Delta G_T = -RT$  InK, where R is the gas constant. On a plot of pH versus log  $a_{Ca^{++}}/a_{Na^+}$  for the above reaction, log (K·A<sub>anor</sub>) is equal to the pH value when log  $a_{Ca^{++}}/a_{Na^+}$  is zero. In order to evaluate the position of the equilibrium boundary it is necessary to specify the activity of the solid phases and water. All of these were assumed to be pure phases with activities of unity except for anorthite. Figure 3 shows that the initial anorthite content of Frio plagioclase is about 35 mole percent and thus would have an activity of about 0.45 (see Saxena and Ribbe, 1972).

Results of the above calculations of the equilibrium boundary for the albitization reaction at 100°, 125°, and 150°C are shown in figure 6. The estimated error on the equilibrium boundary using the errors assigned to the free energy values at 25°C given by Robie, Hemingway, and Fisher (1978), and using standard error estimate formulas (see Fisher and Zen, 1971), is about  $\pm$  1.0 pH units.

It is possible to evaluate whether the Frio pore fluids are in equilibrium with albite + dickite or anorthite + quartz by plotting them on figure 6. Sodium and calcium concentrations in table 5 were corrected to activity values by calculating the ionic strength of the fluid and estimating activity coefficients by the mean salt method (Garrels and Christ, 1965, p. 63). The exact position of the equilibrium boundary for each water plotted in figure 6 is fixed by the temperature of that water.

The waters from the albitization zone and below (large dots, fig. 6) are interpreted to be on the equilibrium boundary or within the albite field, considering the error in the position of the boundaries ( $\pm$  1.0 pH

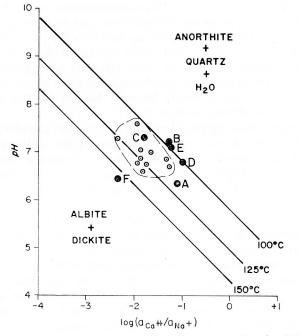


Fig. 6. Equilibrium boundary of albitization reaction:  $2SiO_2 + \frac{1}{2}H_2O + H^+ + Na^+ + CaAl_2Si_2O_8 = NaAlSi_3O_8 + \frac{1}{2}Al_2Si_2O_5 (OH)_4 + Ca^{++} at 100^{\circ}C$ ,  $P_{H_{2O}} = 0.3$  kb;  $125^{\circ}C$ ,  $P_{H_{2O}} = 0.5$  kb;  $150^{\circ}C$ ,  $P_{H_{2O}} = 0.75$  kb. Solid pressure for all boundaries assumed to be 1 atm. Activity of anorthite assumed to be 0.45, other solids and  $H_2O$  assumed to have unit activity.

Frio water analyses (large dots) A through F from table 3. Other water analyses (small dots) are shallow Frio waters (1600-2300 m depths, temperatures 65°-90°C), from Hidalgo County, Texas.

units) and that the *in situ* pH of the waters may be as much as 2.0 pH units less. Thus the water compositions reflect the mineral reactions in the rock.

Also plotted on figure 6 are eleven waters from *above* the albitization zone, ranging in burial depths from 1600 to 2300 m and temperatures ranging from 75° to 90°C. These waters are also near the albite-anorthite equilibrium boundary and, if anything, are probably in the albite + dickite stability field. Therefore waters at depths less than the zone of albitization also appear to favor albitization, yet none has been observed at these *shallower* burial depths.

In the reaction above, silica for albitization is provided by quartz. If silica is assumed to be supplied from pore waters<sup>5</sup> in the form of  $Si(OH)_4$  the reaction becomes:

## $H^+ + 2Si (OH)_4 + Na^+ + anorthite =$

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albite +  $\frac{1}{2}$  kaolinite + Ca<sup>++</sup> + 3.5 H<sub>2</sub>O

<sup>5</sup> In this case silica may be supplied by sources other than quartz, for example, clay diagenetic reactions, see Boles and Franks (1979).

