GL03063

L. J. PATRICK MUFFLER DONALD E. WHITE

AREA

U.S. Geological Survey, Menlo Park, California

EARTH SCIENC

Active Metamorphism of Upper Cenozoic Sediments in the Salton Sea Geothermal Field and the Salton Trough, Southeastern California

Abstract: The Salton Sea geothermal system is entirely within Pliocene and Quaternary sediments of the Colorado River delta at the north end of the Gulf of California. At the time of deposition, these sediments consisted of sands, silts, and clays of uniform original mineralogic composition, but under the elevated temperatures and pressures of the geothermal system they are being transformed to low-grade metamorphic rocks of the greenschist facies. We have studied these transformations by X-ray, petrographic, and chemical analyses of cuttings and core from deep wells that penetrate the sedimentary section.

Temperatures within the explored geothermal system range up to 360° C at 7100 feet. The wells produce a brine containing over 250,000 ppm dissolved solids, primarily Cl, Na, Ca, K, and Fe, plus a host of minor constituents.

The original sediments consisted of detrital quartz, calcite, K-feldspar, plagioclase, montmorillonite, illite, dolomite, and kaolinite. Discrete montmorillonite is converted to illite at temperatures below 100° C, and illite-montmorillonite is completely converted to K-mica at temperatures below approximately 210° C. Ankerite forms by the conversion of calcite, dolomite, or both, at temperatures as low as 120° C, possibly as low as 80° C. Dolomite, ankerite, kaolinite, and Fe⁺⁺ (probably from the brine) react to produce chlorite, calcite, and CO₂ at temperatures as low as 180° C and possibly as low as 125° C. At temperatures greater than approximately 290° to 310° C, iron-rich epidote and K-feldspar become abundant, calcite disappears, and K-mica is sporadic. Detrital Na-Ca plagioclase persists throughout the explored system, and at depth exists out of equilibrium with metamorphic albite. The most common metamorphic assemblage at temperatures of 300° C and above is quartz + epidote + chlorite + K-feldspar + albite \pm K-mica. Pyrite, sphene, and hematite are also sporadically present.

Similar metamorphism occurs in the sedimentary section penetrated by the Wilson No. 1 well, drilled to a depth of 13,433 feet 22 miles south-southeast of the geothermal field. The lower-temperature reactions observed in the Salton Sea geothermal field also occur in Wilson No. 1, but at much greater depths owing primarily to the lower temperature gradient. Temperatures in this well reach only 260° C, insufficient for the formation of epidote and the destruction of calcite and K-mica.

The mineralogical transformations taking place in the Salton Sea geothermal field are metamorphic responses to the elevated temperatures and pressures. Some transformations such as the reaction of dolomite, ankerite, and kaolinite to produce chlorite, calcite, and CO_2 are regional in extent and pose no metasomatic requirements other than that the system be open to H₂O and CO_2 . Other relationships, such as the destruction of calcite and K-mica and the complementary formation of epidote, may involve interchange of elements with the brine.

The Salton Sea geothermal system displays a continuous transition from sediments through indurated sedimentary rocks to low-grade metamorphic rocks of the greenschist facies. This transition encompasses transformations commonly considered as diagenetic, and takes place without the formation of zeolites.

Geological Society of America Bulletin, v. 80, p. 157-182, 9 figs., 2 pls., February 1969

157

CONTENTS

Introduction	158
Geologic setting	160
Sample nature and instrumental technique	163
Cuttings and core from I.I.D. No. 1 well	164
Mineral composition	164
Chemical composition	169
Sportsman No. 1 well	169
Wilson No. 1 well	170
Temperatures of mineral changes	175
Metamorphic environment	177
References cited.	179
Figure	
1. Index map of the Salton Trough	159
2. Map of the Salton Sea geothermal field	160
3. Occurrence of major minerals in cuttings from	
I.I.D. No. 1	165
4. Variation in chemical composition of cuttings	
from I.I.D. No. 1	171
5. Occurrence of major minerals in cuttings from	
Sportsman No. 1	172
6. Occurrence of major minerals in cuttings from	
Wilson No. 1	173
7. Variation in chemical composition of cuttings	
from Wilson No. 1.	175

8 0	8. Mineral occurrence as a function of temperature measured in wells in the Salton Trough 175
3	9. Isothermal section at 325° C through the log
4	fo, log fsT diagram for the Fe-O-S sys-
4	tem
9	
9	Plate
0	
5	1. Photomicrographs of metamorphic epidote See
7	in core from 4920 feet in I.I.D. No. 1 Plate
9	2. Photomicrographs of metamorphosed sand- stone from I.I.D. No. 1
9	Table
ń	1. Wells drilled in the Salton Sea geothermal field
	1960 to 1965
5	2. Chemical analyses (in parts per million) of brine
-	from LLD. No. 1, brine from LLD. No. 3.
1	and water from Wister mudpots 161
•	3 Composition of chlorites from LLD No. 1 geo-

thermal well	166
4. Chemical analyses of cuttings from I.I.D. No. 1	
geothermal well	170
5. Chemical analyses of cuttings from Wilson No.	

INTRODUCTION

The Salton Sea geothermal field is at the southeastern end of the Salton Sea in the Imperial Valley of southeastern California (Fig. 1). Since 1960, 10 wells (Fig. 2 and Table 1) ranging in depth from 1695 to 8100 feet have been drilled for geothermal energy and for the elements carried in solution in the hot geothermal brine (Table 2; Helgeson, 1967, Table 3). The U.S. Geological Survey has co-operated with the private companies that control the wells in the study of the geologic, geochemical, and geophysical aspects of the field. The present paper deals with the mineralogical and chemical changes that occur with depth in the rocks penetrated by the I.I.D. No. 1 and Sportsman No. 1 wells. These changes are compared with those that occur in the Wilson No. 1 well, drilled 22 miles south-southeast of the field to a depth of 13,443 feet. All three wells were drilled in siltstones and sandstones that had similar mineralogical and chemical composition at the time of deposition. Samples from all three wells display both increasing induration and a regular sequence of mineral changes with depth; with increasing depth and temperature, some detrital minerals drop out, whereas other minerals are formed.

White and others (1963) reported on the

mineralogy of four pieces of core from two cored intervals of I.I.D. No. 1 and one piece of core from Sportsman No. 1 and tentatively concluded that these rocks were the product of active metamorphism of relatively young rocks. This conclusion is substantiated and amplified in the present paper. Grubbs (1964) reported on his studies of cuttings and core from I.I.D. No. 1. The early exploration of the Salton Sea geothermal field was summarized by McNitt (1963, p. 31–33).

Various aspects of the Salton Sea geothermal field have recently been described. Muffler and Doe (1968) studied the chemical and mineralogical composition of Colorado River delta sediments and the Cenozoic sedimentary rocks that fill the Salton Trough, and presented isotopic evidence that the detritus of these sediments is of Precambrian age. Doe and others (1966) showed that most of the lead and strontium in the geothermal brine was leached at depth from Cenozoic sedimentary rocks. Skinner and others (1967) described the metalrich scales deposited from the I.I.D. No. 1 geothermal brine during a 90-day production test. Helgeson (1967) discussed some of the physiochemical aspects of rock-water interactions with reference to the Salton Sea geothermal system.

Data presented here from the I.I.D. No. 1

and Sportsman No. 1 wells were collected from samples supplied by O'Neill Geothermal, Inc. Data on the Wilson No. 1 were collected from samples supplied by Standard Oil Company of California. We wish to acknowledge the courtesies and co-operation extended to us by E. T. Anderson of O'Neil Geothermal, Inc., H. W. Diamond of Morton Salt Company, H. C. Helgeson of Shell Development Company (now of Northwestern University), F. A. MacDougall of Shell Oil Company, and R. W. Rex of California Research Corporation (now of the University of California at Riverside).

We are greatly indebted to B. A. Morgan, III, H. P. Taylor, Jr., and E-an Zen for thorough and helpful reviews. This paper has also benefited from the comments and suggestions of M. C. Blake, Jr. and D. S. Coombs.



Figure 1. Index map of the Salton Trough.



Figure 2. Map of the Salton Sea geothermal field.

GEOLOGIC SETTING

The Salton Sea geothermal field lies near the axis of the Salton Trough, which is the sediment-filled northern extension of the structural trough occupied by the Gulf of California (Fig. 1). Various faults of the San Andreas system extend into the Salton Trough from the north-west.

The Salton Trough is filled primarily with silt and fine-grained sand deposited by the Colorado River as part of its delta (Muffler and Doe, 1968). Coarser detritus of local provenance occurs at the edges of the trough. The oldest delta rocks of the trough are probably early Pliocene but may be Miocene. Seismic and gravity data (Biehler and others, 1964) suggest that the maximum depth to basement material of seismic velocity = 5.4 to 6.4 km/sec is 20,000 feet along the axis of the Salton Trough.

The Gulf of California coincides with the intersection of the East Pacific rise and the North American continent, and the general positive heat-flow anomaly of the East Pacific Rise extends into the continent. Heat-flow measurements in the central and southern parts of the Gulf of California average about 3.3 microcal/cm²/sec (Von Herzen, 1963), more than double the oceanic average of about 1.5 microcal/cm²/sec.

The landward extension of this heat-flow anomaly to the north is uncertain, but it almost certainly extends the length of the Salton Trough. Superimposed on the broad anomaly are two areas that have heat flows that are 4-to-10 times normal. Both of these areas are

Well	Company	Town- ship (east)	Range (south)	Sec- tion	Location	Com- pletion date	Depth (feet)	Maximum measured temp. (: C) (Helgeson, 1968)
Sportsman No. 1	O'Neill Geothermal, Inc.	13	11	23	SW14NE14	2-61	4729	310
I.I.D. No. 1	O'Neill Geothermal, Inc.	13	11	23	Center NW¼	3-62	5232	328
Sinclair No. 3	Western Geothermal	13	12	10	NW¼NW¼	5-63	6922	250
River Ranch No. 1	Earth Energy, Inc.	13	11	24	Center of W¼, NW¼	12-63	8100	345
I.I.D. No. 2	Shell Development	13	11	22	NE¼SE¼	12-63	5820	330
Elmore No, 1	Earth Energy, Inc.	13	11	27	NW14SW14	4–64	7117	360
State of Calif. No. 1	Shell Development	13	11	23	SE¼NW¼	5-64	4838	310
Sinclair No. 4	Western Geothermal	13	12	4	SW14SE14	5-64	5306	•••
Hudson No. 1	Earth Energy, Inc.	13	12	13	NW¼SE¼	7-64	6118	•••
I.I.D. No. 3	Imperial Thermal Prod.	13	11	23	Center of North boundary	3-65	1695	200

TABLE 1. WELLS DRILLED IN THE SALTON SEA GEOTHERMAL FIELD, 1960 TO 1965

	I.I.D. No. 1 ¹	I.I.D. No. 3 ²	Wister mudpots
Estimated depth of occurrence	3500-5000 feet	~1575 feet	surface
Temperature of occurrence	~300° C	~105° C	21° C
Density	1.21	1.023	1.014
pH (25° C)	5.2	7.5	7.1
SiO ₂	400	120	59
Al	4.2	2	6(?)
Fe	2290	0.7	0.8
Mn	1400	6.4	0.9
Ca	28,000	1130	79
Mg	54	74	325
Sr	400	85	4
Ba	235	3	<0.2
Na	50,400	10,600	6470
K	17,500	1250	466
Li	215	40	9.6
Rb	135		
Cs	14		
NH4	409	321	34
В	390	100	54
HCO3	>150	1880	4340
SO ₄	5	621	900
Cl	155,000	19,700	8480
F	15	1	14
Br	120	15	
I	18	4.5	••
NO3		9	••
As	12	.16	
Cu	8		.05
Zn	540		
Pb	102		<.3
Ag	1		
Total sulfide as H2S	16		
TOTAL	258,000	35,600	21,240

Table 2. Chemical Analyses (in parts per million) of Brine from I.I.D. No. 1, Brine from I.I.D. No. 3, and Water from Wister Mudpots

¹ I.I.D. No. 1: Values for all constituents except As, Cu, and I are recalculated from analyses of brine and condensed vapor separated at the well head during eruption on April 21, 1966. Mass flow of vapor was 18.8 percent of the total mass flow (H. C. Helgeson, written commun., 1966). Analysis by D. E. Donaldson and C. E. Roberson. Contents of As, Cu, and I are recalculated assuming 18.8 percent vapor from values given by White (1965) for erupted brine alone.

