

# Carbonate alteration minerals in the Salton Sea geothermal system, California, USA

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**ABSTRACT.** Active geothermal systems in fluvial-deltaic sediment of the Salton Trough typically develop a thick, carbonate-cemented sandstone caprock which shows a regular progression of carbonate minerals, mineral reactions, rock-fluid mass transfer, and physical properties on increasing temperature. The Sinclair 3 well contains calcian ankerite at < 175 °C, ankerite from 175 to 195 °C, calcite + minor dolomite from 195 to about 250 °C, and calcite at higher temperatures. The carbonate content of sandstone decreases on increasing temperature from > 45% at < 140 °C to about 10% at > 250 °C. The most abrupt decrease occurs in the 140 to 170 °C range where significant compaction of sandstone occurs as carbonate is reduced to < 25%, and kaolinite reacts to form chlorite. The overall result is the loss of significant Ca, Fe, Mg, and CO<sub>2</sub> from sandstone to the fluid phase on increasing temperature. Reaction of calcian ankerite to ankerite near 175 °C, and of ankerite to calcite and minor dolomite in the 195 to 245 °C range, takes place on a constant carbonate-volume basis by direct replacement of one carbonate by another. The latter reaction produces significant chlorite, with Al derived from solution of detrital feldspar and from the smectite-to-illite transformation. The equilibrium coexistence of calcite with dolomite and ankerite near 200 °C has allowed construction of an isothermal section in the Ca-Mg-(Fe+Mn) carbonate phase diagram and provided a low-temperature constraint on the calcite limb of the calcite-dolomite solvus.

**KEYWORDS:** calcite, dolomite, ankerite, geothermal system, Salton Sea, California, USA.

ONE of the persistent features of the various active geothermal systems in the Imperial Valley-Salton Trough of California, USA, and Baja California, Mexico, is the presence of a carbonate-rich caprock. This paper describes the carbonate mineralogy and mineral chemistry of the cap in the Sinclair 3 geothermal borehole on the southern flank of the Salton Sea Geothermal System (fig. 1) where it is thick and well sampled. The similarities of the various carbonate caps are such that this borehole can be considered a generally representative example.

The gross stratigraphy of the Salton Sea Geothermal System consists of an upper clay-silt-evaporite lacustrine sequence about 400 m thick, and a lower interbedded fluvial-deltaic sandstone-shale sequence (Randall, 1974). The upper lacustrine sequence acts as a stratigraphic permeability cap on the central portions of the geothermal system, where hot fluids are present immediately below this stratigraphic break. On the flanks of the field, where isotherms are much deeper, most sediment is un lithified at the depth of the stratigraphic break. The geothermal system operates in the deeper fluvial-deltaic sequence and has developed its own permeability cap in the form of a carbonate-rich zone in which sandstone is strongly cemented and porosities are generally low. In Sinclair 3, the sampled section of the carbonate cap ranges from about 650 m, where sandstone first becomes sufficiently lithified to survive as well cuttings, to the base of the cap at about 1650 m. The characteristics of the carbonate cap in this well are compared with the much thinner carbonate cap in the Elmore 1 well (fig. 1) located in the central portion of the geothermal system where the carbonate cap occurs directly below the lacustrine to fluvial-deltaic stratigraphic break. The detrital mineralogy of sandstone in Sinclair 3 is essentially identical to that reported in the northern portions of the geothermal field (Muffler and White, 1969; Helgeson, 1968; Muffler and Doe, 1968) and from the central Elmore 1 well (McDowell and Elders, 1980, 1983).

*Method of investigation.* The data and observations for this paper are based on petrographic examination of sandstone cuttings using polished and unpolished thin sections impregnated by clear and blue-stained epoxy, electron microprobe analyses of various minerals using mainly energy dispersive techniques, and X-ray diffraction analyses of both clay fractions and bulk fractions of hand-picked sandstone cuttings. This investigation deals exclusively with well cuttings since little core

