

HYDROTHERMAL CHEMISTRY OF SEAWATER FROM 25° to 350°C*

JAMES L. BISCHOFF** and WILLIAM E. SEYFRIED***

ABSTRACT. Progressive heating of seawater to 350°C causes it to become increasingly acid and depleted in Ca, Mg, and SO₄, because anhydrite and a previously undescribed magnesium oxysulfate are precipitated. Observed composition changes and calculation of activities of dissolved species reveal a progressive increase of HSO₄⁻, HCl⁰, and MgOH⁺ and decrease of HCO₃⁻, CO₃⁼, and CaHCO₃⁺ at temperatures above 150°C. The pH at experimental conditions drops to 3.3, while the buffer capacity of seawater increases from 0.24 meq/pH at 25°C to 54 meq/pH at 350°C.

Theoretical solubilities of brucite, anhydrite, magnesite, dolomite, and calcite were compared to ion-activity products. Comparison of solution composition with theoretical solubilities indicates that carbonate minerals were supersaturated with increasing temperature. The solution composition indicates equilibrium saturation with anhydrite at temperatures $\geq 150^\circ\text{C}$.

INTRODUCTION

Seawater-basalt interaction is rapidly being accepted as an important mechanism for balancing the geochemical budget for several components in the hydrosphere, for producing the ore fluids that precipitate sea-floor metalliferous sediments, and for dissipating the bulk of heat produced during sea-floor spreading.

Conditions of such interaction are poorly defined and, until recently, were believed to be analagous to the Reykjanes geothermal system in Iceland, where the flux of seawater is small relative to the amount of rock contacted and altered, and where temperatures reach nearly 300°C (Tomasson and Kristmannsdottir, 1972; Mottl, Corr, and Holland, 1975). Although changes in the major dissolved species are in qualitative agreement with the proposed role of seawater-basalt-interaction in the geochemical cycle, mobilization of heavy metals is quantitatively unimportant (Mottl, Corr, and Holland, 1975). Experimental studies designed to approximate conditions of the Reykjanes system (Mottl, ms; Bischoff and Dickson, 1975; Seyfried, ms) have yielded similar results. Heavy metals are mobilized from the rock initially but are reprecipitated into the alteration phases in a matter of days. Thus, the geochemical cycle hypothesis was supported, but the metal transport role was not.

It now seems that Reykjanes represents only one specific type of seawater-basalt interaction. Recent mathematical modeling of heat budgets and sea-floor spreading (Lister, 1972; Williams and others, 1974; Wolery and Sleep, 1976) suggests that large volumes of seawater must cycle through spreading centers to account for the required transfer of a major portion of heat. Effective water-rock ratios (total amount of water passing through the system/total amount of rock altered) may be in the range of 50 or 100:1.

We recently reported on an experimental study of seawater-basalt interaction at 260°C and 50:1 water rock ratio, a system chemically dominated by seawater (Seyfried and Bischoff, 1977). This study showed

* Publication authorized by the Director, U.S. Geological Survey

** U.S. Geological Survey, Menlo Park, California 94025

*** Geology Department, Stanford University, Stanford, California 94305

that under water dominated conditions, heavy metals are significantly leached from the rock, are maintained in solution, and show no tendency to reprecipitate with the alteration products. The chemical system in this study was controlled by the seawater rather than the rock, and the solution remained slightly acid throughout the experiment. Thus, high water-rock ratios may be the key to heavy metal transport.

What is it about the chemistry of heated seawater that appears to make it such an effective leaching fluid? The logical extension of the previous experiment was to monitor the chemical behavior of seawater in a closed system at various temperatures. This experiment serves two purposes: (1) to study a system in which all components are originally in a single phase, a system more amenable to thermodynamic interpretation than those including a multicomponent rock phase; (2) to provide information for the extreme case in the spectrum of possible water-rock ratios, that of infinite dilution.

This report includes the results of closed-system experiments on seawater at 70° to 350°C and 500 bars and analyses for Na, Mg, Ca, K, Cl, SO₄, pH, and total dissolved CO₂ species (C_T).

EXPERIMENTAL PROCEDURES

Experiments from 70° to 350°C were carried out in "Dickson" hydrothermal equipment that allowed on-line sampling (Dickson, Blount, and Tunell, 1963), using reaction cells made of gold. Pressure was maintained at 500 bars to represent the approximate pressure of the upper kilometer of crust beneath deep sea spreading centers.

Surface seawater for the experiments was collected off Point Hueheme, southern California, and filtered through 0.1 μ membrane filter (chlorinity = 18.55 ‰). Approximately 100 ml of this water was used for each experiment.

Replicate sampling and pH measurements indicated no further tendency for chemical change after about the first 24 hrs for all experiments. The experiments, however, were continued for approximately one month until termination and final sampling.