² I.I.D. No. 3: Analysis by C. E. Roberson of sample collected at well head March 18, 1965.

³ Wister mudpots: Analysis of all constituents except those noted below by D. E. Donaldson on sample collected April 19, 1966. Analysis for Li by R. Schoen on sample collected November 8, 1963. Al, Fe, Mn, Sr, Cu, and Pb recalculated from quantitative emission spectrographic analysis of evaporated residue by R. E. Mays.

underlain by late Cenozoic sediments of the Colorado delta and are marked by Quaternary volcanism and modern hot-spring activity.

One of these areas is at Cerro Prieto, Baja California, Mexico, about 20 miles southsoutheast of Mexicali (Fig. 1) where a rhyodacite volcano rests on the alluvial surface of the Colorado River delta. East and south of the volcano is an extensive area of very active hot springs and mud pots. The Mexican government has explored this area for geothermal energy (Alonso Espinosa and Mooser, 1964; Anda and Parades, 1964). The second area of anomalous heat flow is the Salton Sea geothermal field, where Rex (1966) reports a natural heat flow of 7 microcal/ cm^2 /sec. Prior to drilling for geothermal power, the surface expressions of this heat flow consisted of Quaternary rhyolitic extrusions, feeble hot springs, and escape of carbon dioxide.

The rhyolite extrusions comprise five separate domes, two of which are topographically joined by reworked pumice and volcanic sediments related to the extrusions (Red Island). Each of the extrusions has a crude domal form (Kelley and Soske, 1936) that is essentially constructional but modified slightly by wave-cut benches related to various stands of late Pleistocene Lake Cahuilla. The extrusions are also partly enveloped by young alluvium and aeolian deposits. The potassium-argon age of one sample of obsidian from Obsidian Butte was determined by R. W. Kistler and John Obradovich to be ~16,000 years.¹ Thicknesses of hydrated rims on obsidian fragments in associated reworked pyroclastics are compatible with this date (R. L. Smith, oral commun., 1964). Three of the extrusions still display weak discharge of gases and water vapor from joints and cracks.

Visible surface discharge from the feeble hot springs around the southeast end of the Salton Sea (Fig. 2) probably does not exceed 20 gal/min. However, neither evaporation nor discharge of thermal water directly into the Salton Sea nor the complex agricultural drainage network of the area can be estimated accurately, and the total natural discharge from the geothermal system could be over 100 gal/min. The major area of hot-spring activity is one mile southeast of Mullet Island; this area is now covered by the Salton Sea. The hotspring groups are aligned along two northwesttrending lineaments (Fig. 2). The northeastern lineament is on the projection of the Mission Creek-Banning fault from its last outcrop just northeast of the Salton Sea. These lines of hot springs probably mark upward leakage of hot water from faults at depth.

The Imperial Carbon Dioxide Gas Field (Rook and Williams, 1942) was in production from 1934 to 1954 but is now abandoned. CO_2 was produced commercially from at least 54 wells from depths ranging from 500 to 700 feet at pressures that initially exceeded hydrostatic (White, 1955). The origin of this CO_2 is discussed later in this paper and also in Muffler and White (1968).

Evidence presented by Muffler and Doe (1968) indicates that sediments deposited in

the Salton Trough have been of similar chemical and mineralogical composition throughout the late Cenozoic. Sediments in and adjacent to historical channels of the Colorado River have uniform mineralogical composition (quartz + calcite + plagioclase + K-feldspar + dolomite + montmorillonite + illite + kaolinite + accessories). Holocene sediments on alluvial fans at the base of mountains adjacent to the Salton Trough, however, differ mineralogically from the Colorado River detritus, primarily in the small amounts of calcite, the absence of dolomite, and the presence of appreciable amphibole and chlorite. These mineralogical criteria distinguish Cenozoic sedimentary rocks derived from the Colorado River from locally derived rocks. This analysis leads to the conclusion that the bulk of the sediment and sedimentary rock in the Salton Trough was indeed derived from the upper Colorado River drainage basin (Muffler and Doe, 1968; Merriam and Bandy, 1965).

The Wilson No. 1 well provides critical evidence supporting this conclusion. This well is located near the axis of the Salton Trough (Fig. 1) and penetrates sediments and sedimentary rocks to a drilled depth of 13,443 feet. The cuttings and core from this well are texturally, chemically, and mineralogically identical to Colorado River delta sediment at depths shallower than 3000 feet. At greater depths the samples are texturally and chemically similar to Colorado River delta sediment but display some mineralogical differences. The mineralogical changes through the deeper 10,000 feet of this well are similar in nature and sequence to the changes that occur at depths less than 2000 feet in the geothermal field.

We show in this paper that the changes in mineralogy with depth in the geothermal field and in Wilson No. 1 correlate primarily with temperature and secondarily with other intensive metamorphic variables. We have found no features that seem better explained by differences in the sources of sediment. In particular, admixture of sediment similar in composition to recent alluvium from the Chocolate Mountains east of the geothermal field appears inadequate to explain the variations in mineralogy with depth in the geothermal field. Any original differences in chemical composition and mineral abundances with depth in the geothermal field and in Wilson No. 1 appear to reflect differences in grain size and sorting rather than differences in provenance.

¹ The sample was collected from a flow ridge of obsidian approximately 1100 feet east of the summit of Obsidian Butte. Analytical data: $K_2O = 4.17$ percent; moles $Ar^{40}/gm = 9.9 \times 10^{-14}$; $\lambda_{\Sigma} = 0.584 \times 10^{-10}$ yr⁻¹; $\lambda_{\beta} = 4.72 \times 10^{-10}$ yr⁻¹; $K^{40} = 1.22 \times 10^{-4}$ gm/gmK. According to Obradovich (written commun., 1967), the age cannot exceed 55,000 years, based on the most extreme argon 40/38 and 38/36 ratios that can be measured on the one mass spectrometer run.

SAMPLE NATURE AND INSTRUMENTAL TECHNIQUE

Cuttings from the I.I.D. No. 1 and Sportsman No. 1 were available from approximately every 100 feet. Cuttings from the Wilson No. 1 were spaced at closer intervals, but were studied only every 100 feet.

Core from the I.I.D. No. 1 was taken at two intervals; 4477 to 4484 feet, and 4917 to 4923 feet. A single sample of core from Sportsman No. 1 at 4662 feet was available. Core from Wilson No. 1 was from 7375 to 7391 feet, 10,455 to 10,476 feet, 11,372 to 11,382 feet, 12,910 to 12,940 feet, and 13,377 to 13,407 feet. The core samples from the I.I.D. No. 1 and Sportsman No. 1 were described briefly by White and others (1963).

In view of the paucity of core, the only way to determine the sequence and nature of the mineral and chemical changes in the sedimentary rocks with depth was to utilize the cuttings. Cuttings have some advantages in the present study in that they approximate a channel sample of the drilled interval, thus smoothing out local differences in lithology such as between adjacent sand and silt beds. On the other hand, cuttings have several severe limitations: (1) some material may be derived from other than the stated interval, especially if sloughing from shallower depths in the well has occurred, (2) cuttings may not represent the stated intervals if much drilling fluid is lost to the wall rocks, and (3) cuttings may be contaminated by drilling additives, including montmorillonite, barite, rubber tires, sawdust, wood chips, and paint. All these additives except montmorillonite and barite can be recognized and removed. Montmorillonite can be washed from the deeper, indurated cuttings and is a severe problem only in the unconsolidated shallow parts of the wells. Barite was a severe contaminant only at depth in the Wilson No. 1.

Fortunately, in coherent rocks such as those found at depth in the Salton Sea geothermal field, the problems of using cuttings are not insurmountable, and their use permits the rapid acquisition of an over-all picture of the mineral changes with depth. In the strictest sense, only the first appearance of a phase with depth is completely reliable; sloughing must be considered for deeper appearances. In the wells considered here, however, sloughing is minor and can be recognized readily if it occurs in any significant amount. For example,

enough kaolinite to be detectable on an X-ray diffractogram at 4000 to 5000 feet depth in I.I.D. No. 1 is clearly anomalous, inconsistent with adjacent samples, and must be due to sloughing from shallower depths. Independent evidence that slumping was usually slight has been provided by very consistent trends in O^{18}/O^{16} in carbonates and silicates with depth (Clayton and others, 1968). The final criterion is essentially a consistency argument; the mineral changes detected by studying cuttings are consistent internally and in relation to available core, temperature data, data from other wells, and geologic considerations. Clearly anomalous and contaminated samples are few and are discarded.

Each sample of cuttings consisted of angular fragments ranging in size from 0.1 mm to 10 mm and had been split several times using unspecified techniques before we acquired them. Using a Jones-type riffle splitter, about 80 grams was split from the sample we received and was crushed to 16 mesh. This 16-mesh product was then split using a microsplitter to about 4 grams, and tramp iron (from the drill string and casing) was removed with a hand magnet. Any obvious contamination from drilling additives was removed at this time. The 16-mesh sample was then ground for 15 minutes in a Fisher mechanical mortar and pestle. Grain size after grinding ranged up to about 40 microns (see Tatlock, 1966, p. 6-9, for a discussion of optimum grain size and grinding time for X-ray diffraction analysis). The samples were then packed in a standard Norelco aluminum sample holder with a 1 \times 2 \times 0.16-cm cavity for the sample. Packing technique was standardized after that of Tatlock (1966, p. 34).

Samples were run on Norelco X-ray diffractometers from 4° 2θ to 36° 2θ at 1°/minute at 400 cps full-scale deflection with Cu radiation. The I.I.D. No. 1 and Sportsman No. 1 data were collected on the same machine at 35 kv and 35 ma, using a focusing monochromator, a scintillation counter, and no β -filter. The Wilson No. 1 data were collected on a different unit at 35 kv and 35 ma, but with a Geiger tube, β -filter, and no focusing monochromator. Peak heights of specific minerals on diffractograms of different samples from I.I.D. No. 1 and Sportsman No. 1 can be compared semiquantitatively, but direct comparison of these data with the Wilson No. 1 data must take into account the differing analytical conditions.

