

# Sediment-sea-water interaction at 200 and 300 °C, 500 bars pressure: The role of sediment composition in diagenesis and low-grade metamorphism of marine clay

EDWARD C. THORNTON  
WILLIAM E. SEYFRIED, JR.

Department of Geology and Geophysics, University of Minnesota, Minneapolis, Minnesota 55455

## ABSTRACT

Experimental interaction of clay-rich marine sediments with sea water at 200 and 300 °C, 500 bars, and a water/rock mass ratio of 5 resulted in the generation of relatively acid, oxidizing conditions. The development of acidity is attributed to the formation of smectite, whereas the oxidation state of the fluids was dependent on the relative proportions of ferromanganese oxide phase, ferrous-rich silicate phases, and organic carbon. An experiment conducted with an oxidized sediment at 300 °C thus produced higher aqueous concentrations of Mn and associated base metals at a relatively high  $fO_2$  ( $\sim 10^{-15}$ ), but an organic carbon-rich sediment yielded fluids characterized by a lower  $fO_2$  ( $\sim 10^{-20}$ ), lower concentrations of Mn, higher Fe, and exhibited substantial thermal alteration and dissolution of organic components. Silica concentrations in the experimental fluids ranged from cristobalite to amorphous silica saturation levels in response to the dissolution of amorphous silica.

Comparison of fluid data and mineralogical assemblages from the Gulf Coast and Salton Sea regions with experimental results suggests that alteration processes in sedimentary basins can, in large part, be attributed to water-rock interaction. Observed differences are apparently due to the higher degree of reaction in the geologic environment and to the increased stability of the illite-chlorite assemblage at the lower silica activity characteristic of geologic fluids.

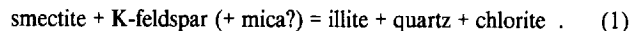
## INTRODUCTION

The interaction of pore fluids with clay-rich sediment during sediment accumulation results in significant changes in fluid chemistry and, to a lesser extent, sediment chemistry and mineralogy. Elucidation of these changes is of fundamental importance in defining the basic chemical processes that occur during the diagenesis and metamorphism of clay-rich sediment.

Pelitic sediments consist primarily of the clay minerals illite, montmorillonite, and kaolinite, detrital chlorite and muscovite, quartz, and varying amounts of feldspar, calcite, and organic matter. This assemblage is relatively stable through diagenesis and persists through low-grade metamorphism (that is, greenschist facies). According to Winkler (1976), the only notable mineralogical changes involve clay-mineral transformations and the increasing crystallinity of mica. As such, it is not generally possible to delineate clearly the transition between diagenesis and metamorphism, although Winkler suggests that metamorphism begins at temperatures somewhat below 200 °C, as deduced in those rock types that produce characteristic assemblages upon the onset of metamorphism. Major

changes in pore-fluid chemistry clearly do occur, however, from the earliest stages of diagenesis and continue into the onset of greenschist metamorphism at 350–400 °C.

Investigations of burial metamorphism in the thick sedimentary sequence of the Gulf Coast region of North America have demonstrated that the most characteristic mineralogical change of shale is an increase in the proportion of illite layers within mixed-layer illite/smectite with depth (Burst, 1969; Zen, 1974; Dunoyer de Segonzac, 1970; Hower and others, 1976; Weaver and Beck, 1971). Hower and others thus demonstrated that, in the temperature interval from  $\sim 50$  to 95 °C, illite/smectite undergoes a conversion from  $<20\%$  to  $\sim 80\%$  illite layers. This change may be regarded as a substitution of  $Al^{+3}$  for  $Si^{+4}$  in the tetrahedral layer and the fixation of  $K^+$  in the interlayer position as a consequence of the increase in negative-charge density. The potassium and aluminum required for this process appear to be derived from the decomposition of potassium feldspar and mica. An increase in the abundance of chlorite in the interval from  $\sim 50$  to 130 °C was also detected, apparently forming from the magnesium and iron lost by the smectite when it underwent conversion to illite. The over-all reaction for this process may be expressed mineralogically by



Hower also suggested that a noninterlayered illite may develop at  $\sim 200$  °C, and illite may recrystallize to form  $2M_1$  dioctahedral mica in the temperature interval from 200 to 300 °C (Maxwell and Hower, 1967).

Analytical data on produced reservoir fluids of the Gulf Coast indicate that salinity tends to increase with depth to a maximum of  $\sim 20\%$ . This increase is generally attributed to membrane filtration (White, 1965; Hanor, 1979; Dickey and others, 1972; Graf, 1982; Kharaka and Berry, 1973) or interaction with evaporites (Hanor, 1979). There is usually a general enrichment in Ca, Sr, Ba, and F, and depletion of Na, K, Mg, and  $SO_4$  relative to sea water (Hanor, 1979), whereas silica concentration is often consistent with quartz saturation. White (1965; see also White and others, 1963) proposed that  $SO_4$  and carbonate decrease, owing to escape of uncharged species such as  $H_2O$ ,  $H_2CO_3$ , and  $H_2S$  through clays during compaction and that enrichment of Ca occurs because of the less-mobile nature of the divalent  $Ca^{2+}$  ion. White also suggested that  $H^+$  increases with depth due to migration of  $H^+$  back across the membrane in response to the escape of Na. It will be shown in this paper, however, that the increase of Ca and decrease in pH, Mg, and  $SO_4$  are also consistent with changes that occur during sediment-seawater interaction.

The studies of Weaver and Beck (1971) and Schmidt (1973) indicated that the salinity of waters within shale does not increase in the manner observed for sands, being generally of lower salinity and of differ-

ent composition. Shale pore fluids are characterized by enrichment of  $\text{SO}_4$  and  $\text{HCO}_3$  and depletion of Cl relative to sea water. Weaver demonstrated that  $\text{SO}_4$  enrichment is readily explained by membrane filtration, being approximately proportional to the decrease in porosity during compaction. The enrichment of  $\text{HCO}_3$  is likely due to oxidation and thermal alteration of organic matter. Cl depletion suggests that this component may be relatively mobile, an observation apparently at variance with the conclusion presented by White (1965). Considerations of mass transfer between compacting shale and adjacent sands may eventually provide the key for understanding the processes controlling salinity and compositional variations in pore fluids of the Gulf Coast region and similar sedimentary basins.

Results of studies of diagenesis and very low grade metamorphism of pelitic sediments of the Gulf Coast may be extended to higher metamorphic grades by comparison with the Salton Sea Geothermal System of southern California, owing to the higher geothermal gradient of the Salton Sea trough. McDowell and Elders (1980) thus observed a metamorphic zonation in the shale of borehole Elmore 1, Salton Sea Geothermal Field, from a dolomite/ankerite zone at temperatures of  $<190^\circ\text{C}$  through a chlorite/calcite zone ( $190\text{--}325^\circ\text{C}$ ) and a biotite zone ( $325\text{--}359^\circ\text{C}$ ). They also noted a regular progression of compositional and textural changes of the layer silicate assemblages through these zones. At temperatures of  $185^\circ\text{C}$ , interlayered illite/smectite was found to contain  $\sim 15\%$  smectite which decreased to  $\sim 5\%$  at  $210^\circ\text{C}$  and assumed a more ordered nature. At  $290^\circ\text{C}$ , smectite was absent. Fine-grained chlorite was observed throughout the chlorite/calcite zone through alteration of detrital-layer silicates and growth within open pores. The changes observed in the layer silicate assemblage thus suggest that reaction 1 may serve as a general expression for metamorphism of pelitic sediment within the Salton Sea Geothermal Field at temperatures  $<290^\circ\text{C}$ . Significant recrystallization was noted at  $300^\circ\text{C}$ ; illite (sericite) and detrital muscovite formed phengite grains, and chlorite grew from small patches to clear grains. Biotite was first observed forming at  $325^\circ\text{C}$  in open spaces and by conversion of chlorite to biotite. Chlorite was found to persist well above the biotite isograd in the shale section but decreased abruptly at  $350^\circ\text{C}$  as biotite increased. Chlorite was absent at  $359^\circ\text{C}$ .

Helgeson (1967, 1968) presented a representative fluid composition for the Salton Sea geothermal reservoir at  $300^\circ\text{C}$ . The solution is a concentrated  $\text{NaCl-CaCl}_2\text{-KCl}$  brine with a total dissolved solids content of 25.9%. Magnesium was nearly depleted at 10 ppm. Helgeson estimated a  $300^\circ\text{C}$  pH of 4.7, a  $\text{H}_2\text{S}$  concentration of 32 ppm, and fugacities of  $\text{S}_2$ ,  $\text{O}_2$ , and  $\text{CO}_2$  of  $10^{-10}$ ,  $10^{-30}$ , and 2.8 atm., respectively, on the basis of fluid-mineral equilibria. The observed concentration of  $\text{SiO}_2$  (400 ppm) is considerably less than quartz solubility at  $300^\circ\text{C}$ . Helgeson (1967) concluded, from equilibrium considerations and mass-transfer calculations, that the Salton Sea brine was probably once sea water or meteoric water that evolved to its present composition through water-rock interaction and concentration through membrane filtration or thermal evaporation.