## SALTON SEA GEOTHERMAL FIELD

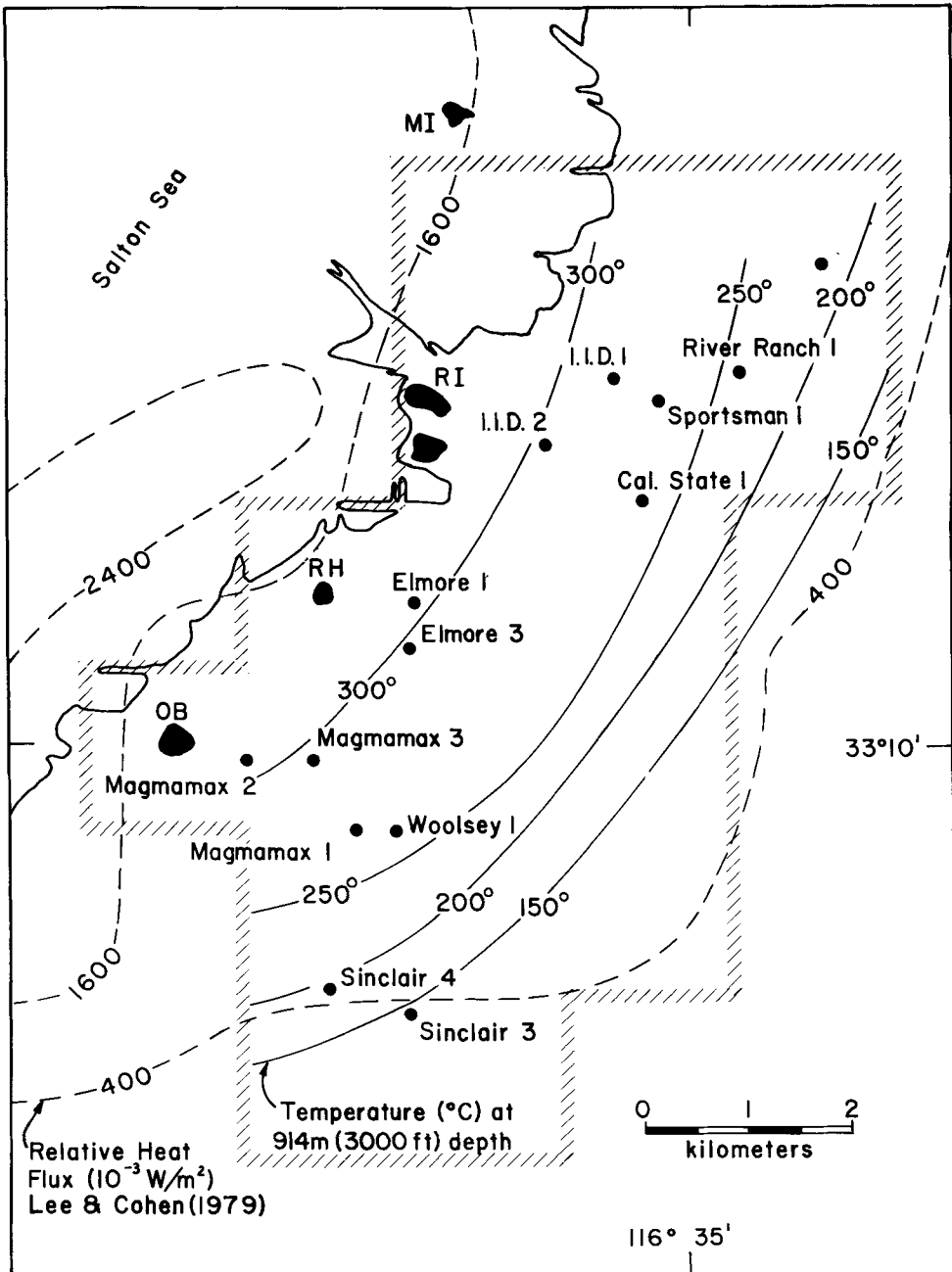


FIG. 1. Location of boreholes in Salton Sea Geothermal Field. Solid lines = temperature ( $^{\circ}\text{C}$ ) at 914 m (3000 ft) depth, modified after Palmer (1975) and Randall (1974). Dashed lines = relative heat flux in  $10^{-3}$  watts/ $\text{m}^2$  from Lee and Cohen (1979). Rhyolite extrusives: OB = Obsidian Butte; RH = Rock Hill; RI = Red Island; MI = Mullet Island.

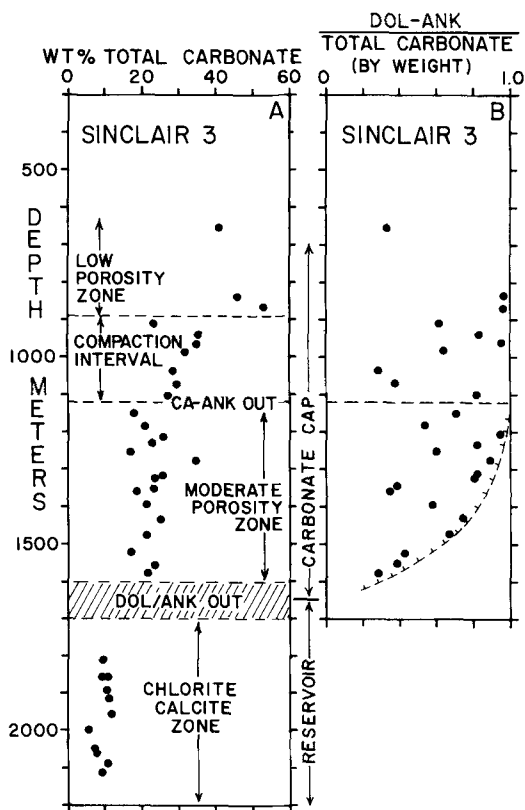


FIG. 2. Variation of weight % total carbonate in solid fraction of sandstone (A) and weight ratio of dolomite-ankerite to total carbonate (B) vs. depth in metres in Sinclair 3 as determined by quantitative X-ray diffraction techniques (Johnson, 1978). Major textural or metamorphic zones are indicated. Hatched dashed line in (B) emphasizes maximum weight ratio of dolomite-ankerite.

was taken during drilling, so that many mineralogical transitions tend to be smeared out with depth and temperature due to the inevitable, but apparently minimal, mixing of cuttings during their ascent to the surface.

**Carbonate mineral distribution.** The general distribution of carbonate minerals in sandstone from Sinclair 3 is shown in fig. 2. The well may be subdivided into four sections, each with distinct petrographic and petrophysical characteristics. The shallowest section, at depths < 900 m (< 140 °C), consists of a low porosity (average 6.4 volume %)\* sandstone with high but variable carbonate content (> 40 wt. %) dominantly of calcian ankerite. A high percentage of highly cor-

\* Porosity in volume % by point counting, all mineralogical percentages in weight % of solid fraction by quantitative X-ray diffraction techniques (Johnson, 1978).

roded floating quartz or feldspar grains with ample evidence of replacement by carbonate is observed.

A sharp petrophysical break near 900 m depth is reflected in an abrupt decrease in carbonate content, an increase in porosity, and strong evidence for removal of so much carbonate cement that significant compaction and detrital grain repacking has occurred. The carbonate content then decreases gradually from ~ 35 wt. % at ~ 950 m to ~ 25 wt. % at 1100 m, continuing the compaction process but still allowing an erratic increase in porosity. While compaction clearly occurs throughout the 900 to 1100 m interval, most compaction occurs in the shallow portion of the interval. Below the compaction interval, from 1160 to 1650 m (255 °C), sandstone has moderate porosities near 16% and carbonate contents near 16 wt. %. On increasing depth the ratio (dolomite + ankerite)/total carbonate, based on quantitative X-ray diffraction analyses (fig. 2b), decreases on increasing depth. Quartz overgrowths and authigenic chlorite are first noted at these depths.

At depths in the 1600-1700 m interval, a second major change occurs as the calcite content drops to about 9 wt. %, the porosity increases to 18-20%, and all dolomite and ankerite are removed. This marks the break between the shallower carbonate cap and the deeper reservoir rocks of the calcite-chlorite zone which persists, in other wells, to temperatures near 325 °C where calcite disappears, biotite and actinolite appear, and the biotite zone is entered.

**Carbonate mineralogy.** The carbonate minerals observed in thin section in sandstone from well Sinclair 3 include detrital calcite and dolomite, and authigenic calcian ankerite (protodolomite?), ankerite, dolomite, and calcite. The authigenic phases have very specific temperature/depth ranges and exhibit a consistent series of reactions.