A prominent peak for each identified mineral was selected, and the height of this peak above background was measured on each diffractogram on which the mineral was detected. The relative abundance of this mineral in successive samples is semiquantitatively proportional to the measured peak height over background of the selected peak on successive diffractograms. We imply no simple correspondence between peak height and absolute abundance. In addition, the relative abundance of different minerals in the same sample can be estimated only in qualitative terms, for the relationship between peak height and the amount of the mineral in the sample is different for each individual mineral (see Schultz, 1964, for a discussion of quantitative interpretation of mineralogical composition from X-ray and chemical data). We scanned each sample only once and made only one mount; however, considering the lack of precision and accuracy inherent in each sample of cuttings, this is all the expenditure of time and effort that can be justified. Replicate analyses, internal standards, and more precise sample preparation are unlikely to affect our general conclusions, and could be justified only if it were possible to insure that all of the sample came from its stated depth. This wholesample X-ray diffraction technique is semiquantitative at best.²

Petrographic techniques were used to a lesser degree and served primarily as control on the diffraction studies, for the detection of phases not readily distinguished on the diffractograms (*for example*, sphene and epidote in small amounts), and for textural information. Thin sections were made approximately every 500 feet from chips selected from cuttings under a binocular microscope. The sandstones are amenable to petrographic work; the siltstones are at or below the lower grain-size limit for effective thin-section study.

The X-ray diffraction analysis of cuttings samples has certain limitations that must be kept in mind. The minerals detected in a cuttings sample do not rigorously define a mineral assemblage of co-existing phases, for the cuttings may be considered as composite "channel" samples. In addition, phases present in amounts too small to be detected on the diffractograms may be significant in specifying the intensive variables that determine a specific assemblage. The distribution of oxides and sulfides is a case in point. Despite these limitations, however, the X-ray diffraction technique does allow an over-all determination of the changes in mineralogy with depth. Owing to the nature of the cuttings samples and the grain size of much of the rocks, this determination could be made using other techniques only at great expense of time and effort, if at all.

CUTTINGS AND CORE FROM I.I.D. NO. 1

The samples from I.I.D. No. 1 display relatively uniform textures and consist of interbedded fine-grained sandstones and siltstones, which are poorly sorted. The sandstones commonly contain considerably more than 10 percent clay-size matrix, and are wackes in the classification of Gilbert (Williams and others, 1955). Bedding in core is subhorizontal (White and others, 1963). The rocks cannot be correlated in detail with upper Cenozoic formations that crop out around the Salton Basin, and show no stratigraphic variation except that the upper 2000 feet has a higher ratio of silt to sand than the lower 3000 feet. Texturally, the sands and silts are similar to modern sediment of the Colorado River delta and to outcropping upper Cenozoic sedimentary rocks of the Salton Basin, interpreted by Muffler and Doe (1968) and by Merriam and Bandy (1965) as part of the Colorado River delta.

With increasing depth in the well, the rocks display progressive mineralogical changes that are the main subjects of this paper. We conclude that these changes are caused by active hydrothermal metamorphism rather than by differences in depositional environment or in provenance. These mineral changes are accompanied by an increase in density and degree of lithification, and the rocks at depth are tough rocks of low metamorphic grade. No schistosity or slaty cleavage is developed but subvertical fractures, some filled with hydrothermal minerals, are observed sporadically.

Mineral composition. Figure 3 shows the distribution of minerals in I.I.D. No. 1 as determined from whole-sample X-ray diffraction. Each mineral has a separate ordinate scale that represents the height of the diffraction peak indicated as measured in inches above back-

² The diffraction data presented in this paper (Figs. 3, 5, 6, and 8) were collected in 1966 and 1967. Preliminary data from each well were collected in 1963 and 1964 under experimental conditions that varied within each series. The earlier data display more scatter and are less reliable than the later data but are qualitatively similar and lead to identical interpretations.





Figure 3. Occurrence of major minerals in cuttings from I.I.D. No. 1. Minerals present only sporadically or in quantities below detection on a whole-sample diffractogram are not shown (anhydrite, sphene, hematite, apatite, biotite, sphalerite, chalcopyrite, and pyrrhotite). Dashed lines indicate anomalies probably due to sloughing from walls at depths shallower than the indicated depth. See text for source of temperature data.

ground on the diffractogram. Several minerals present sporadically in minor quantities are not shown on Figure 3, but are discussed below.

The original depositional mineral suite of the Colorado River delta consists of dominant quartz and calcite and subordinate dolomite, plagioclase, K-feldspar (both monoclinic and triclinic), montmorillonite, illite, and kaolinite (Muffler and Doe, 1968). Minerals such as magnetite, hydrous iron oxides, gypsum, zircon, apatite, leucoxene, clinozoisite, biotite, and chlorite that are present in trace quantities in Colorado River delta sediments are probably also present in the shallow I.I.D. No. I cuttings but are not detected on the whole-sample X-ray diffractograms.

Discrete montmorillonite with a basal spacing of approximately 15A is the dominant clay mineral in Colorado River delta sediment (Muffler and Doe, 1968). In the vicinity of I.I.D. No. 1, montmorillonite is abundant in the surface sediments and to a depth of at least 140 feet in shallow holes bored for temperature measurements. However, whole-sample diffractograms of cuttings from I.I.D. No. 1 display no discrete 15Å peak, even in the shallowest available sample.³ Pronounced asymmetry of the 10Å illite peak to low 2θ suggests the presence of subordinate amounts of interlayered montmorillonite to depths of ~1800 feet.4 In addition, X-ray diffraction studies of oriented air-dryed and glycolated clay-mineral slides at 1070, 1310, and 1470 feet showed detectable interlayered montmorillonite. Neither wholesample X-ray diffraction nor X-ray analysis of oriented slides detected any montmorillonite at depths greater than ~ 1800 feet.

Application of Weaver's (1956) criteria indicate that this montmorillonite is randomly interlayered with illite and suggests a decrease in the amount of expandable interlayered material with depth. However, recent work (Reynolds, 1967) suggests that randomly interstratified illite-montmorillonite does not produce a 001/001 diffraction maximum between ~15Å and ~11Å. Some features considered diagnostic of mixed-layer clays may merely reflect grain size (E-an Zen, written commun., 1967).

Our data thus suggest that montmorillonite, both as a discrete phase and interlayered with illite, is converted to K-mica. The disappearance of interlayered montmorillonite takes place at temperatures below $\sim 210^{\circ}$ C (The approximate temperature corresponding to ~ 1800 feet in I.I.D. No. 1; Helgeson, 1968), and the conversion of discrete montmorillonite at even lower temperatures. These relations are compatible with the experimental work of Khitarov and Pugin (1966). In their experiments, montmorillonite moistened beforehand with 10 percent KC1, dehydrates and converts to 10Å "hydromica" at $\sim 125^{\circ}$ C under pressures of less than 1000 atm.

⁸ Small amounts of discrete montmorillonite were detected on oriented air-dryed and glycolated clay mineral slides but probably represent contaminant from drill mud.

⁴Maxwell and Hower (1967) suggest that this effect may be an intrinsic feature of illites with respect to muscovite and need not indicate mixed layering.

Ankerite occurs as sharply bounded idioblastic rhombohedra disseminated through siltstones and sandstones in the interval between 700 and 1700 feet. Calcite and dolomite also occur in all samples from this interval, and siderite was identified at 940 and 1070 feet. X-ray difraction study of whole samples and mineral separates indicates no compositional gradation between dolomite and ankerite; the positions of the 1014 peaks are constant at 2.92Å for ankerite and 2.89Å for dolomite.

Experimental data on the system CaCO₃-MgCO₃-FeCO₃ (Rosenberg, 1967) at 350° to 550° C show no miscibility gap between ankerite and dolomite, and no indication of a three-phase field of ankerite, dolomite, and calcite. Siderite can co-exist stably with ankerite and calcite at 350° to 550° C but not with dolomite. Unless the phase relations are strikingly different in the temperature range of 120° to 200° C at which the I.I.D. No. 1 ankerite exists, the association of ankerite and dolomite is probably not in equilibrium with any of the other carbonate phases.

The mechanism by which the ankerite forms is not certain. Perhaps the simplest explanation is a reaction of calcite with Mg^{++} and CO_3^{--} from the brine, and with Fe⁺⁺ either from the brine or from detrital iron oxides. A depletion of calcite in the ankerite zone is indicated by the whole-sample X-ray data for I.I.D. No. 1 (Fig. 3) and is supported by the Sportsman No. 1 and Wilson No. 1 data discussed below. The high CO_2 pressures known to exist at shallow depths in the geothermal system would promote CO_3^{--} and drive the reaction forward. The whole-sample X-ray data (Fig. 3) show no depletion of dolomite in the ankerite zone. Partial destruction of dolomite, however, cannot be detected with confidence owing to the closeness of the 1014 dolomite and ankerite peaks. Each peak augments the peak height of the other, leading to exaggerated apparent abundance of both minerals. If a real decrease in dolomite is thus masked in the X-ray data, several reactions involving dolomite become possible. Perhaps the most plausible (taking into account the decrease in calcite) is $2CaCO_3$ + $3CaMg(CO_3)_2$ + $2Fe^{++}$ + $2CO_3^{--}$ $\rightarrow 5CaMg_{.6}Fe_{.4}(CO_3)_2$.

Neither of the above reactions, however, helps to explain why Mg is enriched in the spring waters relative to the brines at depth in the geothermal system. Augmentation of Mg⁺⁺ in the fluid phase at shallow depths may possibly be attained by cation exchange of Fe⁺⁺ from the brine for Mg⁺⁺ in the dolomite to produce ankerite.

Major mineralogic transformations occur between depths of 1200 and 2300 feet in I.I.D. No. 1. Through this interval, kaolinite, dolomite, and ankerite decrease in abundance and disappear, and chlorite becomes abundant.⁵

Seven samples of chlorite from cuttings and

⁵ The identification of chlorite versus kaolinite in the whole-sample X-ray diffractograms is based on the recognition of the 001 and 003 peaks of chlorite (when in sufficient abundance for these peaks to be detected) and on the discrimination of the 004 peak of chlorite (25.2° $2\theta_{Cu}$) and the 002 peak of kaolinite (24.9° $2\theta_{Cu}$). The identifications were corroborated in some samples by separate X-ray analysis of the clay fraction.

TABLE 3.	Compositions o	F CHLORITES	FROM I.I.D.	No. 1	Geothermal	Well
----------	----------------	-------------	-------------	-------	------------	------

[Fe₂O₃, FeO, and MgO determined by wet chemical analysis (Lois M. Jones, analyst). Al^{IV} determined by d_{001} spacing (Shirozu, 1958). Formula used assuming no Fe³⁺ from secondary oxidation: [Mg(Al^{VI}, Fe³⁺)y]_{12-x}Fe_x²⁺ Si_{8-y}Aly^{IV}O₂₀(OH)₁₆. Si, Al^{VI}, and (OH) were not determined; the values given for these constituents are determined by the assumptions inherent in the chlorite formula used.]