Experimental modeling may be used in conjunction with both chemical analyses of subsurface formation fluids and with information regarding mineralogical transformations and alteration of organic matter during diagenesis and metamorphism to define the major chemical processes involved in the development of sedimentary basins such as the Gulf Coast and Salton Sea. In particular, this approach is necessary in order to define the role of sediment composition in controlling fluid chemistry and mineralogical changes during fluid-rock interaction. For these reasons, sediment samples containing varying proportions of pelagic clay, biogenic silica, and a smectite/metalliferous component have been reacted with sea water at  $200$  and  $300^\circ\text{C}$  and 500 bars for presentation in this study. These experiments were conducted at a low water/rock mass ratio (5:1) approx-

imately analogous to that of the natural environment and were conducted with hydrothermal apparatus that allows on-line sampling of fluids during the course of experiments (Seyfried and others, 1979). Changes in fluid chemistry thereby provide a means of monitoring hydrothermal interaction processes and assessing reaction progress and attainment of steady-state conditions.

## PROCEDURES

### Experimental Equipment

Experiments were conducted in the hydrothermal apparatus described by Dickson and others (1963), with modifications by Seyfried and others (1979). This apparatus consists of a gold reaction cell enclosed in a pressure vessel and furnace. The furnace temperature is maintained within  $\pm 2^\circ\text{C}$  by a proportional controller. The reaction cell is sealed with a titanium top, and solution samples are obtained through an internal gold filter and a titanium exit tube by opening a high-pressure sampling valve. Constant hydrostatic pressure is maintained while sampling by pumping water into the pressure vessel around the reaction cell. The assembly is mounted on a rack and continuously rocked through  $180^\circ$  at 20 times per minute. Reaction kinetics are accelerated by suspending the sediment in sea water to insure a maximum surface area of reaction.

Sampling of the aqueous fluid can be accomplished at constant temperature and pressure at any time during the experiment. Quench fluid and reacted sediment are also obtained at the end of each experiment.

### Reactants

Sandia National Laboratories provided the sediments used in this study, which is part of a research program being conducted in the evaluation of potential subseabed disposal sites for nuclear waste. Research at the University of Minnesota has emphasized characterization of the hydrothermal conditions that would develop in the near field sediment environment immediately surrounding a waste canister (Seyfried and others, 1980a; Thornton, 1983). Sediments available for the experiments undertaken represent a variety of North Pacific sedimentary facies types of contrasting compositions, permitting an evaluation of the role of sediment composition in hydrothermal alteration processes.

Sediments were reacted at  $200$  and  $300^\circ\text{C}$  with Copenhagen standard sea water at a water/rock mass ratio of 5. The reactants were characterized on the basis of chemical composition and through mineralogical data derived by X-ray diffraction. Experimental data are presented for two sediment samples; one of these, designated "SM2," is an oxidized marine clay; the other, V36, is more reduced, owing to the presence of abundant organic matter and volcanic debris.

**SM2.** This sediment was obtained from a giant piston core taken at  $30^\circ 20.9' \text{N}$ ,  $157^\circ 50.85' \text{W}$  at  $\sim 5,800\text{-m}$  water depth. SM2 is a dark brown, mixed-layer, smectite-illite clay with clinoptilolite, quartz, fish debris, iron oxides crusts, and amorphous material in the form of silica and ferromanganese oxyhydroxides. This sample is representative of the smectite-rich clay that occurs in the central North Pacific beneath a surficial cover of several metres of illite-rich, pelagic clay (Silva, 1977). A chemical analysis of SM2 is presented in Table 1. SM2 is best defined as pelagic clay with a significant contribution of metalliferous sediment and a minor amount of biogenic silica.

**V36.** This sample is a silty clay composed of quartz, plagioclase, illite, Fe-chlorite, and amorphous silica (radiolarians, diatoms, volcanic glass; Heath, 1981) collected from the western North Pacific (core V36/12-43P, interval 1,025–1,174 cm,  $33^\circ 45.0' \text{N}$ ,  $151^\circ 45.8' \text{E}$ ) at a water depth of

TABLE 1. CHEMICAL ANALYSIS OF SEDIMENTS UTILIZED IN STUDY

Percent	SM2	V36
SiO <sub>2</sub>	51.77	58.31
Al <sub>2</sub> O <sub>3</sub>	13.37	14.79
(Fe <sub>2</sub> O <sub>3</sub> ) <sub>T</sub>	9.09	6.52
MgO	3.49	2.79
CaO	1.29	2.17
Na <sub>2</sub> O	0.79	1.79
K <sub>2</sub> O	3.71	2.63
MnO	1.30	0.21
TiO <sub>2</sub>	0.59	0.70
P <sub>2</sub> O <sub>5</sub>	0.49	0.10
H <sub>2</sub> O <sup>-</sup>	0.94	0.82
H <sub>2</sub> O <sup>+</sup>	12.15	6.87
Total	98.98	97.70
C <sub>inorg</sub>	0.007	<0.0001
C <sub>org</sub>	0.064	0.43
ppm		
Ba	381	681
Co	45	27
Cr	43	79
Cu	276	112
Ni	152	47
Pb	42	28
Sr	203	159
Zn	165	101

Note: samples were washed and dried at 40 °C.

3,185 fathoms. Chemically, it may be characterized as a pelagic clay with a moderate amount of biogenic silica. It also contains 0.43% organic carbon (Table 1), which accounts for its reduced nature and gray-green color.

### Analytical

**Solutions.** Approximately 10 ml of solution was taken per sample. This consisted of ~0.5 ml in a glass gas-tight syringe for total dissolved inorganic CO<sub>2</sub> (ΣCO<sub>2</sub>), and 8 ml for other components. Immediately after sampling, ΣCO<sub>2</sub> was analyzed with a total carbon analyzer (Oceanography International). The 8-ml sample was divided into three aliquots. The first consisted of a 1-ml unfiltered sample for pH determination by a selective ion electrode, and for SO<sub>4</sub>, by ion chromatography (Dionex Corporation). A second 1-ml portion was filtered through a 0.2-μ membrane filter, acidified with ultrapure HNO<sub>3</sub>, and diluted for analysis of SiO<sub>2</sub> and major cations (K, Mg, Ca) using DC-plasma emission spectrometry and atomic absorption spectrophotometry. The remaining portion (~5 ml) was also filtered and acidified but was not diluted. This fraction was analyzed for chlorite (potentiometrically) and for heavy metals and minor elements by DC-plasma emission spectrometry. F was measured with a selective ion electrode.

The following components have been routinely analyzed in solution samples: Mg, Ca, K, SO<sub>4</sub>, SiO<sub>2</sub>, Cl, Sr, Fe, Mn, Zn, Al, Ni, Co, Cr, Ti, Au, Ba, Cu, Pb, B, pH, and ΣCO<sub>2</sub>. Na concentration was calculated by using charge-balance considerations. Uncertainties in reported concentrations are: ±3% for Na, Ca, K, Mg, Σ CO<sub>2</sub> and SiO<sub>2</sub>; ±2% for Cl and SO<sub>4</sub>; ±3% for Fe, Cu, and Mn at >10 ppm and ±10% at <10 ppm; and ±10% for Sr, Zn, Al, Ni, Cr, Ba, B, Au, Pb, and Ti. The reported pH values are accurate to 0.05 pH units. H<sub>2</sub>S was assumed to be negligible in all experiments because of the absence of sulfide odor.

**Solids.** Chemical analyses of sediments (Table 1) were performed by DC-plasma emission spectrometry, using a lithium metaborate fusion technique (Bankston and others, 1979) for major elements and HF-*m*-benzene disulfonic acid digestion for trace elements (Cohen and others, 1975). Sediments were thoroughly washed with distilled, deionized water

and dried at 40 °C before analysis. Organic and inorganic carbon were measured with a total carbon analyzer, and hydration and structural water were estimated by drying the sediments at 105 and 950 °C, respectively.

X-ray diffraction analyses were performed on oriented smear mounts of bulk sediments and alteration products on glass slides, using a Phillips diffractometer and CuKα radiation. Each sample was analyzed three times: untreated from 2° to 60° 2θ at 1° 2θ/min, glycolated from 2° to 30° 2θ at 1° 2θ/min, and heated (1 hr at 550 °C) from 2° to 30° 2θ at 1° 2θ/min.