Rounded, equant grains of detrital dolomite with irregular, often embayed, contacts are noted in trace but persistent amounts in all wells thus far investigated. The grain size and shape of dolomite approaches that of detrital quartz or feldspar in fine-grained sandstone and siltstone. It appears to react very sluggishly as it persists at least to depths of 1523 m (234 °C), and reacts to whatever authigenic carbonate phase is stable at a given temperature. It is rimmed by clear calcian ankerite in optical continuity with the dolomite at shallower depths, by aggregates of small euhedral ankerite rhombs at intermediate depths, or by enehedral aggregates or irregular single crystals of calcite at greater depths. In one grain at 867 m depth, a rounded inclusion train in calcian ankerite outlines the original form of a dolomite grain in which are preserved small relict dolomite patches.

Detrital calcite has a similar appearance to detrital dolomite, with rounded forms showing evidence of embayment by and reaction to the surrounding authigenic carbonate. It seems to persist only in the shallower parts of the well, and to have been completely consumed once temperatures were over  $\sim 200^\circ\text{C}$ .

The only authigenic carbonate observed at depths of  $< 1160$  m (about  $175^\circ\text{C}$ ) in the low porosity zone and compaction interval is calcian ankerite (= protodolomite?). It occurs in a variety of forms and grain sizes ranging from aggregates of minute euhedral rhombs to large, pore-filling, 0.1 mm single crystals. It is clear to turbid, and often shows a light brown or red-brown tint. Ankerite is the only stable authigenic carbonate mineral in sandstone in the 1160–1300 m ( $175$ – $200^\circ\text{C}$ ) depth interval and occurs as aggregates of euhedral rhombs (microspar,  $< 0.05$  mm) which fill or line individual pores. The replacement of calcian ankerite by ankerite, based on microprobe examination, appears to be almost complete by 1276 m depth.

At all depths in the interval 1300–1650 m ( $200$ – $255^\circ\text{C}$ ), ankerite is progressively replaced by calcite. Trace amounts of calcite, not obviously of detrital origin, occur at 1276 m. The ankerite is extensively resorbed, especially along cleavage traces, and often exists only as isolated corroded patches, cores or screens in clear anhedral calcite aggregates or irregular larger single crystals. No calcite rhombs were observed. Often an optical distinction between ankerite and calcite may be made in polished sections due to the greater hardness of ankerite. Both thin section and quantitative XRD analyses (fig. 2b) indicate an erratic but persistent increase in the calcite to dolomite + ankerite ratio on increasing depth or temperature. By 1577 m, only rare irregular ankerite patches were noted. Partially replaced ankerite at 1577 m consists of ragged cores of single ankerite crystals with shadowy, poorly defined domains visible which fade outward into a sea of  $< 5$  mm aggregate calcite by progressively increasing the number of rounded, bleb-like calcite inclusions until no ankerite skeleton remains. Pyrite is visible in the calcite aggregate, and in some areas in the more central portions of pore spaces, larger, clear single crystals of calcite with numerous pyrite inclusions are observed.

In addition to authigenic calcite, small euhedral rhombs and irregular patches of authigenic dolomite are observed at 1431 and 1523 m, and possibly at 1353 m depth. This dolomite is distinct in both size and texture from the rare detrital dolomite still preserved at these depths. Dolomite typically makes up less than 10% of the total carbonate fraction of the sandstone.

*Analytical procedures.* All analyses of carbonate minerals in Sinclair 3, and a few analyses from Elmore 1, were made with a Kevex 5100 energy dispersive system (EDS) mounted on a MAC 400 microprobe in the Institute of Mineral Research at Michigan Tech. The remaining analyses of Elmore 1 carbonates were made using wavelength spectrometers (WDS) on an automated MAC 5 microprobe or a Tracor 880 EDS system at CalTech. All analyses were run at 15 kV using 10 to 15  $\mu\text{m}$  spot sizes, 100 second counting times, and specimen currents of 0.005 microamps or less. The analysis of carbonates by EDS of grains previously run with wavelength methods indicated the same pattern as observed previously for silicates: average EDS analyses showed excellent agreement with average WDS analyses, but the scatter in the EDS analyses was 2 to 3 times that of the WDS analyses.

*Carbonate mineral compositions.* Compositional data on the carbonate minerals from Sinclair 3 are summarized in figs. 3, 4, and 5, and Table I. At 1160 m ( $< 175^\circ\text{C}$ ) calcian ankerite of highly

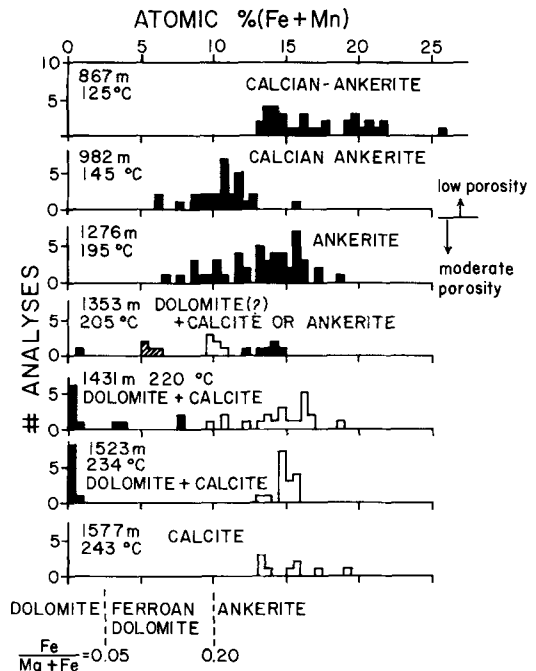


FIG. 3. Histograms of atomic % (Fe + Mn) of carbonates at various depths (m) and temperatures ( $^\circ\text{C}$ ) in the system  $\text{Ca} + \text{Mg} + \text{Fe} + \text{Mn}$ . Stable carbonate mineral assemblage indicated for each depth, with mineral phases in equilibrium in solid shading, relict phases unshaded, and possible intermediate phases in diagonal shading (1353 m only). Nomenclature in part after Deer *et al.* (1962). All detrital phases excluded.

variable composition occurs. In the Ca + Mg + Fe + Mn system, Fe-contents vary from 6 to 25% and Ca-contents from 54 to 61%. The scatter is emphasized in fig. 5, where the two upright triangles and enclosing areas indicate the averages and ranges of two different areas of calcian ankerite in the same sandstone chip, while the inverted triangle and enclosing area indicates those values in a second sandstone chip from the same depth. This calcian ankerite is very similar to the composition of calcian ankerite analysed by Boles (1978) from US Gulf Coast wells at *in situ* temperatures of 140°C or less.