		Atoms per 20 oxygen							
			1	2		5	3		
Depth									Fe
(feet)	Contaminants	Mg	AlVI	Fe ³⁺	Fe ²⁺	Si	Al ^{IV}	(OH)	Fe + Mg
1870	K-mica, quartz, trace calcite	7.32	2.07	0.71	1.90	5.22	2.78	16	.27
2320	K-mica, trace quartz	7.28	2.13	0.61	1.98	5.26	2.74	16	.27
3070	Quartz, K-mica	8.00	2.13	0.35	1.52	5,52	2.48	16	.19
3120	K-mica	7.05	2.08	0.58	2.29	5.34	2.66	16	.29
3610	K-mica, quartz	8.24	2.18	0.44	1.14	5.38	2.62	16	.16
4920	Trace K-feldspar and quartz	6.68	1.95	0,67	2.70	5.38	2.62	16	.32
5020	Trace K-feldspar and quartz	7.05	1.51	1.11	2.33	5.38	2.62	16	.33

core of I.I.D. No. 1 were concentrated by settling in water and were analyzed by partial wet chemistry and X-ray diffraction (Table 3). These chlorites are of clay size (<5 microns), and we were unable to achieve further purification by normal heavy liquid or magnetic techniques. However, because the principal contaminants are K-mica, quartz, calcite, and Kfeldspar, the ratios of Fe++, Fe+++, and Mg are not affected (with the minor exception of some Mg and Fe in K-mica, which is probably phengitic). The formula calculated depends on whether Fe+++ is assumed to be the product of secondary oxidation or whether it is considered as a normal constituent of chlorites (Foster, 1962, p. A16). The latter is viewed as the more probable assumption.

The two deepest chlorite samples (which are also the only two that have no K-mica contamination) are richer in both Fe^{++} and Fe^{+++} than the other samples (this is best shown by the Fe/Fe+Mg ratios in Table 3). Fe/Fe+Mgratios at shallower depths are erratic and perhaps reflect differing concentrations of Fe in their associated interstitial liquids.

Zen (1959, p. 36) proposed the reaction dolomite + kaolinite + quartz + water = calcite + chlorite + carbon dioxide, and noted (Zen, 1960, p. 156–157) that this reaction could explain the calcite-chlorite assemblage found in the Castleton, Vermont, metamorphic rocks. The mineralogic changes indicated by our data from the Salton Sea geothermal system can be incorporated in a similar equation that considers the role of ankerite:

> dolomite ankerite $4CaMg(CO_3)_2 + 5CaMg_{.6}Fe_{.4}(CO_3)_2$

kaolinite

 $+ 2.5 \text{Al}_2 \text{Si}_2 \text{O}_5 (\text{OH})_4 + \text{Fe}^{+3} + \text{H}_2 \text{O} + 1.5 \ 0^{-2}$ chlorite

 $+ 9CaCO_3 + 9CO_2$.

This formulation neglects the possible role of montmorillonite. The iron required could come from the iron-rich brine that permeates the rocks, with oxygen from magnetite and hydrous iron oxides in the sediments, or from montmorillonite.

The formation of chlorite by this reaction does not demand any through-flow of brine or fixation of brine constituents other than H_2O .

For the reaction to take place, however, the system must have available water and must also permit CO_2 to escape. CO_2 produced in this reaction is more than ample to account for the quantity concentrated at shallow depths in the Salton Sea geothermal system (Muffler and White, 1968). Effluents from the thermal springs of the area are also rich in CO_2 .

Epidote is first detected at 3100 feet, is sporadic to 4100 feet, and then abundant to the bottom of the well. Epidote occurs both as veinlets and as idioblastic crystals disseminated in the rock (Pl. 1). The composition of epidote separated from core at 4920 feet is indicated by both optics and X-ray diffraction to be almost exactly Ca₂Al₂Fe⁺³Si₃O₁₂(OH) (Keith and others, 1968).

Calcite gradually decreases in abundance from 2800 to 3900 feet and is sporadic at greater depths. We suspect that some traces of calcite below 4100 feet in I.I.D. No. 1 are due to sloughing in the well from shallower depths, and this suspicion has been confirmed in a few samples by O^{18} studies of cuttings (R. N. Clayton, unpub. data, 1964).

The decrease in calcite and the complementary increase in epidote are considered to be related; that is, Ca^{++} from the calcite is incorporated in the epidote. The liberated CO_2 migrates upward and provides part of the CO_2 of the thermal spring effluents and the shallow reservoirs of the Imperial Carbon Dioxide Gas Field.

Iron in the epidote is almost certainly derived from the iron-rich brine that saturates the rocks. However, iron in the brine is almost all ferrous, whereas iron in epidote is ferric. The mechanism for this oxidation of iron is not clear. Somewhat the same problem is raised by the formation of hematite in the rocks. Silica and alumina in the epidote may be derived from other silicates, most probably muscovite (illite) and quartz. 10Å white mica shows a decrease in abundance at depths greater than 2500 feet. Perhaps the relations can be represented by a complex reaction such as:

 $\begin{array}{ccc} Muscovite & Calcite & Quartz\\ K_2Al_4Si_6Al_2O_{20}(OH)_4 + 4 CaCO_3 + 6 SiO_2 \end{array}$

 $\begin{array}{c} \text{Epidote} \\ + \text{ 2 Fe}^{+3} + 30^{-2} \rightarrow 2\text{Ca}_2\text{Al}_2\text{Fe}^{+3}\text{Si}_3\text{O}_{12}(\text{OH}) \end{array}$

 $\begin{array}{c} & Carbon \\ K-feldspar & Dioxide \\ + 2 KAlSi_3O_8 + 4 CO_2 + H_2O \ . \end{array}$

Calcium, aluminum, and silicon in epidote are not derived primarily from plagioclase, for detrital calcic plagioclase persists in the intensely altered epidote-bearing rocks of I.I.D. No. 1.

The 3.24Å K-feldspar peak plotted on Figure 3 represents both clastic K-feldspar and newly formed K-feldspar. Clastic microcline and monoclinic K-feldspar are present in the modern sediments of the Colorado River delta and in the upper Cenozoic delta rocks exposed around the Salton Basin (Muffler and Doe, 1968). Microcline displaying textural relations indicating a detrital origin persists in most of the metamorphosed rocks at depth in I.I.D. No. 1, and much of the monoclinic Kfeldspar seen in these rocks also is detrital, judging by textural criteria. However, some of the monoclinic K-feldspar at depth displays sharply bounded crystalloblastic forms that suggest a hydrothermal origin. Secondary K-feldspar unequivocally formed in the present geothermal environment occurs as veins transecting the bedding and replaces plagioclase in other wells of the Salton Sea geothermal system, but such relations have not been detected in available samples from I.I.D. No. 1. The K-feldspar considered by textural criteria to be secondary is exclusively monoclinic.

Original detrital plagioclase of the Colorado River delta sediments consists primarily of albite, although subordinate plagioclase as calcic as labradorite is present (Muffler and Doe, 1968). Much of the plagioclase in the most intensely altered and metamorphosed rocks of I.I.D. No. 1 still shows detrital form. Indices of refraction indicate a compositional range from albite to labradorite; the more sodic varieties are dominant.

We did not expect calcic plagioclase to persist into environments favorable for the formation of chlorite, epidote, and albite, particularly in view of the hydrothermal breakdown of calcic plagioclase to albite and other reaction products at Steamboat Springs, Nevada, at depths as little as 200 feet and temperatures as low as 160° C (Schoen and White, 1965; Sigvaldason and White, 1962). We suspect that the extraordinarily high Ca-content of the Salton Sea brine may allow calcic plagioclase to persist metastably to temperatures where breakdown to albite would otherwise occur.

We have identified secondary albite in thin sections of the cleaner medium-grained sandstones. We strongly suspect that secondary albite is also present in the dirty fine-grained sandstones and siltstones, where optical discrimination of felsic minerals is very difficult.

K-feldspar and plagioclase change in abundance with depth, reflecting the interaction of several processes. Variation in the ratio of sand to silt of the Colorado River detritus would cause the abundances of the two feldspars to vary sympathetically; the sands are richer in feldspars than the silts (Muffler and Doe, 1968). Contribution from a local source area (for example, the Chocolate Mountains to the northeast) would be displayed as an increase in both feldspars and as a variation in relative abundance. Hydrothermal augmentation is a third process that is effective, at least locally, at depth. The available data do not permit discrimination of these three processes in the deeper part of I.I.D. No. 1 where both Kfeldspar and plagioclase are augmented (Fig. 3). However, consideration of the mineral distribution in all nine deep wells in the geothermal field fails to show any correlation that can be interpreted stratigraphically, other than the relatively low feldspar content of the upper 2000 feet, reflecting primarily the finer grain size of the younger Colorado River sediments.

Sphene is a ubiquitous, although minor, metamorphic mineral at depths below 2500 feet. It occurs as clots up to 200 microns across, composed of crystals generally averaging 5 to 10 microns but ranging up to 20 microns in the coarser sediments (Pl. 2, fig. 1). This mineral cannot be detected on the whole-sample X-ray diffraction traces, for its major peak (3.23A) is masked by a major peak of K-feldspar, and the minor peaks are all too small to be seen in the quantities present. The maximum amount of sphene that could occur in these rocks is about 2 percent (as calculated from the maximum ${\rm Ti}O_2$ content observed in chemical analyses of cuttings; some TiO2 is undoubtedly incorporated in other minerals). This amount of sphene is too small to appreciably augment the 3.24A K-feldspar peak. Titanium in the sphene is presumably derived from the disseminated leucoxene in the original sediments.

Anhydrite is a sporadic mineral throughout the well and is probably a modification of authigenic gypsum in the original sedimentary rocks (Muffler and Doe, 1968).

Hematite is a common, although minor, constituent of the most highly metamorphosed rocks in the well. For example, in the 4920foot core, hematite co-exists with pyrite, epidote, chlorite, K-feldspar, quartz, and plagioclase. Hematite separated from this core has the following unit-cell parameters: a = b = 5.03Å, c = 13.74Å, $V_r = 100.41$ Å³. Application of this value of V_r to figure 3-28(b) of Nagata (1961) indicates that the hematite is essentially pure Fe₂O₃, assuming that no elements other than titanium substitute for iron in the hematite.

Pyrite is detected by binocular examination of the cuttings at depths greater than 2100 feet and becomes conspicuous on the diffractograms at all depths greater than 3000 feet. Chalcopyrite and sphalerite are present sporadically from 2000 to 5232 feet, the total depth of the well. Chalcopyrite appears in the cuttings as discrete crystals and as veinlets cutting siltstone. Sphalerite occurs as irregular masses in sandstone (Pl. 2, fig. 1) but has not been seen in veinlets. Grubbs (1964) reports that sphalerite occurs from 2130 to 4100 feet and that the color of the sphalerite gradually changes from yellow at the shallowest depths to black at 4100 feet.