Samples were taken at experimental conditions by opening a valve block and allowing the reacted seawater to enter a gas-tight syringe. Aliquots were separated for immediate measurement of pH by micro-combination electrode and C_T by infrared analyzer. Additional acidified aliquots were analyzed for Na, Mg, Ca, and K by flame AA and for Cl by chloridometer (London Co.). SO₄ was analyzed by precipitation with ¹³³Ba inside a dialysis membrane tube. After 24 hrs of washing the entire dialysis tube was counted on a scintillation counter. Analyses of Fe, Mn, Ni, Cu, and Al were carried out by flameless AA (Perkin Elmer HGA 2100), the results indicating that the concentration of these elements in all samples was below our detection limit of approx 5 to 10 ppb. Copenhagen seawater served as a standard or as a standard matrix for all the analyses.

Analytical precision for K, Mg, Ca, and C_T is estimated at 1 percent or better, for Cl at 1 percent, Na at 2.5 percent, and SO_4 at about 2.5 percent at concentrations of 0.027 molal, and about 10 percent at 0.01 molal. pH was measured at 25°C and was generally stable for the first 60 sec and then began to drift in response to CO_2 outgassing. For replicate samples taken over a period of weeks from a single experiment, pH was reproducible within ± 0.02 .

The largest analytical error both in terms of percent of the amount present and in total millimoles of a given species is in the measurement of Na and Cl. A 2.5 percent precision for Na implies an uncertainty of ± 12 millimolal. According to our experimental results (see below), Na and Cl remain unchanged in all the experiments. Analytical uncertainty of the remaining components, therefore, is estimated by assuming constant values of Na and Cl based on initially measured salinity (accurate to four significant figures) and by making a charge balance. These calculations reveal charge balances within 1 to 2 meq/kg and indicate what we consider to be excellent control on the composition of the fluid.

CHANGES IN SEAWATER COMPOSITION WITH TEMPERATURE

Analytical data (table 1, fig. 1) indicate that seawater undergoes considerable chemical modification during heating. Na, K, and Cl remain unchanged, while Ca, Mg, and SO_4 decrease significantly at the higher temperatures. Most significant is the drop in the measured pH (pH_{25°), from 7.63 in the starting seawater to 2.52 for seawater quenched from 350°C. C_T increases slightly from 2.0 millimolal initially to 2.2 or 2.3 millimolal at temperatures above 150°C; this increase is attributed to the oxidation of dissolved organic matter. Surface seawater generally contains between 1 and 5 ppm dissolved organic carbon (Duursma, 1960), and only 3 ppm is sufficient to consume all the dissolved oxygen to form 0.2 millimolal CO_2 .

TABLE 1
pH and analyzed molality of major components in Point Hueneme
seawater at various temperatures and 500 bars

T°C	pH (25°C)	Cl	SO_4	Total CO_2 (C_T)	Na	Mg	Ca	K
25	7.63	0.52	0.027	0.0020	0.45	0.0511	0.0098	0.0097
70	7.7	0.52	0.027	0.0021	0.45	0.0504	0.0099	0.0097
150	6.43	0.52	0.027	0.0022	0.45	0.0504	0.0099	0.0097
200	6.20	0.52	0.020	0.0022	0.45	0.0510	0.0030	0.0097
250	5.80	0.52	0.018	0.0022	0.45	0.0506	0.0015	0.0097
300	3.01	0.52	0.011	0.0022	0.45	0.0438	0.0010	0.0097
350	2.52	0.52	0.009	0.0023	0.45	0.0402	0.0010	0.0097

PRECIPITATION OF SOLIDS AND PRODUCTION OF HYDROGEN IONS

Although the pH under conditions (*in situ* pH) must be different from that measured at room temperature, the low values of pH_{25° indicate that ionizable hydrogen is being produced at high temperature and that the mechanism of production must involve irreversible or only very slowly reversible reactions. Although changing distribution of dissolved species at higher temperatures can produce an acid system at conditions, reequilibration of these species during cooling is very rapid, and the measured pH at room temperature should be little different from that of the starting seawater. Thus, the process forming the acidity must be a result of precipitation of a solid.

The 70°C composition was essentially unchanged from that at 25°C. At 150°C, major components were still unchanged, and the pH_{25° has