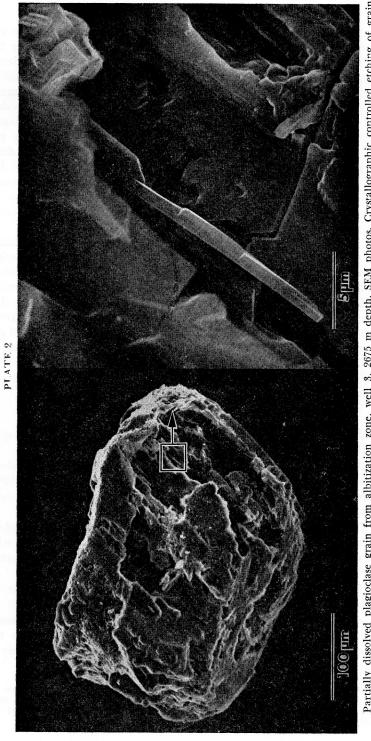
If it is assumed that aqueous silica concentrations are in equilibration with quartz at the appropriate temperatures, the equilibrium boundaries for this new reaction are calculated to be 0.2 to 0.3 pH units higher, at fixed log  $a_{Ca^{++}}/a_{Na^+}$  values, than those shown in figure 6. If aqueous silica concentrations were higher than required for equilibration with quartz, the albite-dickite field would expand even more, and the pore waters shown in table 3 would be even further in the albite-dickite stability field than shown in figure 6.

Apparently these preliminary thermodynamic calculations do not explain adequately the natural process. Possibly the albitization reaction proceeds at an appreciable rate only after a threshold temperature is reached (that is,  $\approx 100^{\circ}$ C). If true, this suggests a step in the albitization process with a critical activation energy that requires temperatures greater than 100°C.

Berner (1978) has shown that feldspar weathering is controlled by surface dissolution rates rather than by the transport rate of ions away from the crystal, evidenced by the presence of solution pits and etching along cracks and cleavages. Microscopic and SEM studies of partially dissolved plagioclase from the Frio albitization zone also exhibit these characteristics showing that surface dissolution is the rate limiting step (pl. 2). The inference from this is that albitization may be indirectly controlled by the strain history of a grain, presence of micro-fractures, and lattice defects formed during crystallization. A kinetic interpretation of the albitization process also suggests that in old strata the albitization process may proceed at lower temperatures than found here. We are presently investigating the temperature dependence of the dissolution rate of plagioclase and its importance to the albitization process.

#### DISCUSSION

One of the interesting aspects of the albitization process is the source of the sodium required for equal volume albitization. In many terrains, albitization apparently results in a net addition of sodium to the rock rather than partition of sodium between solid phases within the rock. The source of the sodium, at least in these Gulf Coast rocks, must be largely the sodium contained in pore fluids. The sodium content of these pore water reflects not only the original sodium in seawater but later diagenetic reactions; for example, the conversion of smectite to illite releases sodium (Boles and Franks, 1979). This clay diagenesis reaction, volumetrically most important in shales, commences at temperatures around 40°C and continues to temperatures at least as high as 150°C. Thus, the released sodium would be available during the albitization process described in this paper. In areas where connate waters from salt diapirs have permeated the overlying Gulf Coast Tertiary section, additional significant sodium will be added to the pore fluids.



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Partially dissolved plagioclase grain from albitization zone, well 3, 2675 m depth. SEM photos. Crystallographic controlled etching of grain suggests grain surface dissolution rates are rate-limiting step in plagioclase dissolution.

Irrespective of the ultimate source of the sodium, in most cases albitization implies sodium mobility, probably on a scale greater than tens of meters. The importance of fluid or ion mobility to albitization is illustrated by cases where albitization is impeded by low permeability fine-grain rocks (Boles and Coombs, 1977) or by early carbonate cementation (for example, Martini, 1968). It is particularly clear in the documented example described here where pore fluids in the albitization zone contain less than 10,000 ppm sodium in solution. A simple mass balance calculation shows that a minimum of about 30 pore volumes would be required to albitize completely the plagioclase found in a typical Frio sandstone from south Texas.<sup>6</sup> This number represents a *minimum* value as it assumes that all sodium can be scavenged from the pore fluid for albitization. The actual value could be an order of magnitude or more greater.