### Distribution of Aqueous Species

Computation of ion activities of aqueous species was performed by "SOLVEQ," a computer program written by Reed (1977). SOLVEQ distributes element concentrations among aqueous species through a series of mass-balance equations containing dissociation constants for complexes. The program assumes electrical neutrality. These equations are solved simultaneously with a Newton-Raphson iteration procedure. The extended Debye Huckle equation is used to compute activity coefficients (Helgeson, 1969). Activities were first computed at 25 °C and 1 bar using the measured pH, concentrations of aqueous components, and a Na value adjusted for electrical neutrality. From this initial distribution, a hydrogen ion mass balance was computed. Activities were then calculated at elevated temperatures and pressures using appropriate dissociation constants for aqueous complexes (Seyfried and Dibble, 1980). Hydrolysis constants of minerals at the experimental conditions calculated from the data of Helgeson and others (1978) were compared with the activity products to determine the extent of saturation of the solutions with respect to selected minerals.

## RESULTS

### Solution Chemistry

**Mg, Ca, Na, K, Cl, SO<sub>4</sub>, and pH.** The major-element chemistry of sea water was significantly modified during all of the experiments performed (Fig. 1 and Table 2). In general, sea water lost Mg and SO<sub>4</sub> and gained K; pH decreased to a minimum value during the first several days of each experiment but increased subsequently as the concentration of Mg was depleted in the fluid. Ca displayed a tendency to decrease initially but subsequently increased. Chloride generally increased slightly during the course of the experiments due to water uptake by hydrated alteration products.

**SiO<sub>2</sub>.** Silica concentrations in solution were controlled primarily by the solubility of amorphous silica in the form of biogenic silica. SiO<sub>2</sub> reached concentrations of 600 to 900 ppm at 200 °C and 1,500 to 2,000 ppm at 300 °C. SiO<sub>2</sub> decreased slightly to <1,250 ppm in the experiment with sediment SM2 after 1,347 hours, apparently due to the elimination of amorphous silica as reactants and the formation of silica-rich alteration phases.

**Fe, Mn, Zn, Cu, Pb, Ni, Cr, Co, Sr, Ba, Al, B, Au, Ti, and F.** Significant heavy-metal mobility was noted in all experiments, varying in relation to changes in redox intensity and pH (Fig. 1 and Table 3). Fe was strongly affected by pH, generally decreasing in concentration as pH rose (for example, SM2 at 300 °C). Fe concentration in solution also was redox sensitive, as illustrated by its relatively low concentration in the experiment performed with oxidized sediment (SM2) and a higher concentration in the experiments containing the more-reduced sediment (V36). Mn exists primarily as Mn(IV) (for example, MnO<sub>2</sub>) in sediment SM2 and behaved as the principal oxidizing agent in that sediment. The Mn concentration of

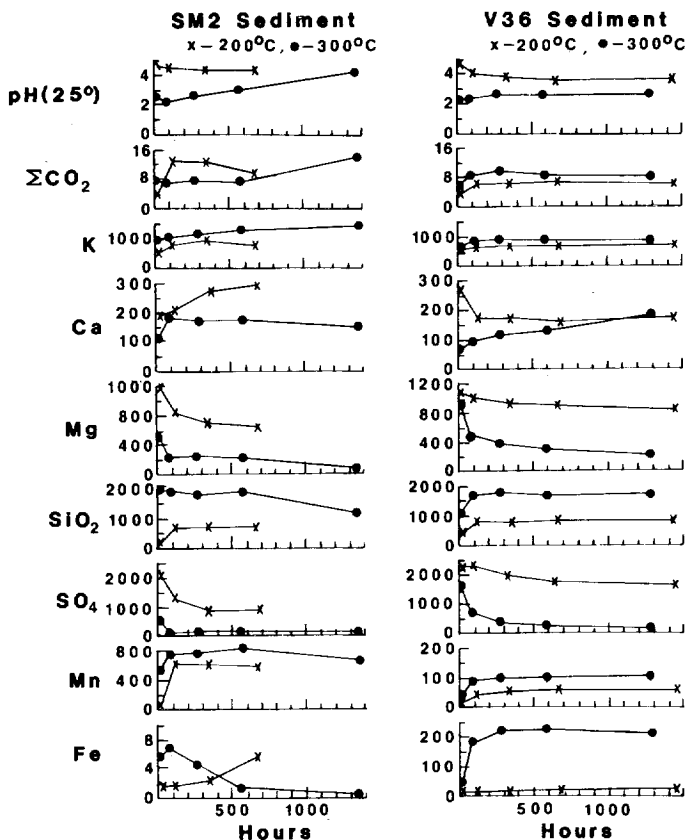


Figure 1. Change in concentration of aqueous components during experimental sediment-sea-water interaction. All data in ppm except for  $\Sigma\text{CO}_2$  (millimolal) and pH.

700 to 800 ppm in the reacted fluid of the SM2 experiment at 300 °C thus reflected the reduction of Mn(IV) to aqueous Mn(II) through the oxidation of organic matter and ferrous iron in the sediment. That  $\text{MnO}_2$  was present in the unreacted sediment in an amount in excess of the reducing agents, and thus capable of maintaining oxidizing conditions during the experiment, was demonstrated by the conspicuous concentrations of Au in solution (1.7 to 1.8 ppm). Mn concentrations were low in the experiments involving the reduced sediment V36, due to the small amount of  $\text{MnO}_2$  originally present. The reduced nature of this sediment is further demonstrated by the low Au concentration in solution (see Discussion below).

Cu and Zn attained concentrations in solution of 60.3 and 19.0 ppm, respectively, in the experiment with SM2 at 300 °C, in response to the oxidizing conditions generated. These elements are present at lower concentrations in the experiments with sediment V36 and were less mobile in the experiments at 200 °C than at 300 °C. Pb reached a concentration of 5.8 ppm in the experiment with SM2 at 300 °C, and 1.10 ppm, with V36 at 300 °C. Ni attained concentrations in solution up to 0.5 ppm with SM2 at 200 and 300 °C; Ti, Cr, and Co concentrations in solution were negligible during all experiments.

Ba concentrations were <0.5 ppm in the reacted fluids of all experiments. Sr concentrations in all experiments declined from an initial seawater value of 7.9 ppm but rose subsequently as Ca-plagioclase and

TABLE 2. CONCENTRATION OF MAJOR AQUEOUS SPECIES (PPM), TOTAL DISSOLVED INORGANIC  $\text{CO}_2$  ( $\Sigma\text{CO}_2$  IN MILLIMOLAL), AND pH DURING SEDIMENT-SEA-WATER INTERACTION

Sample/hr	pH	$\Sigma\text{CO}_2$	Na	K	Ca	Mg	$\text{SiO}_2$	$\text{SO}_4$	Cl
<b>Sediment V36, 200 °C</b>									
SW/0	7.9	2.33	10763	399	412	1297	<.2	2734	19375
1/1.0	4.85	3.06	10909	539	271	1150	498	2325	19466
2/104.0	4.01	6.17	11194	684	172	1043	875	2412	19813
3/332.5	3.90	6.18	10963	703	181	967	904	2019	19307
4/669.0	3.79	6.41	11115	718	160	956	935	1848	19673
5/1442.0	3.80	6.42	10986	705	180	891	953	1709	19444
6/2254.5	3.70	8.22	10812	676	189	859	912	1495	19185
Q/2261.4	5.5	..	..	531	462	836	554	2198	18262
<b>Sediment V36, 300 °C</b>									
SW/0	7.9	2.33	10763	399	412	1297	<.2	2734	19375
1/1.0	2.44	5.32	11060	649	63.8	954	1101	1734	19560
2/93.5	2.49	8.15	10928	798	98.3	529	1790	770	19533
3/284.5	2.72	9.68	10972	858	117	403	1819	456	19422
4/596.0	2.88	8.58	11082	887	136	347	1775	379	19515
5/1297.0	2.85	8.21	10905	921	191	290	1803	260	19277
Q/1608.0	4.52	1.13	..	..	..	..	..	842	..
<b>Sediment SM2, 200 °C</b>									
SW/0	7.90	2.33	10763	399	412	1297	<.2	2734	19375
1/5	4.86	4.38	10853	618	192	1238	217	2030	19822
2/101	4.47	13.19	10479	844	203	864	737	1300	19626
3/341	4.39	12.77	10404	975	271	717	754	851	19667
4/678	4.35	9.97	10685	797	295	659	785	936	19720
Q/706	6.00	..	..	633	659	812	473	1781	..
<b>Sediment SM2, 300 °C</b>									
SW/0	7.90	2.33	10763	399	412	1297	<.2	2734	19375
1/2.0	2.71	7.98	10871	1044	109	562	2064	577	19904
2/79.0	2.34	7.31	10681	1202	184	272	2004	185	19760
3/261.5	2.73	8.00	10884	1281	176	255	1918	161	19998
4/575.3	3.02	7.66	10949	1380	181	208	1981	168	20051
5/1347.0	4.08	14.06	10874	1538	154	137	1246	146	19654
6/2811.0	4.17	12.15	10947	1314	135	114	1239	186	19376

Note: values obtained at 200–300 °C, 500 bars, and water/rock ratio of 5.  
 SW = starting composition of Copenhagen sea water.  
 Q = quench, 25 °C.  
 pH measured at 25 °C; .. not analyzed.

carbonate phases reacted. B attained concentrations in solution in excess of 20 ppm in experiments with sediment SM2 and approached 10 ppm in sediment V36; these data indicate nearly quantitative leaching of B from the sediments, considering the water/rock mass ratio employed. F was measured in the experiment with sediment SM2 at 300 °C, where it was found to reach a maximum value of 6.0 ppm at the pH minimum. Al concentrations in solution were low in all experiments, reaching a maximum of only 0.2 to 0.3 ppm.