At depths greater than 1160 m, the stable ankerite contains some excess calcium (average 52.7% Ca in the Ca + Fe + Mg + Mn system) but is distinctly less calcic than calcian ankerite (fig. 4). The Fe-contents of calcian ankerite and ankerite completely overlap (fig. 3). There is a great deal of scatter in the presumed equilibrium ankerite com-

position at 1276 m depth, and some of the high-Ca analyses may represent relict calcium ankerite not removed during reaction at 150–170°C.

At still greater depths, in the range 1300–1650 m, all analysed ankerite is relict and is being actively replaced by calcite except for a single grain at 1353 m (solid symbol, fig. 3). At 1353 m, rare large ragged patches of ferroan dolomite (diagonal shading, fig. 3) of unknown origin which are in the process of reacting to calcite are noted. Note in fig. 4 the general decrease in Ca-content on increasing temperature. Relict ankerite at 1523 m is distinct in that it has Ca-contents approaching ideal dolomite, and, unlike ankerite at other depths, very restricted ranges in Ca- or Fe-content. The textural evidence, however, strongly suggests that this ankerite is not stable.

Traces of authigenic, apparently equilibrated, dolomite first appear at 1353 m and persist to about 1600 m depth. In most cases the dolomite is very

Table 1. Average carbonate mineral analyses, Sinclair 3

CHIP #	A11	A11	A11	3	2	A11	A11	A11	A11
DEPTH (m)	867	982	1276	1353	1353	1431	1523	1577	1812
TEMP (°C)	125	145	195	205	205	219	234	243	282
MINERAL	CALCIAN ANKERITE	CALCIAN ANKERITE	ANKERITE	RELICT ANKERITE	ANKERITE	RELICT ANKERITE	RELICT ANKERITE	RELICT ANKERITE	NO ANKERITE
#ANALYSES	34	26	14	7	6	24	12	9	
CaO	31.43	32.45	29.07	29.91	29.41	29.90	28.27	29.40	
MgO	9.80	13.77	13.17	15.08	12.92	13.68	13.51	13.41	
MnO	0.29	0.11	0.21	0.42	0.03	0.39	2.15	0.57	
FeO	11.54	7.70	9.97	6.81	9.71	9.71	8.42	9.64	
Equiv. CO <sub>2</sub>	42.62	45.28	43.41	44.34	43.15	44.59	43.43	43.97	
Σ	95.68	99.30	95.82	96.56	95.23	98.27	95.79	96.99	
Ca	1.158	1.125	1.051	1.059	1.070	1.052	1.022	1.050	
Mg	0.502	0.664	0.662	0.741	0.654	0.670	0.679	0.666	
Mn	0.008	0.003	0.006	0.012	0.001	0.011	0.061	0.016	
Fe	0.332	0.208	0.281	0.188	0.276	0.267	0.238	0.269	
CO <sub>2</sub>	2	2	2	2	2	2	2	2	
MINERAL	CALCITE		CALCITE		CALCITE		CALCITE		CALCITE
#ANALYSES	2		9		25		28		36
CaO	50.99		53.60		53.99		53.71		53.26
MgO	0.41		0.84		0.49		0.39		0.57
MnO	0.00		0.44		0.25		0.67		0.59
FeO	1.65		0.93		0.84		0.84		0.81
Equiv. CO <sub>2</sub>	41.48		43.59		43.57		43.51		43.29
Σ	94.53		99.40		99.13		99.13		98.52
Ca	0.965		0.965		0.973		0.969		0.966
Mg	0.011		0.016		0.012		0.010		0.014
Mn	0		0.006		0.003		0.009		0.008
Fe	0.024		0.013		0.012		0.012		0.012
CO <sub>2</sub>	1		1		1		1		1
MINERAL	DOLOMITE		FE-DOLOMITE		DOLOMITE		DOLOMITE		
#ANALYSES	2		4		9		8		
CaO	29.59		30.03		30.39		29.66		
MgO	21.39		17.99		21.45		21.74		
MnO	0.14		0.30		0.15		0.03		
FeO	0.63		3.86		0.58		0.09		
Equiv. CO <sub>2</sub>	47.04		45.76		47.72		47.08		
Σ	98.79		97.95		100.31		98.61		
Ca	0.987		1.030		1.000		0.989		
Mg	0.993		0.858		0.981		1.008		
Mn	0.004		0.008		0.004		0.001		
Fe	0.016		0.104		0.015		0.002		
CO <sub>2</sub>	2		2		2		2		

All energy dispersive analyses (15kV, 0.005 microamperes, 10–30 μm spot sizes). Total iron as FeO.

pure (figs. 3, 5, Table I) and approaches ideal dolomite in composition. At 1431 m, a few authigenic rhombs of ferroan dolomite were noted, and appear to be in textural equilibrium. In fig. 5, tie lines have been drawn between coexisting calcite and dolomite (solid lines) and between ferroan dolomites and calcite (dashed lines).

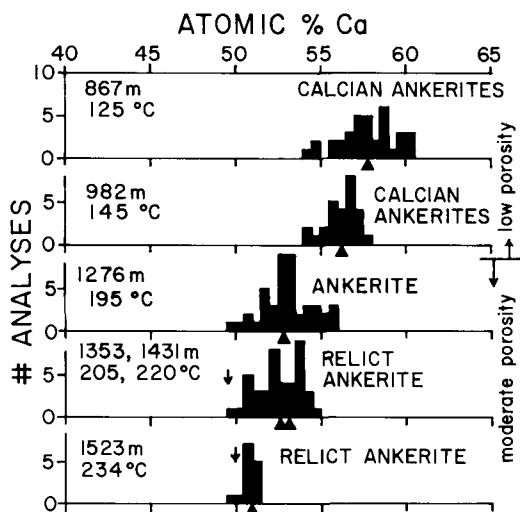


FIG. 4. Histograms of atomic %Ca in ankerites at various depths (m) and temperatures (°C) in the system Ca+Mg+Fe+Mn. Phase nomenclature and equilibrium/relict status as indicated. Triangles indicate average compositions, arrows indicate authigenic dolomite composition.