Data presented in this paper suggests that Frio albitization effectively goes to completion within a 300 m zone. Assuming the rocks within the albitization zone (2.7 km) are about 32 m.y. old, the mean subsidence rate of the section is about  $8.4 \times 10^{-5}$  m/yr. Thus the *time* required for the section to pass *through* the albitization zone is  $3.6 \times 10^6$  yrs, and the minimum flow rate required would be about 290 cc fluid/ $3.6 \times 10^6$  yrs through 100 cc rock or 80 cc of fluid would have to flow through 10 cc of pore space in  $10^6$  yrs in order for complete albitization to occur. Although I have no independent data against which the flow rates can be checked, they provide an estimate of fluid mobility that can be tested in future studies.

#### SUMMARY

This study of plagioclase albitization in a modern burial setting has shown the following:

1. Albitization of plagioclase in Oligocene Gulf Coast sandstone occurs at 2500 to 2800 m burial depths, temperatures of 110° to 120°C, fluid pressures of about 0.2 to 0.5 kb, and total overburden pressures of about 0.58 to 0.66 kb.

2. The albitization zone is characterized by partially albitized plagioclase grains in which nearly pure albite coexists with calcic plagioclase. Grains within this zone are albitized by a solution-precipitation process rather than by solid state diffusion.

3. By-products of the albitization process commonly include clay minerals such as kaolinite and nearly pure calcite (Fe-Mg free).

4. Albitization does not require abnormal salinities or extremely high sodium concentrations. In this study, pore fluids with less than  $10,000 \text{ mg/1 Na}^+$  appear to be close to the equilibrium boundary for albitization.

<sup>6</sup> This calculation assumes complete equal volume albitization of plagioclase in a rock with 20 percent plagioclase of initial composition  $An_{30}$  (fig. 3), porosity in the albitization zone of 10 percent (Lindquist, 1976, p. 126), and a pore fluid with 4600 mg/l Na<sup>+</sup> (table 3, analysis B).

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5. Albitization may be controlled by grain surface dissolution rates. Unfavorable reaction rates may prevent albitization at shallow levels where pore fluid compositions are over-saturated with respect to albite + clay.

6. Albitization requires pore fluid or ion mobility, probably on a scale of at least 10's of meters. In Frio sandstones minimum flow rates on the order of 80 cc fluid/10 cc pore/106 yrs are required.

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#### REFERENCES

- Bailey, E. B., and Grabham, G. W., 1909, Albitization of basic plagioclase feldspar: Geol. Mag., v. 6, p. 250-256.
- Berner, R. A., 1978, Rate control of mineral dissolution under earth surface conditions: Am. Jour. Sci., v. 278, p. 1235-1252.
- Boles, J. R., 1978, Active ankerite cementation in the subsurface Eocene of southwest
- Boles, J. R., and Coombs, D. S., 1977, Zeolite Facies alteration of sandstones in the Southland Syncline, New Zealand: Am. Jour. Sci., v. 277, p. 982-1012.
  Boles, J. R., and Franks, S. G., 1979, Clay diagenesis in Wilcox sandstones of southwest Texas: implications of smectite diagenesis on sandstone cementation: Jour. Sed. Potter Jour. Sed.
- Petrology, v. 49, p. 55-70. Burst, J. R., Jr. 1969, Diagenesis of Gulf Coast clayey sediments and its possible re-
- lationships to petroleum migration: Am. Assoc. Petroleum Geologists Bull., v. 53, p. 73-93.
- p. 75-55.
  Coombs, D. S., 1954, The nature and alteration of some Triassic sediments from south-land, New Zealand: Royal Soc. New Zealand Trans., v. 82, p. 65-109.
  Dickinson, W. R., Ojakangas, R. W., and Stewart, R. J., 1969, Burial metamorphism of the late Mesozoic Great Valley sequence, Cache Creek, California: Geol. Soc. America Bull., v. 80, p. 519-526. Fisher J. R., and Zen, E-an, 1971, Thermochemical calculations from hydrothermal
- phase equilibrium data and the free energy of H2O: Am. Jour. Sci., v. 270, p. 297-314.