$\Sigma\text{CO}_2$ . Total dissolved inorganic  $\text{CO}_2$  increased in all experiments to 10 millimolal or more (Fig. 1 and Table 2). Organic carbon or  $\text{CH}_4$  determinations were not attempted during the experiments, but a mild organic odor accompanied by a yellowish coloration of fluids in the experiment with V36 at 300 °C indicated the presence of a significant amount of a dissolved organic component. Preliminary ion chromatographic analysis indicates that this component consists largely of organic acids.

### Alteration Products

Mineralogical changes in sediment SM2 involved a transition from a mixed smectite-illite component to a product containing smectite and less of the mixed-layer clay, as indicated by X-ray diffraction analysis. Clinoptilolite dissolved entirely. A reduction in the intensity of the reflection of plagioclase suggests that it also underwent partial reaction.

As smectite formed, the abundances of  $\text{SiO}_2$ -rich amorphous material and plagioclase in sediment V36 were reduced somewhat. Chlorite and illite showed little change. The organic carbon content of the sediment was found to decrease from 0.43% before reaction to 0.18% after reaction at 200 °C, and to 0.13% after reaction at 300 °C. The total inorganic carbon concentrations of the experimental solutions (Table 2) are too low

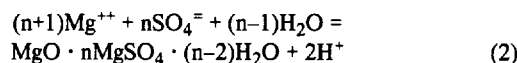
to account for the decrease in organic carbon observed. The aqueous concentrations of Fe and Mn are also lower than would be expected if ferromanganese oxyhydroxide phases had oxidized substantial amounts of organic material. Most of the decrease in organic carbon of the sediment thus is attributed to loss by dissolution during thermal alteration. This explanation is substantiated to some degree by the presence of an organic odor in the solution samples.

Anhydrite was identified as an alteration product of all experiments, both microscopically and by X-ray diffraction.

## DISCUSSION

### Chemical Exchange and pH Regulation during Sediment-Sea-water Interaction

Experiments in the sediment-sea-water system at 200 and 300 °C indicate that acidity develops due to Mg removal from solution (Seyfried and others, 1980a). Bischoff and Seyfried (1978) demonstrated that at temperatures above 250 °C at 500 bars, sea water loses Mg due to the precipitation of Mg-hydroxysulfate hydrate (MHSH). This mechanism for  $\text{H}^+$  generation may be written as



where  $3 \leq n \leq 5$ . This reaction is probably important during the first few hours of our experiments. Sulfate is also removed from solution as anhydrite, however, and reaction 2 is soon superseded by reactions involving

TABLE 3. CONCENTRATION OF TRANSITION METALS AND TRACE ELEMENTS IN SOLUTION SAMPLES (PPM) DURING SEDIMENT-SEA-WATER INTERACTION

Sample/hr	Fe	Mn	Zn	Cu	Pb	Ni	Cr	Co	Ba	Sr	Al	B	Au	Ti	F
Sediment V36, 200 °C															
SW/0	<.01	<.01	<.01	<.01	<.01	<.01	<.01	<.01	0.03	7.9	<.01	4.4	<.01	<.01	1.3
1/1.0	5.5	19.6	0.9	1.70	..	..	..	0.01	0.23	3.4	0.34	5.5	<.03	.01	..
2/104.0	12	48.9	1.0	0.45	..	..	..	0.01	0.23	2.0	0.14	7.1	0.06	.01	..
3/332.5	17	55.5	1.0	0.56	..	..	..	<.01	0.16	1.9	0.14	7.7	0.14	<.01	..
4/669.0	23	61.9	1.3	0.42	..	..	..	<.01	0.28	1.8	0.18	7.8	0.12	.01	..
5/1442.0	36	61.8	..	0.39	..	..	..	..	0.10	2.6	0.16	8.2	0.12	..	..
6/2254.5	34	65.4	1.4	0.27	..	..	..	..	0.11	2.7	0.16	9.2	0.04	..	..
Q/2261.4	28	56.5	<.5	0.01	..	..	..	..	0.17	5.8	0.18	7.6	<.05	..	..
Sediment V36, 300 °C															
SW/0	<.01	<.01	<.01	<.01	<.01	<.01	<.01	<.01	0.03	7.9	<.01	4.4	<.01	<.01	1.3
1/1.0	30.3	36.3	1.7	2.8	0.66	..	..	..	0.09	1.1	0.23	7.6	<.1	..	..
2/93.5	181	86.5	6.8	8.4	0.97	..	..	..	0.16	0.8	0.14	9.5	0.20	..	..
3/284.5	231	99.7	8.5	9.4	1.10	..	..	..	0.22	1.0	0.12	9.1	0.24	..	..
4/596.0	229	103	8.0	7.4	1.09	..	..	..	0.28	1.0	0.12	9.0	0.24	..	..
5/1297.0	218	108	9.1	3.3	..	..	..	..	0.37	1.4	0.13	9.4	0.24	..	..
Q/1608.0	..	..	6.8	1.5	..	..	..	..	0.28	3.2	0.28	8.4	0.22	..	..
Sediment SM2, 200 °C															
SW/0	<.01	<.01	<.01	<.01	<.01	<.01	<.01	<.01	0.03	7.9	<.01	4.4	<.01	<.01	1.3
1/5	1.54	56.8	2.3	..	..	0.50	..	0.02	0.08	2.8	0.31	8.5	0.09	.01	..
2/101	1.60	605	2.1	..	..	0.35	..	0.02	0.08	3.4	0.22	22.4	1.30	.01	..
3/341	2.10	614	2.24	..	..	0.30	..	0.02	0.14	4.3	0.26	24.0	1.40	.01	..
4/678	5.70	582	2.9	..	..	0.48	..	0.02	0.18	4.5	0.29	24.0	1.30	.01	..
Q/706	0.16	576	0.74	..	..	0.37	..	0.02	0.12	9.3	0.46	23.0	0.05	.01	..
Sediment SM2, 300 °C															
SW/0	<.01	<.01	<.01	<.01	<.01	<.01	<.01	<.01	0.03	7.9	<.01	4.4	<.01	<.01	1.3
1/2.0	5.9	520	9.6	2.7	0.53	0.25	0.04	0.24	0.22	1.3	0.12	17.5	1.20	.01	5.0
2/79.0	6.7	756	16.2	11.5	..	0.43	0.04	0.09	0.38	2.0	0.12	22.6	1.70	.01	6.1
3/261.5	4.2	777	16.4	43.8	5.75	0.40	0.05	0.09	0.49	2.3	0.17	23.0	1.70	.01	3.7
4/575.3	1.3	807	19.0	54.5	3.50	0.50	0.07	0.06	0.42	2.8	0.17	23.1	1.80	.01	3.0
5/1347.0	0.2	700	17.6	57.7	0.52	0.45	0.01	0.03	0.41	2.9	0.21	23.8	1.66	.01	2.2
6/2811.0	0.2	657	17.4	60.3	0.41	0.54	0.01	0.02	0.44	2.4	0.18	24.2	1.60	.01	1.1

Note: values obtained at 200-300 °C, 500 bars, and water/rock ratio of 5.

SW = starting composition of Copenhagen sea water.

Q = quench, 25 °C.

pH measured at 25 °C; .. not analyzed.

sea-water Mg and  $\text{SiO}_2(\text{aq})$  derived from the dissolution of quartz and amorphous silica. This process can be illustrated by the reaction



The formation of smectite either as a distinct phase or as a talc-like unit within existing clay minerals thus is probably the most important mechanism for producing the acidity observed during these experiments. This process is substantiated by the observation that smectite is a dominant alteration product.