Thin-section study of the sandstones indicates that overgrowths of quartz on original subangular detrital grains of quartz are common at depth. The original detrital forms can commonly be observed by outlines of inclusions (Pl. 2, fig. 2).

Chemical composition. Samples of cuttings were chemically analyzed at depth intervals of approximately 500 feet (Table 4), using splits of the samples studied by X-ray diffraction. The variation in chemical composition with increasing depth (Fig. 4) reflects the changing mineral content of the rocks, and several oxides in the rocks at depth are significantly augmented or depleted.

Several oxides decrease significantly with depth and correlative increasing temperature and pressure. The decrease of CO2 with depth is related to the breakdown of dolomite and ankerite at 1500 to 2400 feet and the gradual decrease in the abundance of calcite below 2800 feet. CaO decreases from 2300 feet to 4500 feet, owing to the breakdown of calcite, and only partial fixing of the released CaO in newly formed epidote; the remaining CaO presumably dissolves in the brine. The high CaO at 5210 feet reflects the abundant epidote in the sample. The large decrease in \tilde{H}_2O^- between 0 and 2000 feet is due primarily to the breakdown of montmorillonite and hydrous ferric oxides; H₂O+ shows little significant change.

Total iron remains fairly constant at shallow

depths but increases sharply below ~ 3700 feet, correlative with the abundant epidote, chlorite, pyrite, and hematite at depth. Although total iron is nearly constant at shallow depths, FeO increases and Fe₂O₃ decreases in the uppermost 1300 feet. Ferric iron in the original sediments is present in appreciable amounts only in the hydrous ferric oxides and magnetite. Accordingly, some of the ferrous iron required for the formation of ankerite must be derived from reduction of ferric iron originally in the sediments rather than directly from the brine.

The high FeO at depths below ~ 3800 feet correlates primarily with the abundant chlorite. The high Fe₂O₃ in the pyrite-rich sample at 5210 feet is illusory, for in these rapid-rock analyses Fe in pyrite is reported as ferric iron.

MnO and TiO₂ show little change with depth. MgO, although occurring as an essential or significant constituent in dolomite, ankerite, chlorite, illite, and montmorillonite, is very nearly constant with depth. All of the Mg in the original clastic carbonates and clay minerals is evidently represented at depth by Mg in chlorite, and very little has been dissolved or redistributed by the brine. Analyses of brine from I.I.D. No. 1 (Table 2) show a remarkably low proportion of Mg to Ca (54/28,000, or 0.0019), in spite of the fact that Mg is abundant and is available for solution in the brine as successive Mg-bearing minerals become unstable. One of the authors (White) has been impressed with the crude relationship between Mg/Ca and temperature in natural waters; the ratio tends to be high at low temperatures (3.2 in ocean water) and is low at high temperatures. This helps to explain why Mg is relatively immobile in the thermal system and why, with upward migration of thermal brine, the proportion of Mg to total dissolved solids increases slightly.

Variations in K_2O , Na_2O , SiO_2 , or Al_2O_3 in response to the hydrothermal environment are obscured in great part by variation in the ratio of sand to silt in the original detritus. The relatively low Na_2O and SiO_2 with correlative high Al_2O_3 in the 1000- to 2000-foot interval reflect the higher proportion of silt and clay in these samples. Likewise, the relatively high Na_2O and K_2O at depth reflect in part the more abundant sands. However, the very high K_2O at 4090 and 4485 feet may well reflect hydrothermal addition of K-feldspar.

SPORTSMAN NO. 1

The Sportsman No. 1 well is located ap-

Depth (feet)	Near surface²	460	890	1310	1680	2220	2840	3520	4090	4485	5210
SiO ₂	56.0	56.2	59.2	51.5	51.6	55.0	57.9	57.5	57.1	57.3	58.7
Al_2O_3	12.7	12.1	11.9	15.6	14.1	13.7	13.6	15.6	16.2	15,2	15.0
Fe ₂ O ₃	3.5	2.7	2.1	2.0	1.8	1.5	1.3	2.0	1.6	2.0	4.4
FeO	.6	1.0	1.7	2.8	2.8	2.7	2.8	2.6	5.8	5.3	4.0
MgO	2.8	3.3	2.5	3.2	3.2	3.1	2.7	3.2	2.6	3.2	2.8
CaO	6.8	7.7	6.5	6.0	8.7	8.5	7.1	6.6	3.3	2.6	6.0
Na2O	1.1	1.3	1.1	. 87	1.1	1.2	1.8	2.5	1.5	2.0	1.3
K_2O	2.6	2.5	2.6	2.8	3.0	2.9	3.6	4.7	6.9	6.5	4.0
H ₂ O ⁻	3.7	3.0	2.2	2.7	1.6	.68	.53	.24	.22	.68	.18
H_2O^+	3.6	3.1	3.0	2.7	3.7	3.7	2.9	2.2	3.1	3.1	2.4
TiO_2	.58	.50	.52	.62	.61	.61	.61	.75	.72	.72	.70
P_2O_5	.18	.16	.15	.16	.18	.18	.17	.19	.20	.18	.21
MnO	.05	.06	.07	.04	.02	.04	.08	.12	.13	.13	.10
$\rm CO_2$	5.6	6.1	6.1	7.1	7.5	5.9	4.4	1.7	.62	.56	.06
Total Total iron	100	100	100	1003	100	100	99	100	100	99	100
as FeO	3.8	3.4	3,6	4.6	4.4	4.0	4.0	4.4	7.2	7.1	8.0

TABLE 4. CHEMICAL ANALYSES¹ OF CUTTINGS FROM I.I.D. NO. 1 GEOTHERMAL WELL

¹ Rapid chemical analyses using X-ray fluorescence supplemented by methods described in Shapiro and Brannock (1962). Analysts: Paul Elmore, Sam Botts, Gillison Chloe, Lowell Artis, and H. Smith.

² Mean of 6 modern Colorado River delta sediments.

 3 Total at 1310 depth includes 1.7 percent reported as "volatiles other than H₂O and CO₂." This probably represents carbonaceous material (lignite) present in small quantities.

proximately one-fourth mile east of the I.I.D. No. 1 well. The Sportsman well also penetrates fine-grained, poorly sorted sandstones and siltstones of the Colorado River delta throughout its entire depth. Although the lack of recognized stratigraphic horizons precludes any detailed correlation between the wells, no evidence suggests significant stratigraphic differences or major structural displacements between the wells. However, fault displacements of small magnitude almost certainly have occurred, and one cannot assume that rocks at a given depth in Sportsman No. 1 correlate precisely with rocks at the same depth in I.I.D. No. 1.

Variations in mineral content of the Sportsman No. 1 with depth are, as in I.I.D. No. 1, due to hydrothermal metamorphism in the high-temperature environment of the geothermal system. Although cuttings samples were not available at depths shallower than 700 feet and between 970 and 2010 feet, the available samples indicate (Fig. 5) that the distribution of minerals with depth and temperature in Sportsman No. 1 is very similar to that in I.I.D. No. 1. Kaolinite, dolomite, and ankerite are present in the interval from 700 to 970 feet but are conspicuously absent at all greater depths. Chlorite is detected in only one of the

four samples from 700 to 970 feet but is abundant in all samples from greater depths. These mineral relations are similar to those observed in I.I.D. No. 1, and substantiate the reaction of kaolinite, dolomite, and ankerite to produce chlorite inferred from the I.I.D. No. 1 data. As in I.I.D. No. 1, montmorillonite decreases in abundance with depth, and 10Å mica is absent in the most intensely metamorphosed rocks at depths greater than 4100 feet, where mica may have been converted to K-feldspar. Calcite, abundant at depths shallower than 3900 feet, is essentially absent at greater depths, whereas epidote and pyrite are abundant below 4000 feet. Indeed, all the metamorphic minerals detected in the better sampled I.I.D. No. 1 are also detected in Sportsman No. 1, and the metamorphic reactions inferred from I.I.D. No. 1 may also be inferred from Sportsman No. 1 at equivalent temperatures and depths.

WILSON NO. 1

The Wilson No. 1 well is a dry oil test drilled in 1963 by Standard Oil Co. of California in the SW1/4 sec. 20, T. 14 N., R. 15 E. Through its total depth of 13,443 feet, the well penetrates fine-grained, poorly sorted sandstones and siltstones of the Colorado River delta (Muffler and Doe, 1968). Although mineral changes do occur with increasing depth, they are best explained by diagenetic processes and weak hydrothermal metamorphism and do not reflect stratigraphic or provenance discontinuities. Detailed temperature-depth profiles from the well are not available, but rock temperature at the bottom of the well is approximately 260° C (R. W. Rex, oral commun., 1964). The linear temperature gradient interpolated from this temperature is 60° C per km or 1° C per 50 feet of depth, which is about twice the gradients observed in the Los Angeles and Ventura basins (Philippi, 1965).

The low-temperature mineralogical transformations outlined for the I.I.D. No. 1 well are detected also in the Wilson No. 1 cuttings (Fig. 6). The order of mineral changes in the two wells is identical, although each change extends over a much greater depth range in Wilson No. 1 than in the much hotter I.I.D. No. 1 (Fig. 3). Temperatures in Wilson No. 1 evidently are not sufficiently high or fluid compositions are not appropriate for the development of epidote, pyrite, and hematite. However, veinlets of galena occur in core from 11,372 feet.

Ankerite is the first new mineral to form with increasing depth, as in I.I.D. No. 1 and Sportsman No. 1, and ankerite similarly drops out at shallower depths (and lower temperatures) than does dolomite. The relations among kaolinite, dolomite, ankerite, and chlorite in Wilson No. 1 are compatible with the reaction inferred from the I.I.D. No. 1 data. As in I.I.D. No. 1, there is a zone in which both kaolinite and chlorite are present, and a somewhat larger zone in which both dolomite and chlorite are present. Dolomite persists to the bottom of Wilson No. 1, but abruptly decreases in abundance below 12,500 feet, and we suspect that dolomite is absent at depths only a little greater than the bottom of the well.

Discrete montmorillonite, the dominant clay mineral of the Holocene Colorado River delta sediments (Muffler and Doe, 1968), does not occur at depths greater than 4200 feet in Wilson No. 1. Montmorillonite is common at shallower depths, both in whole-sample diffractograms



Figure 4. Variation in chemical composition of cuttings from I.I.D. No. 1. Data plotted at zero depth are the means of chemical analyses of six Holocene sediments from the Colorado River delta in the Salton Trough.



4,

BEST AVAILABLE ESTIMATES OF TEMPERATURES WITHIN WELL AFTER DRILLING

Figure 5. Occurrence of major minerals in cuttings from Sportsman No. 1. Minerals present only sporadically or in quantities below detection on a whole-sample diffractogram are not shown. Epidote is present sporadically in cuttings from 3440 to 3830 feet and is common at greater depths, although not in sufficient abundance to appear on the whole-sample X-ray diffraction traces.