The carbonate mineral compositions from Elmore 1 are summarized in Table II. Note that in this well, located in central portion of the geothermal area where the carbonate cap is shallow, very thin, and poorly sampled, euhedral ankerite rhombs show no signs of replacement by calcite. Thus calcite appears to coexist in equilibrium with ankerite at depths of 439 m and temperatures near 190°C. Texturally, calcite is always later than ankerite, as the few existing ankerite rhombs are invariably surrounded by pore filling calcite. This paragenetic relationship is consistent with observations in the equivalent carbonate cap of the nearby Cerro Prieto Geothermal system in Mexico, where ankerite rhombs commonly line pore walls, with the pore interiors either open or filled with coarse grained, anhedral micritic calcite. Trace amounts of optically almost invisible, texturally ambiguous dolomite occur in Elmore 1 in sandstone chips containing ankerite. The dolomite, identified almost entirely by microprobe, shows none of the

typical embayed textures of detrital dolomite observed in other sandstones in Elmore 1 and Sinclair 3. Its Fe-content, while low, is distinctly higher than that of typical detrital dolomite, which is almost Fe-free. This dolomite is thus assumed to be authigenic.

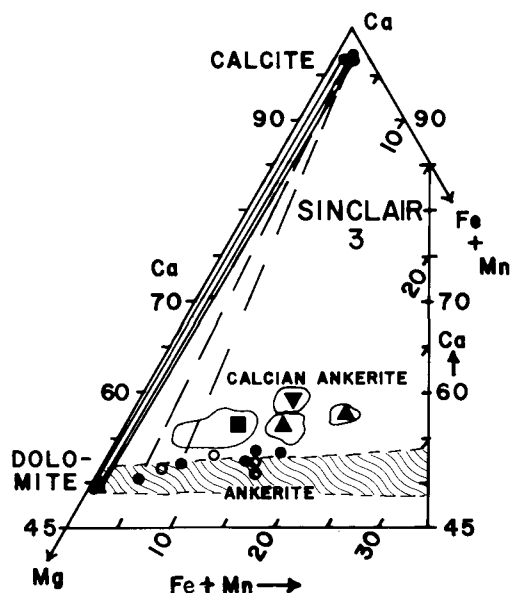


FIG. 5. Average compositions of carbonate minerals at various depths in Sinclair 3 in system Ca-Mg-(Fe+Mn) in atomic %. Solid symbols indicate equilibrated phases, open symbols relict phases. Triangles and square indicate average calcian ankerite composition (see text for further discussion). Coexisting phases connected by the lines, dashed where tentative. Shaded area indicates compositional range of ankerites in biotite zone metamorphic rocks after Essene (1983).

Manganese is a ubiquitous minor element in authigenic carbonate (Tables I, II). The most manganiferous ankerite and calcite occur at the base of the carbonate cap at 1523 m. This general pattern may be repeated in Elmore 1, as ankerite and calcite are most Mn-rich at the base of the carbonate cap at 439 m (190°C), while calcite from the deeper chlorite-calcite zone contains significantly less MnO.

*Carbonate phase relationships.* Very little experimental work has been done on the phase relationship of carbonate minerals at temperatures less than 400°C, and essentially no work has been done on the calcite limb of the calcite-dolomite/ankerite solvus when Fe or Mn are present in the system. The presence of apparently coexisting calcite and

Table II. Average analyses of carbonate minerals from borehole Elmore 1, Salton Sea Geothermal Field. All wavelength dispersive analyses (15kV, 0.005 microamperes, 5-10  $\mu\text{m}$  spot sizes) unless otherwise indicated.

DEPTH	439	439	439	923.5	1064
TEMP. ( $^{\circ}\text{C}$ )	190	190	190	306	322
CHIP #	2	1+5	3	A11	A11
#ANALYSES	10	9	4	5	4
MINERAL	CALCITE	CALCITE	CALCITE	CALCITE	CALCITE
	(EDS)				
CaO	54.37	50.98	50.90	52.45	51.36
MgO	0.22	0.47	0.49	0.11	0.27
MnO	0.35	1.37	1.44	0.28	0.44
FeO	0.87	1.31	1.66	0.09	0.35
Equiv. CO <sub>2</sub>	43.66	42.17	42.40	42.08	41.10
$\Sigma$	99.46	96.30	96.89	95.01	93.52
Ca	0.977	0.948	0.942	0.988	0.981
Mg	0.006	0.012	0.013	0.005	0.008
Mn	0.005	0.020	0.021	0.006	0.007
Fe	0.012	0.019	0.024	0.002	0.005
CO <sub>2</sub>	1	1	1	1	1

#ANALYSES	4	10	10
MINERAL	DOLOMITE	ANKERITE	ANKERITE
		(EDS)	
CaO	29.80	29.11	29.28
MgO	20.17	11.87	11.00
MnO	0.35	1.05	1.45
FeO	0.89	11.56	11.70
Equiv. CO <sub>2</sub>	46.17	43.54	43.08
$\Sigma$	97.38	97.15	96.51
Ca	1.012	1.049	1.064
Mg	0.950	0.595	0.558
Mn	0.014	0.030	0.042
Fe	0.024	0.325	0.334
CO <sub>2</sub>	2	2	2

dolomite (Sinclair 3, Elmore 1) or calcite and ankerite (Elmore 1) at temperatures near 200  $^{\circ}\text{C}$  can be regarded as a natural 'experiment' from which some insight into the carbonate phase relationships may be gained.

The compositional trends of calcite coexisting with dolomite or ankerite are indicated in figs. 6 and 7. In both figures it is clear that the solvus limb, at temperatures near 200  $^{\circ}\text{C}$ , is oriented such that Mg increases as Fe + Mn increase. In fig. 7, a linear least-squares fit through individual wavelength dispersive analyses (A), or individual wavelength dispersive and average energy dispersive analysis (B), extrapolates to pure CaCO<sub>3</sub>. Thus, in the Fe-Mn free system, the calcite limb of the solvus is predicted to lie within 0.05% of pure calcite. The general agreement between WDS and EDS analyses lends confidence to this extrapolation. Emphasis in curve fitting has been put on WDS analyses because of their lower detection limits and greater precision. Calcite coexisting with dolomite usually contains < 3.5% (Fe+Mn)CO<sub>3</sub>, while that coexisting with ankerite contains > 3.5%

(Fe+Mn)CO<sub>3</sub>. Note that these calcites have an Fe:Mn ratio near 1:1 (fig. 7c), so that the predicted solvus limb extends from the Ca-Mg join into the quaternary system on the 1:1 Fe:Mn plane. The compositional trend observed for these natural calcites is at a high angle to the solvus limb trend (dashed line, fig. 6B) predicted from thermodynamic analysis of the Ca-Mg-Fe system by Bickle and Powell (1977).