The length of time that solution pH remains acidic depends upon sediment mineralogy. Reaction of carbonates or the hydrolysis of anhydrous silicate phases, for example, serves to titrate  $\text{H}^+$ , and pH will remain low only as long as enough Mg remains in solution to replace the  $\text{H}^+$  consumed by reaction of these minerals. In the experiment with sediment SM2 at 300 °C, pH thus remained below 3 until reaction of clinoptilolite, illite, and a minor amount of calcareous material resulted in partial neutralization of acidity and the removal of the bulk of Mg from solution (Table 2 and Fig. 1). In contrast, the fluid chemistry from the 300 °C V36 experiment remained acidic due to the lack of "reactive" minerals, particularly calcareous material and K-bearing phases (Table 1). The results of the experiments with these two sediments at 200 °C further substantiate these deductions; note, in particular, the higher values of  $\Sigma\text{CO}_2$ , K, and pH, and lower Mg concentrations in solution for SM2 relative to V36, respectively.

The effect of sediment-sea-water interaction on solution chemistry, including pH, can be graphically illustrated through the use of mineral-activity diagrams. These diagrams conveniently illustrate mineral stability fields relative to solution composition. Their use thus can reveal a great deal concerning solution-mineral equilibria and alteration processes. As an example of this approach, mineral-activity diagrams for the  $\text{MgO-CaO-K}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$  system at 300 °C, 500 bars, have been constructed using appropriate thermochemical data (Wolery, 1978; Helgeson and others, 1978); superimposed on these diagrams are the activity ratios of cations and  $\text{H}^+$  calculated using the solution data of the experiments at 300 °C (Fig. 2).

Reaction paths defined by the data illustrated in Figure 2 demonstrate that pH changes are related to mineralogical reactions involving the exchange of  $\text{H}^+$  for  $\text{Ca}^{++}$ ,  $\text{Mg}^{++}$ , and  $\text{K}^+$ . The data from the experiment at 300 °C with sediment SM2 clearly illustrate the general direction of the reaction path. Initially, the activity ratios decrease as  $\text{H}^+$  is released into solution by the hydrolysis of water in conjunction with the formation of smectite (reaction 3); thus the activity ratios of the solution lie well within the stability field of Mg-beidellite, a dioctahedral smectite. The reaction path subsequently reverses as  $\text{H}^+$  in solution is removed by the hydrolysis of the primary silicate minerals and the activity ratios move toward the boundary between Mg-beidellite and Mg-saponite, an analog for triocta-

hedral smectite. The experiment with sediment V36 demonstrates a similar, although less pronounced, evolution of solution chemistry close to the saponite-beidellite boundary at steady state.

The application of mineral-activity diagrams in this manner is valid, however, only if it can be demonstrated that the fluids being considered are near saturation with respect to the solid phases presented. This point is especially important inasmuch as a solution field is not included in Figure 2. The degree of saturation of some representative phases thus is presented in Table 4 on the basis of the aqueous speciation performed by SOLVEQ and from hydrolysis constants computed from the thermochemical data of Helgeson and others (1978) and Wolery (1978).

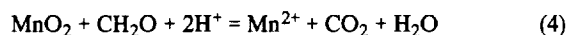
This information illustrates that the experimental fluids were supersaturated with respect to Mg-nontronite (ferric dioctahedral smectite) and saturated to moderately undersaturated with respect to Mg-saponite. A smectite-rich assemblage thus was stable under the experimental conditions, supporting the hypothesis that smectite precipitation is a viable mechanism for promoting the generation of  $\text{H}^+$  through the formation of additional talc-like interlayers or discrete smectite phases.

As further illustrated in Figure 2, the activity ratios of pertinent aqueous species in the experiments are far removed from the stability fields of the zeolite and feldspar minerals, and, indeed, stability fields do not exist for minerals such as chlorite, illite, or calcite under the experimental and compositional conditions for which these diagrams were constructed. It is only through reaction with these phases that acidity can be neutralized.

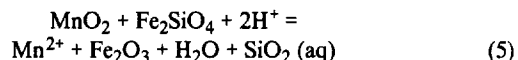
### Redox Equilibria

$\text{MnO}_2$ - and  $\text{Fe}_2\text{O}_3$ -containing phases are ubiquitous components of marine sediments and are commonly accompanied by significant amounts of organic carbon and ferrous iron, the latter incorporated in detrital material such as chlorite, volcanic debris, or magnetite. This assemblage promotes vigorous redox reactions at elevated temperatures and pressures which greatly affect solution chemistry and alteration processes.

Reaction of  $\text{MnO}_2$  with organic carbon and components containing ferrous iron can be illustrated as



and



where  $\text{CH}_2\text{O}$  and  $\text{Fe}_2\text{SiO}_4$  represent organic matter and ferrous iron phases, respectively. Pore solutions in sediment containing  $\text{MnO}_2$  in excess of organic matter and ferrous iron thus will be characterized by high Mn concentrations and low Fe concentrations. Sediments containing a larger amount of organic matter will ultimately reduce all  $\text{MnO}_2$ -containing

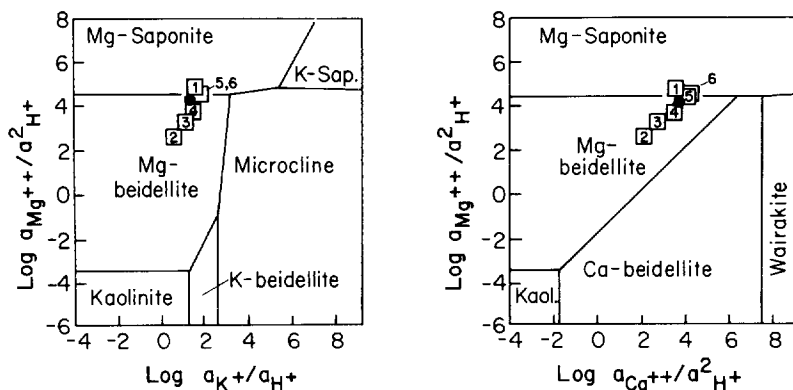


Figure 2. Mineral activity diagrams for the  $\text{MgO-CaO-K}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$  system at 300 °C, 500 bars, and amorphous silica saturation ( $a_{\text{SiO}_2} = 10^{-1.48}$ ). Data points represent the activity ratios for solution samples (squares = SM2, 300 °C; filled circles = V36, 300 °C, 1,297 hr).

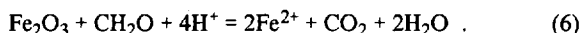
TABLE 4. DEGREE OF SATURATION (LOG IAP/K) OF EXPERIMENTAL FLUIDS WITH RESPECT TO SELECTED MINERALS AT 300 °C AND 500 BARS PRESSURE.

Sample/hr	Quartz	Am. silica	Calcite	Anhydrite	MHSH	Mg-nontronite	Mg-saponite	Illite	Clinocllore
Sediment V36, 300 °C									
1/1.0	0.25	-0.18	-5.29	0.33	-0.32	4.08	0.85	-3.14	-4.00
2/93.5	0.46	0.02	-5.50	0.11	-1.12	5.08	-0.98	-3.88	-8.20
3/284.5	0.46	0.03	-5.24	-0.01	-1.41	5.79	-0.96	-3.84	-8.20
4/596.0	0.45	0.02	-5.02	0.03	-1.46	6.43	-0.50	-5.16	-7.29
5/1297.0	0.46	0.02	-5.11	-0.02	-1.80	5.71	-1.40	-3.80	-8.85
Sediment SM2, 300 °C									
1/2.0	0.52	0.09	-5.25	-0.13	-1.29	4.56	0.10	-3.38	-6.64
2/79.0	0.51	0.08	-6.29	-0.70	-2.76	0.80	-4.99	-5.56	-15.56
3/261.5	0.49	0.06	-5.65	-0.66	-2.57	2.44	-3.01	-4.20	-14.07
4/575.3	0.51	0.07	-5.27	-0.57	-2.51	2.80	-1.96	-3.50	-9.77
5/1347.0	0.30	-0.13	-4.28	-0.58	-2.48	3.02	-0.62	-2.26	-6.36
6/2811.0	0.30	-0.14	-4.34	-0.49	-2.42	3.19	-0.69	-2.77	-6.51

$\text{SiO}_2 = \text{SiO}_2(\text{aq})$ ; Log K (quartz) = -1.91; Log K (amorphous silica) = -1.48.  
 $\text{CaCO}_3 + \text{H}^+ = \text{Ca}^{2+} + \text{HCO}_3^-$ ; Log K = -1.54.  
 $\text{CaSO}_4 = \text{Ca}^{2+} + \text{SO}_4^{2-}$ ; Log K = -8.93.  
 $\text{MgO} \cdot 4\text{MgSO}_4 \cdot 2\text{H}_2\text{O} + 2\text{H}^+ = 5\text{Mg}^{2+} + 4\text{SO}_4^{2-} + 3\text{H}_2\text{O}$ ; Log K = -5.59.