Garbarini, J. M., and Carpenter, A. B., 1978, Albitization of plagioclase by oil field brines: Geol. Soc. America Abs. with Programs, v. 10, p. 406. Garrels, R. M., and Christ, C. L., 1965, "Solutions, Minerals, and Equilibria": New

York, Harper and Row Pub. Co., 450 p. Iijima, A., and Utada, M., 1972, A critical review on the occurence of zeolites in

sedimentary rocks in Japan: Japanese Jour. Geology Geography, v. 42, p. 61-83. Jones, P. H., 1969, Hydrodynamics of geopressure in the northern Gulf basin: Jour.

Petroleum Tech., v. 21, p. 803-810. Kastner, M., and Siever, R., 1979, Low temperature feldspars in sedimentary rocks: Am. Jour. Sci., v. 279, p. 435-479. Kharaka, Y. K., Carothers, W. W., and Brown, P. M., 1978, Origins of water and

- Kharaka, T. K., Caroniers, W. W., and Drown, T. H., 1976, Origins of water and solutes in the geopressured zones of the northern Gulf of Mexico Basin: Dallas, Texas, Soc. Petroleum Engs., Preprint SPE 7505, 8 p.
   Lindquist, S. J., ms, 1976, Sandstone diagenesis and reservoir quality, Frio Formation (Oligocene), south Texas: M.A. thesis, Univ. Texas Austin, Texas, 148 p.

1977, Secondary porosity development and subsequent reduction, over-pressured Frio Formation sandstone (Oligocene), south Texas: Gulf Coast Assoc.

Geol. Soc. Trans., v. 27, p. 99-107. Loucks, R. G., Bebout, D. G., and Galloway, W. E., 1977, Relationship of porosity formation and preservation to sandstone consolidation history — Gulf Coast Lower Tertiary Frio Formation: Gulf Coast Assoc. Geol. Soc. Trans., v. 27, p. 109-120.

Martini, J., 1968, Etude pétrographique des Grès de Taveyanne entre arve et Giffre (Haute-Savoie, France): Schweizer. min. pet. Mitt., v. 48, p. 539-654.
Merino, E., 1975, Diagenesis in Tertiary sandstones from Kettleman North Dome, California: I. Diagenetic mineralogy: Jour. Sed. Petrology, v. 45, p. 320-336.
Murray, G. E., 1960, Geologic framework of Gulf Coastal Province of United States, in Shepard, F. P., and otners, eds., Recent Sediments, northwestern Gulf of Mexico, Twice Obleheme Are Area Betrolupy Coalegiet Public p. 5-28.

Shepard, F. P., and otners, eds., Recent Sediments, northwestern Gulf of Mexico, Tulsa, Oklahoma, Am. Assoc. Petroleum Geologist Pub., p. 5-33.
Perry, E., and Hower, J., 1970, Burial diagenesis in Gulf Coast pelitic sediments: Clay and Clay Minerais, v. 18, p. 165-177.
Pettijohn, F. J., Potter, P. E., and Siever, R., 1973, "Sand and Sandstones": New York, Springer-Verlag Pub. Co., 618 p.
Robie, R. A., Hemingway, B. S., and Fisher, J. R., 1978, Thermodynamic properties of minerals and related substances at 298.15 K and 1 Bar (10<sup>6</sup> pascals) pressure and at higher temperatures: U.S. Geol. Survey Bull. 1452, 456 p.
Saxena, S. K., and Ribbe, P. H., 1972, Activity-composition relations in feldspars: Contr. Mineralogy and Petrology, v. 37, p. 131-138.
Surdam, R. C., 1973, Low-grade metamorphism of tuffaceous rocks in the Karmutsen Group, Vancouver Island, British Columbia: Geol. Soc. America Bull., v. 84, p. 1911-1922.
Wright, T. L., 1968, X-ray and optical study of alkali feldspar: U an X-ray method for the state of the state of the study of alkali feldspar: U an X-ray method for the state of the study of alkali feldspar: U an X-ray method for the study of alkali feldspar.

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Wright, T. L., 1968, X-ray and optical study of alkali feldspar: II an x-ray method for determining the composition and structural state from measurements of 20 values for three reflections: Am. Mineralogist, v. 53, p. 88-104.