The empirical phase relationships between calcite and dolomite/ankerite are shown in the Ca-Mg-(Fe+Mn) system in fig. 8, with the most accurately determined tie lines and probable solvus limits indicated for temperatures near 200  $^{\circ}\text{C}$ . These tie lines are in reasonable agreement with those reported in Essene (1983) for greenschist facies metamorphic rocks. In this figure, the most (Fe+Mn)-rich compositions of calcite and ankerite are indicated by the rectangles at the end of the two solvus trends. Siderite has been persistently reported in low concentrations (< 2% by weight, up to 9% maximum) in shale from the shallow portions of the geothermal system. No siderite has

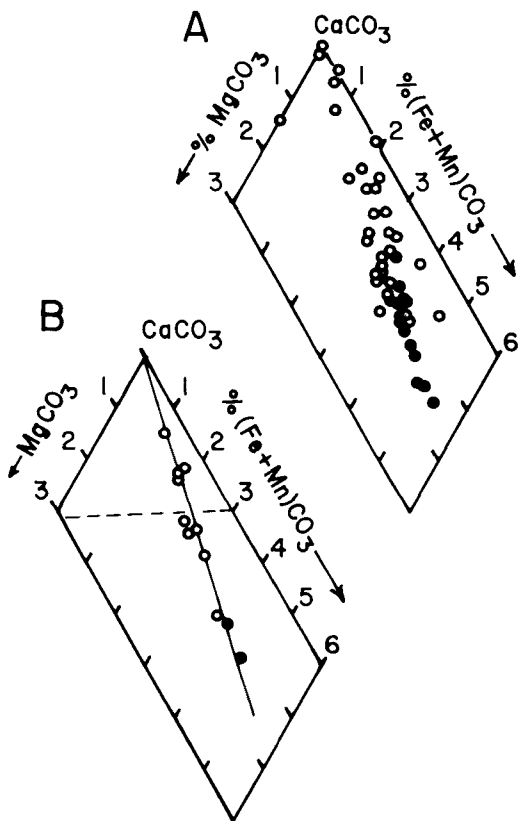


FIG. 6. Composition of calcite coexisting with dolomite or ankerite in Ca-rich portion of Ca-Mg-(Fe + Mn) system, in mol. %. A: Individual WDS (solid circles) and EDS (open circles) analyses from Elmore 1, 439 m depth (190 °C). B: Average WDS (solid circles) and EDS (open circles) analyses from Elmore 1, 439 m depth (190 °C) and Sinclair 3, 1523 m depth (234 °C). Solid line indicates linear regression trend from fig. 7 and provides estimate of calcite solvus limb position near 200 °C for 1:1 Fe:Mn ratio calcites. Dashed line in B shows solvus trend predicted by Bickle and Powell (1977) based on thermodynamic analysis of Mn-free Ca-Mg-Fe system.

been observed in any of the sandstones investigated despite extensive search. The presence of siderite in interbedded shales from these wells, however, suggests that the fluid phase is near saturation in siderite. If so, the (Fe + Mn)-rich limits observed for the carbonates may be close to the three phase ankerite-calcite-siderite assemblage as indicated in the figure.

The extrapolated, (Fe + Mn)-free carbonate composition at 200 °C has been used to construct the calcite limb of the dolomite-calcite solvus in the CaCO<sub>3</sub>-MgCO<sub>3</sub> system (fig. 9). The high-temperature end of the solvus has been drawn to be

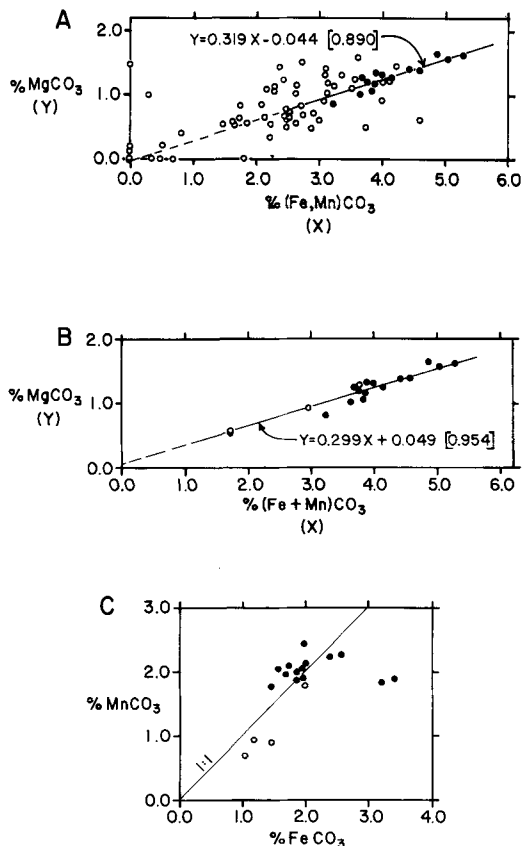


FIG. 7. Composition of calcite coexisting with dolomite or ankerite in mol. %. A: Individual WDS (solid circles) and EDS (open circles) analyses from Elmore 1, 439 m (190 °C) and Sinclair 3, 1523 m (234 °C). Linear regression (correlation coefficient in brackets) calculated using WDS analyses only. B: Individual WDS (solid circles) and average EDS (open circles) analyses from Elmore 1, 439 m (190 °C). All points used in regression, correlation coefficient in brackets. C: Same data as B, 1:1 Fe:Mn line shown for reference.

consistent with the unpublished 2 kbar experimental data of Fanelli and Wyllie (see Essene, 1983), since they also used electron microprobe rather than X-ray methods to determine phase compositions. No pressure correction has been made. The dashed line near 200 °C indicates the probable position of the solvus for calcites containing 5% (Fe + Mn)CO<sub>3</sub> based on fig. 8. We suggest that this calcite solvus be used as a working solvus for low-temperature, low-pressure geothermometry.