$\text{Mg-nontronite} + 7.32\text{H}^+ = 4.66\text{H}_2\text{O} + 0.165\text{Mg}^{2+} + 0.33\text{Al}^{3+} + 3.67\text{SiO}_2(\text{aq}) + 2\text{Fe}^{3+}$ ; Log K = -15.16.  
 $\text{Mg-saponite} + 7.32\text{H}^+ = 4.66\text{H}_2\text{O} + 3.165\text{Mg}^{2+} + 0.33\text{Al}^{3+} + 3.675\text{SiO}_2(\text{aq})$ ; Log K = -3.97.  
 $\text{Illite} + 8\text{H}^+ = 5\text{H}_2\text{O} + 0.6\text{K}^+ + 0.25\text{Mg}^{2+} + 2.3\text{Al}^{3+} + 3.5\text{SiO}_2(\text{aq})$ ; Log K = -3.97.  
 $14\text{A-Clinocllore} + 16\text{H}^+ = 12\text{H}_2\text{O} + 5\text{Mg}^{2+} + 2\text{Al}^{3+} + 3\text{SiO}_2(\text{aq})$ ; Log K = 20.78.

phases, and  $\text{Fe}_2\text{O}_3$  will be the dominant oxidizing agent; that is, ferrous iron will enter solution in response to the reaction



The experimental results were clearly influenced by the redox processes presented above. Reaction of sediment SM2 with sea water thus

yielded distinctly oxidizing fluids characterized by high Mn/Fe ratios (Fig. 1). This sediment contained sufficient  $\text{MnO}_2$  to oxidize virtually all of the organic carbon (0.05%) and ferrous iron available (reactions 4 and 5). Sediment V36, in contrast, generated more reducing fluids characterized by low Mn/Fe ratios, owing to the relatively high organic carbon content (0.43%) and low  $\text{MnO}_2$  of the sediment. Hematite therefore acted as the primary oxidizing agent, releasing ferrous iron to solution as organic carbon was oxidized (reaction 6).

Evaluation of the degree of oxidation of organic carbon by mass-balance calculations utilizing  $\text{CO}_2$  concentration is not possible because several sources contribute this component to solution. That is, in addition to oxidation of organic carbon, aqueous  $\text{CO}_2$  may also be generated by dissolution of carbonate minerals and by thermal alteration of organic matter.

### Estimation of Oxygen Fugacity

Quantitative evaluation of the oxidation potential of fluids derived from these experiments is extremely difficult because of our inability to define, specifically, the stable phases involved in redox reactions and because of uncertainties in the thermochemical data base for even generalized phases involved in these reactions. The solubility of Au from the reaction cell, however, has proven to be useful for this purpose, as the redox couple is defined in terms of only one solid phase (Au) and the aqueous Au-complexes, of which  $\text{AuCl}_2^-$  is of primary importance. Thermodynamic data from Helgeson (1969), together with *in situ* activities calculated by SOLVEQ from the measured pH and from concentrations of Au and Cl in the fluids, may be used to estimate  $f\text{O}_2$  as follows:



In the experiment with the oxidizing sediment (SM2),  $f\text{O}_2$  was found to range from  $10^{-13}$  to  $10^{-17}$  at 300 °C, whereas  $f\text{O}_2$  computed for the experiment utilizing sediment V36 at 300 °C was  $\sim 10^{-20}$  (Fig. 3).

### Mobility of the Base Metals and Boron

The experimental data presented here indicate that significant metal mobility occurs during hydrothermal interaction of seawater and sediment at 300 °C (Table 3). Dissolved Fe appeared to increase in concentration primarily in response to low pH in experiments, but it fell late in the experiment with SM2 due to an increase in pH. It was also apparent in

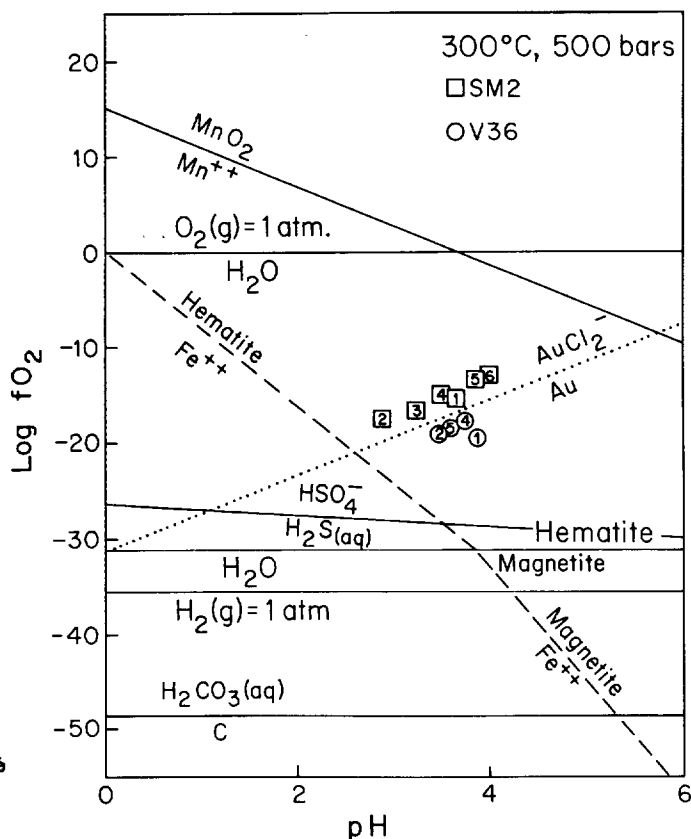


Figure 3. Relationship of redox couples and chemistry of experimental solution samples as a function of  $f\text{O}_2$  and pH at 300 °C, 500 bars. Boundaries drawn assuming an activity of  $10^{-6}$  for aqueous species.

that experiment that Pb decreased as pH increased, after attaining a concentration of at least 6 ppm. Mn concentration increased in response to reduction of  $MnO_2$ , primarily by organic matter (reaction 4). Cu clearly was mobilized by oxidation, attaining concentration levels an order of magnitude higher in the experiment with SM2 at 300 °C than in the experiment with V36. Cu appears to have been completely leached from sediment SM2, reaching a concentration in excess of 60 ppm. Significant amounts of Zn are also mobilized; in the experiment with SM2, it reached 19 ppm, and with V36, it reached 9 ppm.

These data suggest that Cu-bearing solutions accompanied by Zn and Pb may evolve in sedimentary basins characterized by oxidizing conditions, whereas Zn and Pb will predominate in a more reducing environment (Thornton and Seyfried, 1981). Analysis of reservoir fluid from the Salton Sea has demonstrated that appreciable amounts of metals are being mobilized through the interaction of the brine with continental clastic sediments (Helgeson, 1967, 1968). This fluid may be similar to that involved in the formation of the Sullivan deposit, an example of the class of sediment-hosted stratiform sulfide deposits. These deposits have generally come to be regarded as syngenetic or very early diagenetic in origin, being produced by hydrothermal exhalatives in a shallow-marine basin (Gustafson and Williams, 1981). The presence of  $H_2S$  in the Salton Sea brine indicates a somewhat reducing environment for fluid evolution, and Pb and Zn predominate over Cu. These observations are consistent with the predominance of Pb-Zn sulfides in most deposits of the Sullivan type.

The Salton Sea brine also has a high content of boron (390 ppm) which apparently was also leached from the sediments. It is of interest to note that tourmalinites are associated with the Sullivan deposit (Ethier and Campbell, 1977; Slack, 1980). A high boron content was observed in the experimental fluids at 200 and 300 °C; sediment V36 released 10 ppm boron to solution, and SM2 released >20 ppm (Table 3). This represents nearly quantitative leaching of boron from the sediments, which originally contained 100 to 150 ppm.

#### The Role of Silica Activity in Clay-Mineral Transformations

A discrepancy is apparent when the solid products of the experiments are compared to the mineralogical assemblages generated during the diagenesis and low-grade metamorphism of clay-rich sediment. That is, the experiments have generally demonstrated the formation of smectite at the expense of illite and chlorite, although the reverse is true in the two geologic examples considered in the introductory section.