BEST AVAILABLE ESTIMATES OF TEMPERATURE WITHIN WELL AFTER DRILLING

Figure 6. Occurrence of major minerals in cuttings from Wilson No. 1. Minerals present only sporadically or in quantities below detection on a whole-sample diffractogram are not shown (anhydrite, barite, pyrite, galena). Barite powder derived from the drilling mud contaminates the cuttings at depths greater than 3800 feet and particularly at depths greater than 10,900 feet, and the cuttings could not be completely freed from this contaminant. Although natural barite was observed in small quantity in thin section of core at 11,455 feet depth, any natural barite that may be in the cuttings at depths is masked by the barite contaminant.

and in oriented clay mineral slides, but some contamination by drill-mud montmorillonite cannot be precluded. Accordingly, 4200 feet is the maximum depth for the persistence of discrete montmorillonite in Wilson No. 1, as compared to the maximum depth of 1000 feet in I.I.D. No. 1. Proportionate depths of montmorillonite in the two wells and similar proportions for distributions of some other minerals suggest that the observed montmorillonite is largely natural rather than a drill-mud contaminant.

Illite, subordinate to montmorillonite in the original Colorado River delta sediment, persists throughout Wilson No. 1. At depths less than 11,000 feet, illite with approximately 25 percent interlayered montmorillonite is also present; X-ray traces of oriented clay slides show a conspicuous sharpening of the 10Å peak upon glycolation, as well as the development of a low, broad peak in the 11-to-16Å range. Using the criteria of Weaver (1956), there is some suggestion that the percentage of interlayered expandable material decreases with depth.

At depths greater than 11,000 feet, the illite contains no detectable montmorillonite layers. The 10Å peak is sharp and displays no change in shape upon glycolation. We have not yet been able to concentrate the K-mica sufficiently to determine whether or not there is a polymorph change of K-mica with increasing depth.

The changes in montmorillonite and illite with depth in Wilson No. 1 are similar to those in I.I.D. No. 1 but occur at considerably greater depths. Our observations in both wells are compatible with those of Burst (1959), who described the progressive diagenetic conversion of montmorillonite to illite in the subsurface Wilcox Formation of the Gulf Coast. Burst found that interlayered illite-montmorillonite displayed a progressive loss of swelling characteristics with depth, and that at depths greater than 14,000 feet no swelling characteristics were evident. The depths below which no swelling was evident in Wilson No. 1 and I.I.D No. 1 are, respectively, ~11,000 feet and ~1800 feet.

In addition, Burst suggested conversion of montmorillonite to chlorite, which he found to be more abundant at depth than near the surface. He did not consider the possible role of kaolinite in this relationship, for kaolinite appears to be a minor constituent of the Gulf Coast rocks considered (Burst, 1959, p. 335). In the Salton Sea geothermal field and Wilson No. 1, however, conversion of kaolinite is the dominant reaction, although montmorillonite may be involved to some extent.

Chemical analyses of cuttings from Wilson No. 1 are available for six samples to a depth of 9420 feet (Table 5; Fig. 7). The analyses of cuttings from depth differ little from those of the shallower samples or from the average of six Holocene silts and sands from the Colorado River delta in the Salton Basin. The mineralogical changes of Figure 10 are not reflected in differences in the bulk chemical composition through the deepest sample of Table 5. There

Depth (feet)	2040	3580	4680	6600	7800	9420
SiO ₂	57 7	56.6	55.7	55.8	53.4	54.5
AloOa	12.5	13.8	13.7	12.7	13.9	13.6
Fe ₂ O ₃	3.3	2.4	2.9	2.8	2.0	1.8
FeO	.82	1.8	1.4	1.5	2.3	2.7
MgO	2.3	3.1	2.7	2.7	2.9	3.4
CaŎ	6.3	6.0	6.6	6.4	7.3	7.4
Na ₂ O	1.0	1.1	1.1	.85	1.0	.58
K ₂ O	2.1	2.7	2.3	2.4	2.8	3.1
H_2O^{-}	3.3	2.1	2.8	2.0	1.7	1.1
H_2O^+	4.0	3.4	4.0	3.4	3.6	3.3
TiO ₂	.54	.58	.56	.55	.58	.57
P_2O_5	.15	.17	.16	.16	.17	.19
MnO	.06	.05	.08	.08	.07	.07
$\rm CO_2$	5.3	6.0	5.9	6.3	7.6	7.7
Total	99	100	100	98	99	100
Total Fe as FeO	3.79	3.96	4.01	4.02	4.1	4.32

TABLE 5. CHEMICAL ANALYSES¹ OF CUTTINGS FROM WILSON NO. 1 WELL

¹Rapid chemical analyses using X-ray fluorescence supplemented by methods described in Shapiro and Brannock (1962). Analysts: Paul Elmore, Sam Botts, Gillison Chloe, Lowell Artis, and H. Smith.



Figure 7. Variation in chemical composition of cuttings from Wilson No. 1. Data plotted at zero depth are the means of chemical analyses of six Recent sediments from the Colorado River delta in the Salton Trough.

is no significant over-all addition or removal of iron or magnesium in the formation of chlorite from dolomite and kaolinite, or in the formation of ankerite. The progressive decrease of H_2O^- and complementary slight increase of most other constituents with depth is due to the diagenesis or weak metamorphism that has affected the rocks. The progressive decrease of H_2O^- reflects in part the breakdown of discrete montmorillonite at shallow depths, and the breakdown of montmorillonite interlayered with illite at depths greater than 4000 feet. Fe₂O₃ decreases with depth (as in the shallower 4000 feet of I.I.D. No. 1), and FeO shows a complementary increase.

TEMPERATURES OF MINERAL CHANGES

The mineralogical data of Figures 3, 5, and 6 are re-plotted on Figure 8 in order to show the relationships between mineral occurrence and temperature that are common to I.I.D. No. 1, Sportsman No. 1, and Wilson No. 1. The correspondence of temperatures of mineral changes in the three wells is only approximate, but considering the many sources of imprecision in the data, it appears significant.

The temperature data for I.I.D. No. 1 and Sportsman No. 1 (Figs. 3, 5, and 8) are taken from Figure 4 of Helgeson (1968) and are the best available estimates of temperatures within the wells after drilling. These data were collected intermittently in undisturbed wells from November 1963 through August 1966, and according to Helgeson (1968) have an over-all uncertainty range of \pm 5° C.

However, these temperature-depth profiles need not represent the original formation temperatures before drilling. The temperature gradient in a geothermal well can be severely distorted by several phenomena: (1) Fluid circulated during drilling cools the rock adjacent to the well, and temperatures measured too soon after drilling ceases are low. (2) Upflow of hot fluids in a producing well heats the ground adjacent to the well, particularly near the surface where the temperatures were originally lowest. (3) Convection may occur in a standing well, causing near-surface temperatures to be too high and deep temperatures to be too low. (4) Aquifers at differing pressures can be connected and "short-circuited" by the well, with resulting circulation of fluid either upward or downward.

The temperatures shown on Figures 3 and 6 for I.I.D. No. 1 and Sportsman No. 1 were measured several years after drilling; thus, cooling by drilling fluid is not significant. I.I.D. No.



ZOU Temperature in C*

Figure 8. Mineral occurrence as a function of temperatures measured in wells in the Salton Trough. Dashed lines indicate interpolation across intervals where cuttings are not available. Dotted lines indicate only the uncertainties in detection of the particular mineral. Uncertainties in temperature measurement and in extrapolation of measured temperatures to ground temperatures prior to drilling are discussed in the text. Minor original detrital chlorite not shown. Contaminants derived from sloughing at shallow depths in the well also not shown.

1 produced in excess of 500,000 pounds per hour of brine and steam during testing in 1962, and was tested intermittently after that time. It is therefore possible that the measured gradient is slightly high because of the testing but probably not by a significant amount. Helgeson (1968) concludes that the effects of convection in the I.I.D. No. 1 and Sportsman No. 1 wells are negligible, but O¹⁸ evidence presented by Clayton and others (1968), suggests that convection cannot be discounted. The measured temperatures in the upper parts of the drilled wells may be significantly higher than pre-drilling formation temperatures. The metamorphic reactions proposed from data from the I.I.D. No. 1 and Sportsman No. 1 wells may then occur at temperatures somewhat lower than shown on Figures 3 and 5.

The temperatures shown on Figures 6 and 8 for Wilson No. 1 were calculated assuming a straight-line gradient from the bottom-hole temperature of ${\sim}260^\circ$ C estimated by R. W. Rex (oral commun., 1964). Temperatures at intermediate depth, computed by this straightline gradient, are probably too low. Thermal conductivity of rocks of identical mineral composition increases with decreasing porosity because of the very low conductivity of water in pores. Average porosity decreases with depth in Wilson No. 1 owing to compaction, and therefore the temperature-depth curve would be expected to be convex to higher temperatures. This consideration may explain why ankerite and chlorite form at apparently lower temperature in Wilson No. 1 than in I.I.D. No. 1.

The major discrepancy between the temperatures at which minerals are found in I.I.D. No. 1 and the temperatures of the corresponding minerals in Wilson No. 1 lies in the fact that ankerite and dolomite persist to appreciably higher temperatures in Wilson No. 1. This discrepancy may reflect the inability of CO_2 to escape readily from the rocks in Wilson No. 1.

The available evidence suggests strongly that the observed mineral occurrences and the metamorphic transformations inferred from these occurrences reflect the present (predrilling) temperature environment and not some previous higher temperatures. We have detected no evidence of retrograde metamorphism. The natural expressions of the geothermal system (for example, the hot springs, the Holocene extrusions, and the shallow CO_2 reservoirs) all point to an active system. (The masking modern delta alluvium,

however, precludes observation of any direct evidence of more extensive hot spring activity in the past.) The deepest rocks are no older than late Pliocene, and the rocks in the geothermal field itself are mostly, if not entirely, Pleistocene; this leaves little time for a major temperature climax and reversal. Continuing sedimentation up to modern times provides increasing depths of cover and equivalent increasing insulation, assuming other factors to remain constant. In addition, O18 studies indicate that the carbonates in the rocks of the geothermal system are in or near isotopic equilibrium with the present geothermal fluids at temperatures at (or slightly below) temperatures measured in the various wells (Clayton and others, 1968).

Figures 3, 5, 6, and 8 all show apparent overlap between minerals on the opposite sides of the reactions proposed in this paper. For example, in I.I.D. No. 1, kaolinite, dolomite, ankerite, and chlorite occur together from 1300 feet to 1800 feet at temperatures of 155° C to 210° C; epidote and calcite occur together at depths of 3100 feet to 3800 feet and temperatures of 295° C to 310° C. Qualitatively similar overlaps have been found in all wells throughout the geothermal field and are not due merely to sloughing of cuttings from higher levels in the well, although this is a minor contributing factor. Major factors responsible for the overlap may include:

(1) Non-univariancy of the reactions, owing to dependence on factors such as fugacity of oxygen, fugacity of CO_2 , and the degree to which the reactions are open to constituents of the brine. In particular, the decarbonation reactions are dependent on the ease of escape of CO_2 from the system, and thus on porosity and permeability of the rocks.

(2) Non-stoichiometry of the phases, allowing a given reaction to proceed over an interval of temperature or other physical parameters.