**Discussion.** The distribution of authigenic minerals in Sinclair 3 is summarized in Table III. Anhydrite is erratically distributed as a minor (< 2%) cementing phase throughout the well.



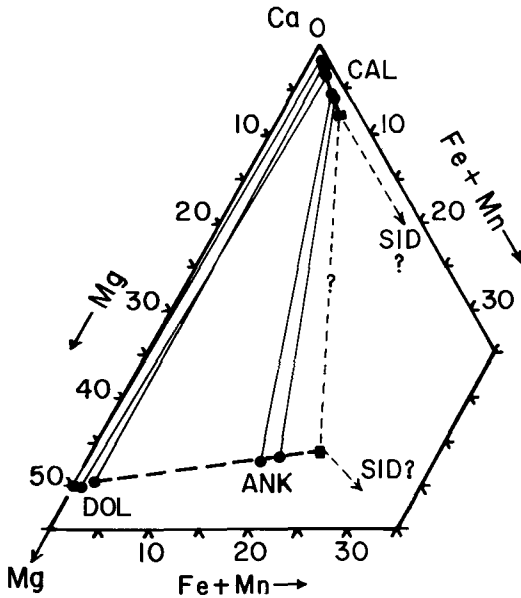


FIG. 8. Summary of coexisting calcite and dolomite-ankerite from Elmore 1 and Sinclair 3 in Ca-Mg-(Fe+Mn) system in atomic %, average analyses. The probable position of calcite (heavy solid line) and dolomite-ankerite (heavy dashed line) solvus limbs at temperatures near 200°C are indicated, and the most (Fe+Mn)-rich individual analyses are indicated by rectangles at each of solvus limb trends. A possible 3-phase calcite-ankerite-siderite assemblage is indicated by the short dashed lines and arrows.

Occasionally, as at 1141 m, it makes up to 40% by volume of some sandstone chips. These anhydrite-rich zones may represent relict evaporitic units, as cuttings ranging from anhydrite-rich sandstone to pure anhydrite are progressively more abundant in the shallower portions of the geothermal field. In the shallowest portions of many wells, they represent the only lithified non-shale cuttings observed.

The initial authigenic assemblage in Sinclair 3 is calcian ankerite + kaolinite + illite/smectite + pyrite + anhydrite. This assemblage, based on information from other wells, is characteristic of sandstone at temperatures of < 150°C. In the shallow, low-porosity zone calcian ankerite has extensively replaced quartz and feldspar. Sericite (illite/smectite) often appears to nucleate on detrital grain boundaries or to form networks along carbonate-carbonate contacts. Pyrite also occurs along such carbonate-carbonate contacts. There is little evidence of sericite replacement of feldspar in this zone. Authigenic chlorite is absent, and only large, rounded detrital chlorite is observed. Minor (< 3% by weight) but persistent amounts of

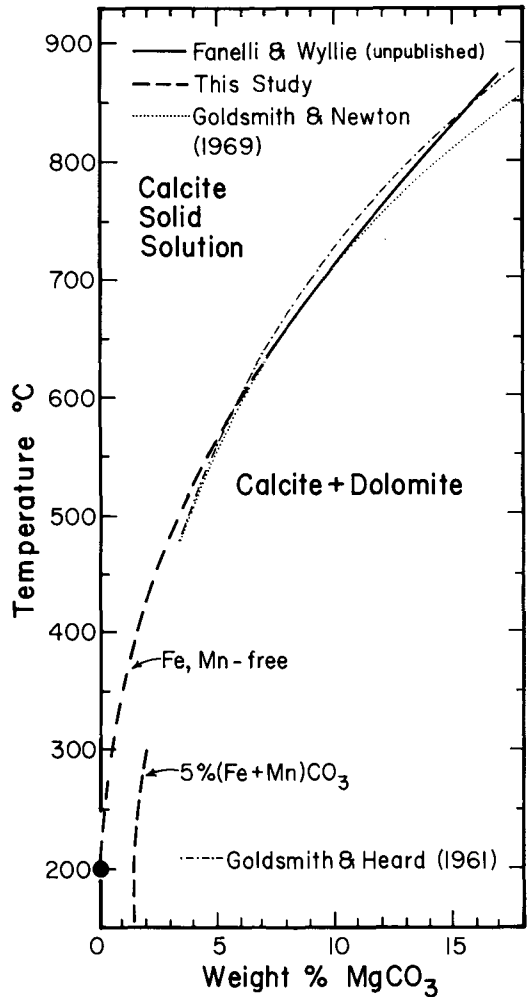


FIG. 9. Calcite limb of calcite-dolomite solvus in temperature (°C)-CaCO<sub>3</sub>-MgCO<sub>3</sub> diagram. Heavy dashed line marks position of projected (Fe+Mn)-free solvus from figs. 7-9 drawn to be consistent with 2 kbar experimental solvus at higher temperatures (heavy solid line) of Fanelli and Wyllie (unpublished). Estimated position of solvus at low temperatures with 5% (Fe+Mn)CO<sub>3</sub> in calcite (Fe = Mn) also shown. Other solvus estimates as indicated.

kaolinite are reported in X-ray diffraction analyses of sandstone cuttings.

At the top of the compaction interval near 900 m, X-ray analyses indicate kaolinite disappears and chlorite appears on increasing depth. Zen (1959) proposed that the reaction:

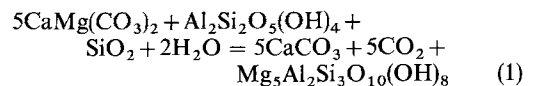
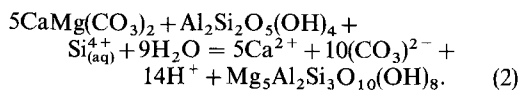


Table III. Distribution of authigenic minerals in borehole  
Sinclair 3.