Aqueous silica concentrations in the experiments were consistently higher than was the level for quartz saturation (commonly being much closer to amorphous silica or cristobalite saturation) and appear to be controlled by the amount of amorphous silica-bearing phases initially present in the sediment. The experiments with sediment V36 were near amorphous silica saturation throughout their duration due to the large amount of amorphous silica originally present (Table 2). The experiments with sediment SM2, in contrast, indicate that a lower concentration of aqueous silica was present at 200 °C; at 300 °C, silica decreased initially from amorphous silica saturation to a level nearer cristobalite saturation. This behavior may be ascribed to the limited amount of amorphous silica originally present in SM2 (Table 1). Additional information in regard to the role of sediment composition in controlling aqueous silica activity may be obtained from data presented by Seyfried and others (1980b) for an experiment conducted at 300 °C with pelagic clay from the North Pacific. This sample consisted primarily of a detrital quartz-illite component with essentially no amorphous silica. Fluids obtained were consequently near cristobalite saturation throughout the experiment (for example, 939 ppm  $SiO_2$  in solution at 1,243 hr). The prevention of equilibration of silica in

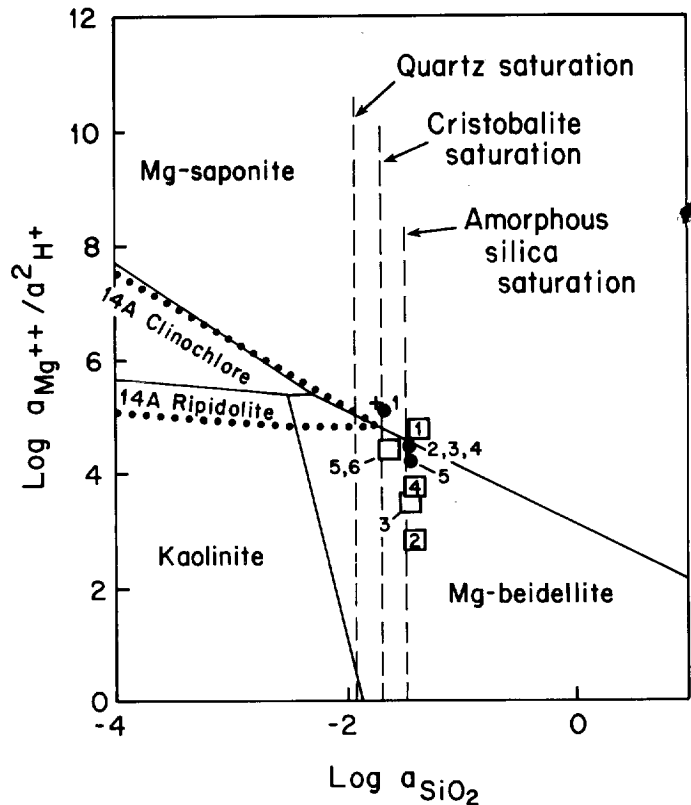


Figure 4. Mineral-activity diagram for the  $MgO-SiO_2-Al_2O_3-H_2O$  system at 300 °C, 500 bars. Data points represent activities of components of experimental solution samples (+ = sediment B, 300 °C, 1,243 hr (Seyfried and others, 1980b); squares = SM2, 300 °C; filled circles = V36, 300 °C). Stability field of ripidolite is outlined by filled circles.

experimental fluids, with respect to quartz, a major phase present in all of the sediments, appears to be due to the sluggish kinetics of quartz growth under acidic conditions (Seyfried and Mottl, 1982).

The role of silica concentration in fluids, with respect to the stability of smectite relative to illite (or muscovite), may be readily seen in reaction 1. That is, a high silica level approaching amorphous silica saturation will serve to stabilize smectite relative to illite by driving reaction 1 to the left. Conversely, silica concentrations in solution near quartz saturation (for example, Salton Sea geothermal fluids) will tend to stabilize illite relative to smectite. A similar relationship also exists between smectite and chlorite. As illustrated in Figure 4, smectite is increasingly stable in comparison to chlorite at relatively high silica concentrations. It follows that smectite formation in the experiments having fluids saturated with respect to amorphous silica will occur more readily than those undersaturated with respect to amorphous silica. The experiments with sediments V36 and, to a lesser degree, SM2, thus produced smectite as a reaction product, whereas pelagic clay, which is devoid of amorphous silica-containing components, produced Mg-chlorite at 300 °C (Seyfried and others, 1980b). Chlorite would certainly be expected to be more stable in the geologic environment where sufficient time is available to permit pore fluid to equilibrate with quartz. It should be noted, in addition, that the sediments of the Salton Sea trough and the Gulf Coast region are largely of detrital origin. They have rather low amorphous silica contents and hence might be expected to yield chlorite and illite upon burial. Conversely, smectite may be stable during



burial metamorphism in marine basins characterized by a larger component of siliceous organisms such as diatoms and radiolarians. For example, hydrothermal alteration of diatom-rich sediments in the southern trough of the Guaymas Basin, Gulf of California, is characterized by smectite, not chlorite or illite, even though temperatures of alteration approached 200 °C (Stout and Campbell, 1983). Furthermore, Lonsdale and others (1980) described near-surface, hydrothermally altered rocks from the northern trough of the Guaymas Basin. These rocks were altered at temperatures as high as 280 °C and once again contained smectite in association with iron-rich talc and pyrrhotite. Apparently, the diatom-rich nature of these sediments results in SiO<sub>2</sub> concentrations in solution much in excess of quartz saturation. This leads to formation of smectite, rather than relatively silica-poor phases, such as chlorite.

The stability of chlorite at 300 °C is strongly affected by compositional variations. To illustrate this, the stability fields of both the Mg end member, clinocllore, and a chlorite containing both Fe and Mg, ripidolite, are presented in Figure 4 under conditions typical during our experiments. It is apparent from the illustration that the inclusion of a ferrous-iron component increases the stability field of chlorite to quartz saturation and possibly to cristobalite saturation, in agreement with the presence of chlorite in the reaction products of the experiment conducted with the pelagic clay. Precise definition of chlorite stability will not be possible, however, until sufficient thermodynamic data are available for the compositional end members to permit accurate assessment of solid solution through site-mixing approximations (Stoessel, 1983; Helgeson and others, 1978).

## SUMMARY

Experimental interaction of sediment and sea water at 200 and 300 °C, 500 bars, and at a water/rock mass ratio of 5 resulted in significant changes in fluid chemistry. These included a decrease in Mg and SO<sub>4</sub> and an increase in Na, K, SiO<sub>2</sub>, Cl, ΣCO<sub>2</sub>, Fe, and Mn. Cu, Zn, Pb, and B also increased during reaction, primarily in response to the low pH and moderately to highly oxidizing conditions generated. Reaction products observed during these experiments included smectite, smectite/chlorite, anhydrite, and cristobalite.

In an effort to utilize the experimental results in defining the alteration processes operating in the geologic environment, fluid chemistry and mineralogical assemblages resulting from diagenesis and metamorphism of pelitic sediments in the Gulf Coast and Salton Sea regions were considered. Differences between the experimental and geologic examples appear to arise primarily from kinetic effects associated with the relatively short duration of the experiments. Fluids in the geologic environment are therefore generally near saturation with respect to quartz, but the experimentally derived fluids were closer to cristobalite or amorphous silica saturation. Fluids in the geologic environment also have a higher pH and are more reducing, possibly as a result of an increased degree of reaction between fluid and ferrous iron-bearing silicates. Geologic assemblages are commonly dominated by chlorite and illite or muscovite, rather than smectite, probably due largely to the lower silica content of the geologic fluids. Smectite-rich assemblages, however, may be anticipated in marine basins containing sediments with a substantial amorphous silica content.

## ACKNOWLEDGMENTS

The authors wish to acknowledge the support of Sandia National Laboratories under the subseabed disposal program. The final manuscript benefited greatly from the comments of L. R. Gardner (University of South Carolina) and an anonymous reviewer. We also gratefully acknowledge the contribution of R. Knoche (University of Minnesota), who

performed sediment and fluid analyses. D. R. Janecky (Los Alamos National Laboratory) contributed significantly through the acquisition of thermodynamic data used in the evaluation of mineral stability.