(3) Kinetic considerations, including the history of the temperature regime at any given point and the rates of reaction (influenced in part by the relatively low solubilities in the brine of some constituents such as Mg and Al). The importance of disequilibrium is indicated by the persistence of dolomite in the presence of ankerite-calcite or ankerite-calcite-siderite, and by the persistence of detrital plagioclase having a wide range in An content.

In summary, the following are our best estimates of the lower temperature limits of the reactions proposed in this paper. The formation of ankerite by the conversion of calcite, dolomite, or both, takes place at temperatures below 120° C, possibly as low as 80° C. The reaction of dolomite, ankerite, and kaolinite to produce chlorite, calcite, and CO_2 can occur at temperatures lower than 180° C and possibly as low as 125° C. Epidote can form as low as 290° C. Conversion of montmorillonite to illite may begin at essentially surface temperatures; montmorillonite disappears as a discrete phase at about 100° C, and illite-montmorillonite is converted to K-mica at temperatures below 210° C.

METAMORPHIC ENVIRONMENT

The mineral assemblage of the most intensely metamorphosed rocks in I.I.D. No. 1 and Sportsman No. 1 is quartz + epidote + chlorite + K-feldspar + albite + pyrite \pm hematite \pm sphene \pm K-mica, and \pm metastable Na-Ca plagioclase. Anhydrite, pyrrhotite, sphalerite, and chalcopyrite are minor phases present only locally. The assemblage is com patible with the quartz-albite-muscovitechlorite subfacies of the greenschist facies (Turner and Verhoogen, 1960, p. 534–537).

The Salton Sea geothermal system displays a continuous transition from sediments through indurated sedimentary rocks to low-grade metamorphic rocks of the greenschist facies, without passing through the zeolite facies. This transition encompasses transformations commonly considered as diagenetic (Taylor, 1964, p. 417-418; Winkler, 1965, p. 6, Fig. 1), and the temperatures at which important mineralogic reconstitution has taken place are quite reasonable for the deeper parts of many sedimentary basins where the geothermal gradient is not anomalously high. One might predict that mineral transformation similar to those observed in the Salton Trough should be taking place in other basins, and indeed the data of Burst (1959) do indicate that very similar diagenetic transformations occur at depth along the Gulf Coast.

Most of the rocks penetrated by Wilson No. 1 and many of the rocks of the Salton Sea geothermal field itself are not readily distinguished from ordinary sedimentary rocks. That is, one would describe a given specimen of core as a sandstone or siltstone, not as a metamorphic rock, although the specimen would be recognized as an indurated and lithified sedimentary *rock*, not an unconsolidated *sediment*. However, virtually all the rocks at depth have undergone mineralogic change since deposition. This change is a progressive metamorphism in response to increasing depth, increasing temperature, and changing chemical environment. The resultant metamorphic rocks are more porous than common metamorphic rocks, possibly owing to the low pressure and probable short duration of the metamorphism, relative to metamorphism as commonly inferred.

Metamorphism in the Salton Sea geothermal system is indisputably hydrothermal in that hot brine permeates almost the entire system and undoubtedly contributes to and promotes the metamorphic reactions. In the part of the Salton Trough penetrated by the Wilson No. 1 well, however, the movement of solutions is probably not much greater than in ordinary sedimentary basins and metamorphic environments.

The mineralogical and chemical interaction of rocks and hot water is commonly termed "hydrothermal alteration" rather than metamorphism, particularly when the rocks in question are spatially related to fractures, veins, or disseminated ore. However, considering that hydrothermal alteration can be treated in the same manner as metamorphism (Creasey, 1959; Burnham, 1962; Helgeson, 1967), the discrimination of hydrothermal alteration and hydrothermal metamorphism appears primarily semantic; either term could be applied to the Salton Sea system. Hydrothermal alteration generally involves the formation of more hydrous mineral assemblages and progressive metamorphism, less hydrous assemblages. If judged by this criterion, the metamorphic aspects of the Salton Sea system should be emphasized.

The Salton Sea metamorphism is pervasive throughout at least 100 cubic miles in the explored geothermal system alone. When one considers the low-temperature transformations taking place at depths as shallow as 3000 feet in Wilson No. 1, 22 miles from the geothermal field, the volume of metamorphosed rock becomes truly regional in extent. Some minerals (for example, epidote and hematite) are concentrated along fractures at depth in the geothermal field, yet these minerals are also disseminated throughout metamorphosed sandstones and siltstones. The distribution of ankerite and chlorite (the principal lowtemperature metamorphic minerals) and the conversion of montmorillonite to K-mica are not controlled by fractures or permeable zones.

These minerals occur throughout even the most impermeable claystones.

Inasmuch as no schistosity is developed, the metamorphic rocks of the Salton Sea geothermal system are analogous to the products of burial metamorphism (Coombs, 1961, p. 214) but without the development of zeolites.

There is no evidence that the metamorphism of the Salton Sea geothermal field is contact metamorphism (that is, directly related to an intrusive body), although the high temperature gradient, the rhyolite extrusions, and the sporadic dikes penetrated by geothermal wells other than those described here, suggest the presence of a large intrusive body at depths of at least 15,000 feet.

The mineral reactions inferred in this paper take place in response to at least five general variables: (1) Temperature, (2) Total pressure, (3) The ratio of the activity of CO_2 to the activity of H_2O (a CO_2/aH_2O), (4) Fugacity of oxygen, and (5) Activities of other dissolved species in the brine.

Temperature is clearly the dominant intensive variable, particularly for the reactions involving production of chlorite. In all three wells discussed here, as well as the other eight wells in the geothermal field, the changes in mineralogical composition are progressive with increasing temperature, and the sequence of mineral changes is the same in all wells.

Total pressure cannot be related simply to mineralogical changes, although it probably influences stability fields to a small degree. Pressure is certainly very important in the induration and lithification of the rocks, resulting in an increase in density from less than 2.0 at the surface to as much as 3.0 at 4000 to 5000 feet in I.I.D. No. 1 (T. H. McCulloch, written commun., 1963).

The activity of CO₂ relative to that of H₂O appears to be an important factor in determining whether or not zeolite-bearing assemblages are stable under very low-grade metamorphic conditions (<250° C). Zen (1961) has suggested that at low values of aCO2/aH2O, zeolites are stable, whereas alternative assemblages become stable at higher aCO_2/aH_2O under the same temperature and total pressure. Zeolites are absent in the Salton Sea geothermal system, where independent evidence points to relatively high aCO2/aH2O at shallow depths. The decarbonation reactions that take place at depth in the Salton Sea geothermal system liberate abundant CO2. Much of this CO2 apparently migrates upward

and laterally, and is concentrated in permeable sands at relatively shallow depths (Muffler and White, 1968). CO_2 has been produced commercially from depths of approximately 600 feet in the geothermal system at static well-head pressures of up to 17 atm (Rook and Williams, 1942). Hydrostatic pressure at these depths is also about 17 atm. A relatively high $aCO_2/$ aH_2O is also favored by the lowering of aH_2O by the abundant salts in solution in the brine.

The absence of zeolites in the rocks of the Salton Sea geothermal system is in contrast to the abundance of zeolites in low-grade metamorphic terrains in New Zealand (Coombs and others, 1959) and elsewhere. In addition, zeolites are common hydrothermal minerals at temperatures of 150° C to 250° C in other geothermal systems, notably Wairakei, New Zealand (Steiner, 1955) and Yellowstone (Fenner, 1936). In contrast to the carbonatebearing clastic rocks of the Salton Sea geothermal system, the rocks of both Wairakei and Yellowstone are volcanic and contain no primary calcite or dolomite from which CO₂ could be derived.

The fugacity of oxygen is probably an important variable in determining the stability and composition of several iron-bearing minerals in the geothermal system. Keith and others (1968) show that two hydrothermal epidotes (one from I.I.D. No. 1 well and the second from I.I.D. No. 2 well) formed at essentially the same temperature (320° C) and hydrostatic pressure but have appreciably different contents of ferric iron. The high-iron epidote is associated with chlorite, hematite, and pyrite; the intermediate-iron epidote with pyrite and ironbearing tremolite⁶ but no chlorite or hematite. Differing oxygen fugacity between the fluids associated with the two samples of epidote is the most likely mechanism to account for these observed differences in composition and association (Keith and others, 1968).

Assuming equilibrium, the co-existence of pyrite and hematite in a number of samples from I.I.D. No. 1, including the core that contains the high-iron epidote described by Keith and others (1968), places close limits on the possible fugacities of oxygen and sulfur. Using the thermochemical data presented by Holland

⁶ Tremolite has not been detected in I.I.D. No. 1, Sportsman No. 1, or Wilson No. 1, but is present in at least two other wells in the geothermal field (to be reported on at a later date).

(1965), calculations similar to those expressed in Figure 4 of Holland (1959) indicate that at 325° C, rocks containing both pyrite and hematite have oxygen fugacities of 10^{-25} to 10^{-27} atm and sulfur fugacities of $10^{-5.7}$ to $10^{-7.3}$ atm (Fig. 9). The indicated sulfur fugacities are appreciably higher than the value of $10^{-10.2}$ atm determined for co-existing pyrite-pyrrhotite and pyrrhotite-sphalerite at 6612 feet in River Ranch No. 1 well (Skinner



Figure 9. Isothermal section at 325° C through the log f₀₂-log f₈₂-T diagram for the Fe-O-S system (*after* Holland, 1959) using the thermochemical data presented by Holland (1959) and Holland (1965).

and others, 1967). The fugacity of oxygen in an assemblage containing both pyrite and pyrrhotite but with no magnetite should be less than 10^{-31} atm, assuming equilibrium (Fig. 9). Thus, both f_{S_2} and f_{O_2} seem to have an appreciable range within the Salton Sea geothermal system. This analysis suggests that magnetite may be present as a metamorphic mineral in the Salton Sea geothermal system, but to date none has been identified.

Activities of other constituents dissolved in the brine are undoubtedly important in determining the observed mineral associations, but available samples and data do not permit a detailed analysis. We infer that the high activity of Ca++ in the brine may be important in allowing the detrital Na-Ca plagioclase to persist at temperatures where, in other hydrothermal systems low in dissolved Ca++, plagioclase has broken down to albite and other products. The high-iron content of the brine may be important in promoting the formation of ankerite, chlorite, and pyrite. Experimental work of others (Orville, 1963; Hemley, 1959; Hemley and Jones, 1964) and consideration of natural hydrothermal systems (White, 1965) indicate that the K+/Na+, K+/H+, and Na⁺/H⁺ ratios in the brine influence the relations of the feldspars, micas, and clays found in the Salton Sea geothermal system.