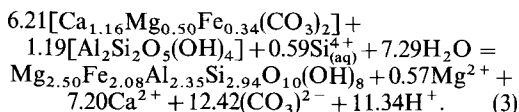
	Assemblage	Characteristics
	Calcian ankerite, minor kaolinite illite/smectite, pyrite, anhydrite	<7% porosity, >40% carbonate cement
----- 130-140°C (920±50 m) solution, kaolinite rxn -----		
Compaction Interval	Calcian ankerite, minor chlorite, illite/smectite, pyrite, anhydrite	<12% porosity, 35 to 25% carb. on inc. temperature
----- 150-170°C (1000-1140 m) CaAnk+Ank rxn -----		
	Ankerite, minor chlorite, illite/smectite, pyrite, anhydrite	<17% porosity, 20-25% carbonate
----- ~195°C (~1300 m) Ank+calcite rxn begins -----		
Carbonate cap = clay carbonate facies	Calcite + chlorite + quartz, minor illite/smectite, dolomite, pyrite, anhydrite	13-20% porosity 20-25% carbonate
===== 250-280°C (1600-1800 m) =====		
Chlorite- calcite zone, greenschist facies = reservoir rocks	Calcite+chlorite + quartz + illite, minor feldspar, pyrite, anhydrite, sphene	~20% porosity, 7-11% carbonate

was operative within the clay-carbonate facies, and was responsible for the coexistence of calcite and chlorite. In Sinclair 3, the kaolinite-to-chlorite transition occurs in the presence of calcian ankerite, where quartz is not stable and calcite not a product of the reaction. Reaction 1 is thus a limiting reaction for the concentration (activity) of aqueous silica,  $\text{Ca}^{2+}$ , and  $(\text{CO}_3)^{2-}$  in the fluid phase. A more realistic reaction is:



The above reactions could be adjusted using thermodynamic activities to allow for the addition of Fe and Al to chlorite, and of Fe and Ca to dolomite in the natural minerals. However, the activity-composition relationships of both chlorite and ankerite are very poorly understood at present.

If the actual mineral compositions are used, and the assumption is made that ankerite is the only source of Fe or Mg for chlorite, reaction 2 becomes:



An average chlorite composition from a depth of 1353 m was used, as this is the shallowest available chlorite analysis from this well.

There is a possibility that the kaolinite-to-chlorite reaction is metastable. Detrital layer silicate

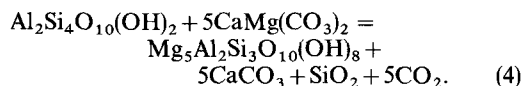
minerals such as biotite, muscovite, and chlorite are preserved metastably to temperatures as high as 200°C with no evidence of chemical re-equilibration (McDowell and Elders, 1983) in highly cemented sandstone from Elmore 1. On increasing temperature, the abrupt removal of carbonate cement at the base of the carbonate cap and movement of fluid into sandstone initiates reaction of the detrital layer silicates. A similar situation may occur in Sinclair 3, with kaolinite preserved metastably in the low porosity zone, and reaction to chlorite near 900 m depth initiated when significant cement was removed and fluid access occurred.

At the base of the compaction interval, calcian ankerite reacts to ankerite, and only ankerite is observed at greater depths. Throughout this interval the carbonate content decreases slightly and porosity increases very little. Thus the calcian ankerite-to-ankerite reaction, in which almost 25% of the rock is transformed, is close to a constant volume reaction. The Fe/Mg ratio of the original calcian ankerite is preserved in the reaction, while Ca and  $\text{CO}_2$  are lost to the fluid phase. No other phases can be shown to participate in this reaction.

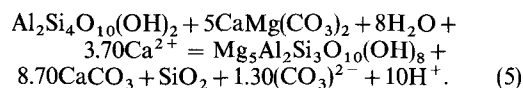
The first evidence of reaction of ankerite to calcite occurs at 1315 m (200°C) and by 1400 m (215°C) almost all sandstone chips show evidence of this reaction. Relict ankerite is still observed at 1577 m (243°C). Since total carbonate content and porosity remain constant in this entire interval, the ankerite to calcite reaction also appears to be a

constant volume reaction as far as the carbonate minerals are concerned. This reaction is responsible for the first abundant (up to 8%) authigenic chlorite observed in Sinclair 3. In addition, the following other changes are observed: (1) quartz overgrowths first occur; (2) authigenic dolomite occurs in trace amounts; (3) alteration of feldspar to illite is significant; (4) the K-feldspar content (bulk X-ray) decreases; (5) illite/15% smectite transforms to illite (clay X-ray); and (6) pyrite is produced. The non-equilibrium solution of detrital K-feldspars provides a local Al source for chlorite formation, as well as K for the smectite to illite transformation (Hower, *et al.*, 1976; Boles and Franks, 1979). The transformation of smectite to illite may also be an Al source.

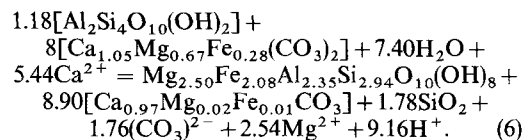
A plausible equilibrium mineralogical reaction that represents the reaction of ankerite to calcite with the production of chlorite may be written if the pyrophyllite component of illite/smectite clay is regarded as an Al-source:



This reaction does not satisfy the observation that the volume of calcite produced is approximately equal to the volume of ankerite reacted, although it may be useful as a limiting reaction. If a constant carbonate-volume restriction is added, and dolomite is regarded as the only Mg-source for chlorite formation, reaction 4 becomes:



Reaction 5 may then be modified using the actual mineral compositions as follows:



Since the volume of carbonate minerals reacted is significantly greater than that of the layer silicate minerals, it is clear that these reactions account for a small portion of the actual chemical exchange. The dominant reaction is that of the constant volume conversion of ankerite to calcite, which consumes Ca and releases significant Fe, Mg, and CO<sub>2</sub> to the fluid phase.

The prograde reaction sequence involves significant mass transfer between sandstone and fluid phase. In the compaction interval (130–170°C)

significant removal of Ca, Mg, Fe, and CO<sub>2</sub> from rock to fluid phase occurs, with most of that change occurring near 130°C (reaction 3). Deeper in the compaction interval, the similar Fe/Mg ratios of calcian ankerite and ankerite imply that, along with an absolute reduction in sandstone carbonate, Fe and Mg are lost in fixed proportions to the fluid phase. The Ca consumed by the deeper ankerite-to-calcite reaction may have been supplied by the shallower calcian ankerite-to-ankerite reaction, but both reactions produce significant amounts of Fe, Mg, and CO<sub>2</sub>. A further reduction in carbonate content from about 20 to 10% at the base of the carbonate cap implies further loss of all carbonate mineral components from sandstone.

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