## REFERENCES CITED

- Bankston, D. C., Humphris, S. E., and Thompson, G., 1979, Major and minor oxide and trace element determination in silicate rocks by direct current plasma optical emission echelle spectrometry: *Analytical Chemistry*, v. 51, p. 1218-1225.
- Bischoff, J. L., and Seyfried, W. E., 1978, Hydrothermal chemistry of seawater from 25° to 350 °C: *American Journal of Science*, v. 278, p. 838-860.
- Burst, J. F., 1969, Diagenesis of Gulf Coast clayey sediments and its possible relation to petroleum migration: *American Association of Petroleum Geologists Bulletin*, v. 53, p. 73-93.
- Cohen, R. S., Hemmes, P., and Puffer, J. H., 1975, *m*-Benzene disulfonic acid (BDS) as a superior accompanying acid for routine silicate rock analysis: *Chemical Geology*, v. 16, p. 307-309.
- Dickey, P. A., Collins, A. G., and Fajardo, M. I., 1972, Chemical composition of deep formation waters in southwestern Louisiana: *American Association of Petroleum Geologists Bulletin*, v. 56, p. 1530-1533.
- Dickson, F. W., Blount, C. W., and Tunell, G., 1963, Use of hydrothermal solution equipment to determine the solubility of anhydrite in water from 100 °C to 275 °C and from 1 bar to 1,000 bars pressure: *American Journal of Science*, v. 261, p. 61-78.
- Dunoyer de Segonzac, G., 1970, The transformation of clay minerals during diagenesis and low-grade metamorphism: A review: *Sedimentology*, v. 15, p. 281-346.
- Ethier, V. G., and Campbell, F. A., 1977, Tourmaline concentrations in Proterozoic sediments of the southern Cordillera of Canada and their economic significance: *Canadian Journal of Earth Sciences*, v. 14, p. 2348-2363.
- Graf, D. L., 1982, Chemical osmosis, reverse chemical osmosis, and origin of subsurface brines: *Geochimica et Cosmochimica Acta*, v. 46, p. 1431-1448.
- Gustafson, L. B., and Williams, N., 1981, Sediment-hosted stratiform deposits of copper, lead, and zinc: *Economic Geology*, Seventy-fifth Anniversary Volume, p. 139-178.
- Hanor, J. S., 1979, The sedimentary genesis of hydrothermal fluids, in Barnes, H. L., ed., *Geochemistry of hydrothermal ore deposits* (2nd edition): New York, John Wiley and Sons, Inc., p. 137-172.
- Heath, G. R., 1981, Site qualification and multibarrier assessment: *Subseabed Disposal Annual Report*, January to December 1980, Sandia National Laboratories, Albuquerque, New Mexico.
- Helgeson, H. C., 1967, Solution chemistry and metamorphism, in Abelson, H. L., ed., *Researches in geochemistry*, Volume 2: New York, John Wiley and Sons, Inc., p. 362-404.
- , 1968, Geologic and thermodynamic characteristics of the Salton Sea Geothermal System: *American Journal of Science*, v. 266, p. 129-166.
- , 1969, Thermodynamics of hydrothermal systems at elevated temperatures and pressures: *American Journal of Science*, v. 267, p. 729-804.
- Helgeson, H. C., Delany, J. M., Nesbitt, H. W., and Bird, D. K., 1978, Summary and critique of the thermodynamic properties of rock-forming minerals: *American Journal of Science*, v. 278-A, 229 p.
- Hower, J., Eslinger, E. V., Hower, M. E., and Perry, E. A., 1976, Mechanism of burial metamorphism of argillaceous sediment: I. Mineralogical and chemical evidence: *Geological Society of America Bulletin*, v. 87, p. 725-737.
- Kharaka, Y. K., and Berry, F. A., 1973, Simultaneous flow of water and solutes through geologic membranes. I. Experimental investigation: *Geochimica et Cosmochimica Acta*, v. 37, p. 2577-2603.
- Lonsdale, P., Bischoff, J. L., Burns, V. M., Kastner, M., and Sweeney, R. E., 1980, A high-temperature hydrothermal deposit on the seabed at a Gulf of California spreading center: *Earth and Planetary Science Letters*, v. 49, p. 8-20.
- Maxwell, D. T., and Hower, J., 1967, High-grade diagenesis and low-grade metamorphism of illite in the Precambrian Belt Series: *American Mineralogist*, v. 52, p. 843-857.
- McDowell, S. D., and Elders, W. A., 1980, Authigenic layer silicate minerals in borehole Elmore 1, Salton Sea Geothermal Field, California, USA: *Contributions to Mineralogy and Petrology*, v. 74, p. 293-310.
- Reed, M. H., 1977, Calculation of hydrothermal metasomatism and ore deposition in submarine volcanic rocks with special reference to the West Shasta district, California [Ph.D. thesis]: Berkeley, California, University of California, 107 p.
- Schmidt, G. W., 1973, Interstitial water composition and geochemistry of deep Gulf Coast shales and sands: *American Association of Petroleum Geologists Bulletin*, v. 57, p. 321-337.
- Seyfried, W. E., Jr., and Dibble, W. E., Jr., 1980, Seawater-peridotite interaction at 300 °C and 500 bars: Implications for the origin of oceanic serpentinites: *Geochimica et Cosmochimica Acta*, v. 44, p. 309-321.
- Seyfried, W. E., Jr., and Mottl, M. J., 1982, Hydrothermal alteration of basalt by seawater under seawater-dominated conditions: *Geochimica et Cosmochimica Acta*, v. 46, p. 985-1002.
- Seyfried, W. E., Jr., Gordon, P. C., and Dickson, F. W., 1979, A new reaction cell for hydrothermal solution equipment: *American Mineralogist*, v. 64, p. 646-649.
- Seyfried, W. E., Jr., Thornton, E. C., and Janecky, D. R., 1980a, Seawater-sediment interaction at 300 °C, 500 bars: Implications for seabed disposal of nuclear wastes: *International Symposium on Water-Rock Interaction*, 3rd, Edmonton, Canada, Proceedings, p. 135-137.
- , 1980b, Seawater-sediment interaction at elevated temperatures and pressures: Implications for the near field chemical environment: *Seabed Disposal Annual Report*, January 1, 1979 through December 1979, Sandia National Laboratories, Albuquerque, New Mexico.
- Silva, A. J., 1977, Physical processes in deep-sea clays: *Oceanus*, v. 20, no. 1, p. 31-40.
- Slack, J. F., 1980, *Tourmaline—A prospecting guide for massive base-metal deposits in the Penobscot Bay area, Maine*: Maine Geological Survey Special Economic Studies Series, v. 8, 25 p.
- Stoessel, R. K., 1983, A solid solution model for chlorites: *Geological Society of America Abstracts with Programs*, v. 15, p. 698.
- Stout, P. M., and Campbell, A. C., 1983, Hydrothermal alteration of near-surface sediments, Guaymas Basin, Gulf of California, in Larue, D. K., and others, eds., *Cenozoic marine sedimentation, Pacific margin, U.S.A.*: Society of Economic Paleontologists and Mineralogists, Pacific Section Meeting, Sacramento, California, p. 223-231.
- Thornton, E. C., 1983, Experimental and theoretical modeling of sediment-seawater hydrothermal interaction at constant temperature and in a thermal gradient: Implications for the diagenesis and metamorphism of marine clay and the seabed disposal of nuclear waste [Ph.D. thesis]: Minneapolis, Minnesota, University of Minnesota, 193 p.
- Thornton, E. C., and Seyfried, W. E., Jr., 1981, Experimental hydrothermal alteration of sediments: A model for stratiform copper mineralization and the boron anomaly: *Geological Society of America Abstracts with Programs*, v. 13, p. 567.
- Weaver, C. E., and Beck, K. C., 1971, Clay-water diagenesis during burial: How mud becomes gneiss: *Geological Society of America Special Paper* 134, 96 p.
- White, D. E., 1965, Saline waters of sedimentary rocks: *American Association of Petroleum Geologists Memoir*, v. 4, p. 342-366.
- White, D. E., Hem, J. D., and Waring, G. A., 1963, Chemical composition of subsurface waters: *U.S. Geological Survey Professional Paper* 440-F, p. F1-F67.
- Winkler, H.G.F., 1976, *Petrogenesis of metamorphic rocks*: New York, Springer-Verlag, 334 p.
- Wolery, T. J., 1978, Some chemical aspects of hydrothermal processes at mid-oceanic ridges—A theoretical study [Ph.D. thesis]: Evanston, Illinois, Northwestern University, 263 p.
- Zen, E.-An, 1974, Burial metamorphism: *Canadian Mineralogist*, v. 12, p. 445-455.

MANUSCRIPT RECEIVED BY THE SOCIETY APRIL 25, 1984

REVISED MANUSCRIPT RECEIVED MARCH 18, 1985

MANUSCRIPT ACCEPTED MARCH 30, 1985

PUBLICATION NO. 1077 OF THE SCHOOL OF EARTH SCIENCES, DEPARTMENT OF GEOLOGY AND GEOPHYSICS, UNIVERSITY OF MINNESOTA