REFERENCES CITED

- Alonso Espinosa, Héctor, and Mooser, Federico, 1964, El pozo M-3 del campo geotermico del Cerro Prieto, B. C., Mexico: Asoc. Mexicana Geólogos Petroleros Bol., v. 16, nos. 7-8, p. 163-178.
- Anda, L. F., de, and Paredes, E., 1964, La falla de San Jacinto y su influencia sobre la actividad geotermica en el valle de Mexicali, B. C., Mexico: Asoc. Mexicana Geólogos Petroleros Bol., v. 16, nos. 7–8, p. 179–181.
- Bichler, S., Kovach, R. L., and Allen, C. R., 1964, Geophysical framework of northern end of Gulf of California structural province, *in* vanAndel, T. H., and Shor, G. G., Jr., *Editors*, Marine Geology of the Gulf of California—a symposium: Am. Assoc. Petroleum Geologists Mem. 3, p. 126–143.
- Burnham, C. W., 1962, Facies and types of hydrothermal alteration: Econ. Geology, v. 57, no. 5, p. 768-785.
- Burst, J. F., Jr., 1959, Postdiagenetic clay mineral environmental relationships in the Gulf Coast Eocene, in Swineford, A., *Editor*, Clays and clay minerals: Internat. Ser. Mons., Earth Sci., v. 2, p. 327-341.
- Clayton, R. N., Muffler, L. J. P., and White, D. E., 1968, Oxygen isotope study of calcite and silicates of the River Ranch well, Salton Sea geothermal area, California: Am. Jour. Sci. (in press).
- Coombs, D. S., 1961, Some recent work on the lower grades of metamorphism: Australian Jour. Sci., v. 24, no. 5, p. 203-215.
- Coombs, D. S., Ellis, A. J., Fyfe, W. S., and Taylor, A. M., 1959, The zeolite facies, with comments on the interpretation of hydrothermal systems: Geochim. et Cosmochim. Acta, v. 17, nos. 1–2, p. 53–107.
- Creasy, S. C., 1959, Some phase relations in the hydrothermally altered rocks of porphyry copper deposits: Econ. Geology, v. 54, no. 3, p. 351-373.
- Doe, B. R., Hedge, C. E., and White, D. E., 1966, Preliminary investigation of the source of lead and strontium in deep geothermal brines underlying the Salton Sea geothermal area: Econ. Geology, v. 61, no. 3, p. 462-483.

Fenner, C. N., 1936, Bore-hole investigations in the Yellowstone Park: Jour. Geology, v. 44, p. 225-315.
Foster, M. D., 1962, Interpretation of the composition and a classification of chlorites: U.S. Geol. Survey Prof. Paper 414-A, 33 p.

Grubbs, D. K., 1964, Ore-bearing magmatic and metamorphic brine from the Salton Sea volcanic domes geothermal area, Imperial County, California (Abs.): Virginia Jour. Sci., v. 15, n.s., no. 4, p. 333; *also*, 1963, Virginia Univ., Charlottesville, Virginia, M.S. thesis.

Helgeson, H. C., 1967, Solution chemistry and metamorphism, *in* Abelson, P. H., *Editor*, Researches in Geochemistry, v. 2: New York, New York, John Wiley and Sons, Inc., p. 362-404.

---- 1968, Geologic and thermodynamic characteristics of the Salton Sea geothermal system: Am. Jour. Sci., v. 266, no. 3, p. 129–166.

- Hemley, J. J., 1959, Some mineralogical equilibria in the system K₂O-Al₂O₃-SiO₂-H₂O: Am. Jour. Sci., v. 257, no. 4, p. 241–270.
- Hemley, J. J., and Jones, W. R., 1964, Chemical aspects of hydrothermal alteration with emphasis on hydrogen metasomatism: Econ. Geology, v. 59, no. 4, p. 538-567.
- Holland, H. D., 1959, Some applications of thermochemical data to problems of ore deposits. I. Stability relations among the oxides, sulfides, sulfates and carbonates of ore and gangue metals: Econ. Geology, v. 54, no. 2, p. 184–233.

----- 1965, Some applications of thermochemical data to problems of ore deposits. II. Mineral assemblages and the composition of ore-forming fluid: Econ. Geology, v. 60, no. 6, p. 1101–1166.

Keith, T. E. C., Muffler, L. J. P., and Cremer, Marcelyn, 1968, Hydrothermal epidote from the Salton Sea geothermal field, California: Am. Mineralogist (in press).

Kelley, V. C., and Soske, J. L., 1936, Origin of the Salton volcanic domes, Salton Sea, California: Jour. Geology, v. 44, no. 4, p. 496-509.

- Khitarov, N. I., and Pugin, V. A., 1966, Behavior of montmorillonite under elevated temperatures and pressures: Geochemistry Internat., v. 3, no. 4, p. 621-626.
- Maxwell, D. T., and Hower, John, 1967, High-grade diagenesis and low-grade metamorphism of illite in the Precambrian Belt series: Am. Mineralogist, v. 52, nos. 5-6, p. 843-857.
- McNitt, J. R., 1963, Exploration and development of geothermal power in California: California Div. Mines and Geol. Spec. Rept. 75, 45 p.

Merriam, R., and Bandy, O. L., 1965, Source of upper Cenozoic sediments in Colorado River delta region: Jour. Sed. Petrology, v. 35, no. 4, p. 911–916.

Muffler, L. J. P., and Doe, B. R., 1968, Composition and mean age of detritus of the Colorado River delta in the Salton Trough, southeastern California: Jour. Sed. Petrology, v. 38, p. 384–399.

Muffler, L. J. P., and White, D. E., 1968, Origin of CO₂ in the Salton Sea geothermal system, southeastern California, U.S.A.: XXIII Session Internat. Geol. Congress, Prague, August 1968, v. 17, Genesis of mineral and thermal waters, p. 185–194.

Orville, P. M., 1963, Alkali ion exchange between vapor and feldspar phases: Am. Jour. Sci., v. 261, no. 3, p. 201–237.

Philippi, G. T., 1965, On the depth, time and mechanism of petroleum generation: Geochim. et Cosmochim. Acta, v. 29, no. 9, p. 1021–1050.

- Rex, R. W., 1966, Heat flow in the Imperial Valley of California (Abs.): Am. Geophys. Union Trans., v. 47, no. 1, p. 181.
- Reynolds, R. C., Jr., 1967, Interstratified clay systems—Calculation of the total one-dimensional diffraction function: Am. Mineralogist, v. 52, nos. 5–6, p. 661–672.
- Rook, S. H., and Williams, G. C., 1942, Imperial carbon dioxide gas field: California Div. Oil and Gas, California Oil Fields-Summ. Operations, v. 28, no. 2, p. 12-33.
- Rosenberg, P. E., 1967, Subsolidus reactions in the system CaCO₃-MgCO₃-FeCO₃ between 350° and 550° C: Am. Mineralogist, v. 52, nos. 5–6, p. 787–796.
- Schoen, Robert, and White, D. E., 1965, Hydrothermal alteration in GS-3 and GS-4 drill holes, Main Terrace, Steamboat Springs, Nevada: Econ. Geology, v. 60, no. 7, p. 1411–1421.
- Schultz, L. G., 1964, Quantitative interpretation of mineralogical composition from X-ray and chemical data for the Pierre Shale: U. S. Geol. Survey Prof. Paper 391-C, 31 p.

Shapiro, Leonard, and Brannock, W. W., 1962, Rapid analysis of silicate, carbonate, and phosphate rocks: U. S. Geol. Survey Bull. 1144-A, p. A1-A56.

Nagata, Takesi, 1961, Rock magnetism: Tokyo, Maruzen Co., Ltd., 350 p.

- Shirozu, Hauo, 1958, X-ray powder patterns and cell dimensions of some chlorites in Japan, with a note on their interference colors: Mining Jour., v. 2, no. 4, p. 209–223.
- Sigvaldason, G. E., and White, D. E., 1962, Hydrothermal alteration in drill holes GS-5 and GS-7, Steamboat Springs, Nevada: U. S. Geol. Survey Prof. Paper 450-D, p. D113-D117.
- Skinner, B. J., White, D. E., Rose, H. J., and Mays, R. E., 1967, Sulfides associated with the Salton Sea geothermal brine: Econ. Geology, v. 62, no. 3, p. 316-330.

Steiner, A., 1955, Wairakite, the calcium analogue of analcime, a new zeolite mineral: Mineralog. Mag., v. 30, no. 230, p. 691-698.

Tatlock, D. B., 1966, Rapid modal analysis of some felsic rocks from calibrated X-ray diffraction patterns: U. S. Geol. Survey Bull. 1209, 41 p.

Taylor, J. H., 1964, Some aspects of diagenesis: Adv. Sci. (London), v. 20, p. 417-436.

Turner, F. J., and Verhoogen, John, 1960, Igneous and metamorphic petrology, 2d ed.: New York, New York, McGraw-Hill Book Co., 694 p.

- Von Herzen, R. P., 1963, Geothermal heat flow in the gulfs of California and Aden: Science, v. 140, no. 3572, p. 1207-1208.
- Weaver, C. E., 1956, The distribution and identification of mixed-layer clays in sedimentary rocks: Am. Mineralogist, v. 41, nos. 3-4, p. 202-221.
- White, D. E., 1955, Thermal springs and epithermal ore deposits: Econ. Geology, 50th Anniversary Volume, Part 1, p. 99-154.
 - 1965, Saline waters of sedimentary rocks, *in* Fluids in subsurface environments—a symposium: Am. Assoc. Petroleum Geologists Mem. 4, p. 342–366.
- White, D. E., Anderson, E. T., and Grubbs, D. K., 1963, Geothermal brine well—Mile-deep drill hole may tap ore-bearing magmatic water and rocks undergoing metamorphism: Science, v. 139, no. 3558, p. 919–922.
- Williams, H., Turner, F. J., and Gilbert, C. M., 1955, Petrography: San Francisco, W. H. Freeman and Co., 406 p.

Winkler, H. G. F., 1965, Petrogenesis of metamorphic rocks: New York, Springer Verlag, 220 p.

Zen, E-an, 1959, Clay mineral-carbonate relations in sedimentary rocks: Am. Jour. Sci., v. 257, no. 1, p. 29-43.

------ 1960, Metamorphism of Lower Paleozoic rocks in the vicinity of the Taconic Range in west-central Vermont: Am. Mineralogist, v. 45, p. 129–175.

---- 1961, The zeolite facies-an interpretation: Am. Jour. Sci., v. 259, no. 6, p. 401-409.

Publication Authorized by the Director, U. S. Geological Survey Manuscript Received by The Society May 6, 1968 Revised Manuscript Received July 23, 1968



Figure 1. Metasandstone; epidote (E), quartz (Q), plagioclase (P), pyrite (Py). Partly crossed polars.



1.0 mm

Figure 2. Epidote veinlet cutting metasiltstone (st) and metasandstone (ss), the latter rich in epidote and in pyrite (Py). Partly crossed polars.

PHOTOMICROGRAPHS OF METAMORPHIC EPIDOTE IN CORE FROM 4920 FEET IN I.I.D. NO. 1

MUFFLER AND WHITE, PLATE 1 Geological Society of America Bulletin, v. 80, no. 2



Figure 1. Sphalerite (Sl) and sphene (Sp) in metamorphosed wacke from 3520 feet. Plane light.



Figure 2. Metasandstone from 4920 feet, showing interlocking quartz crystals (Q) and relic detrital shapes outlined by inclusions. Plagioclase (P), epidote (E), pyrite (Py). Partly crossed polars.

PHOTOMICROGRAPHS OF METAMORPHOSED SANDSTONES FROM I.I.D. NO. 1

MUFFLER AND WHITE, PLATE 2 Geological Society of America Bulletin, v. 80, no. 2