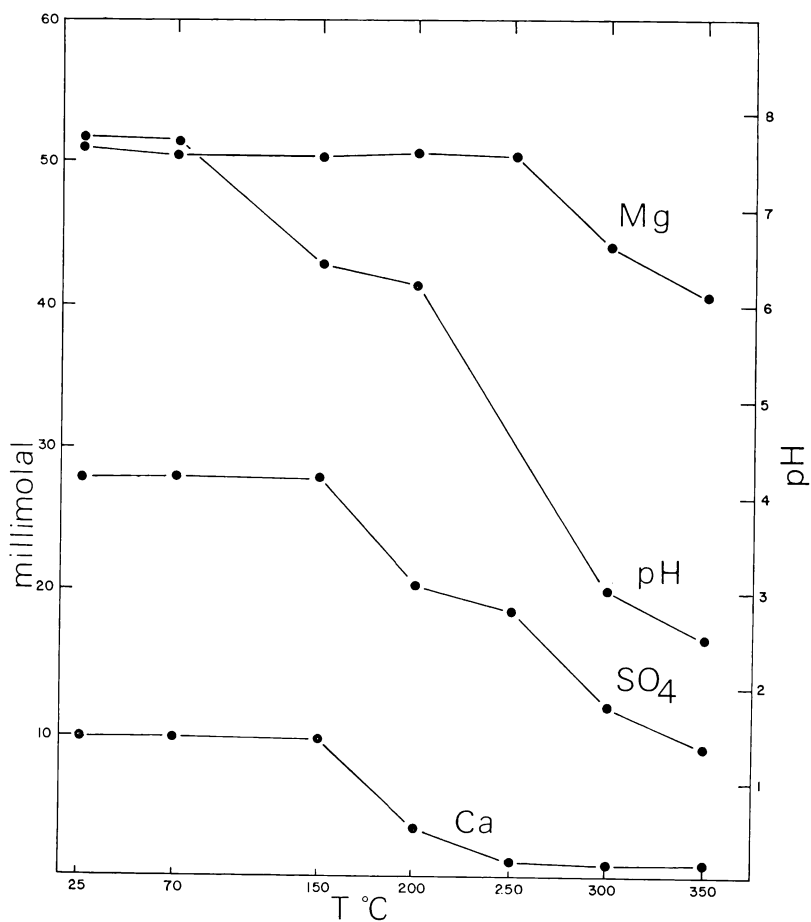


Fig. 1. PH and molality of Mg, Ca, and SO₄ in Point Hueneme seawater from 25° to 350°C at 500 bars.

dropped only slightly to 6.7. Between 150° and 200°C, Ca and SO₄ began to decrease (both by the same 6.8 millimolals (tables 1 and 2)), indicating the precipitation of anhydrite. Further precipitation of anhydrite was evident at 250°C (tables 1 and 2) at which point an additional 2 millimolal of both Ca and SO₄ were removed from solution. Anhydrite was the only precipitate at 200° and 250°C and amounted to about 1 g per kg of seawater (table 3). Inasmuch as the precipitation of anhydrite produces no ionizable hydrogen, the slight pH_{25°} drop from 7.6 at 25°C to 5.8 at 250°C and the accompanying 10 percent increase in C_T (0.2 millimolal) are caused by oxidation of dissolved organic matter.

Between 250° and 300°C, Mg began to precipitate (table 1). Ca continued to precipitate within this interval but in significantly smaller amounts than SO₄ (tables 1 and 2). In addition, pH_{25°} dropped dramatically to 3.01. Further changes in these same components were seen at 350°C, where more Mg, Ca, SO₄ were removed, and pH_{25°} dropped to 2.52 (table 1). Thus, at 300° and 350°C the precipitate was composed of Ca, Mg, and SO₄ and presumably contained OH⁻ to account for the H⁺ increase.

COMPOSITION OF PRECIPITATE

Changes in the composition of the fluid (table 1) allow an estimate of the composition of the precipitate for 300° and 350°C. The amounts of precipitated Mg, Ca, and SO₄ in millimolal are readily calculated (table 2). The gain in total ionizable hydrogen (presumably equal to the amount of OH⁻ precipitated) is equal to C_T plus molality of H⁺ at 25°C provided the pH_{25°} is less than 5.5. This is because initially produced H⁺ must first titrate all HCO₃⁻ which is essentially equal to C_T in seawater at 25°C to CO₂. Further additions of ionizable hydrogen are reflected in equivalent changes in pH. Choosing 0.8 as the activity coefficient of H⁺ at 25°C, ionizable hydrogen gains of 3.52 and 6.07 millimolal were calculated for 300° and 350°C, respectively (table 2).

TABLE 2

Mass balance relations between Ca, Mg, and SO₄ loss and ionizable hydrogen gain in Point Hueneme seawater. Concentrations in millimolal

T°C	SO ₄ loss	Ca loss	Mg loss	ionizable hydrogen gain	SO ₄ loss-Ca loss	Mg loss-1/2H gain
70	-	-	-	-	-	-
150	-	-	-	-	-	-
200	6.9	6.8	-	-	0.1	-
250	8.4	8.32	-	-	0.08	-
300	15.3	8.74	7.3	3.52	6.56	5.54
350	17.5	8.76	10.4	6.07	8.74	7.37

Increase in ionizable hydrogen is equal to molal H⁺ (estimated from pH_{25°}) + C_T for pH_{25°} < 5.5

SO₄ loss for these temperatures exceeds Ca loss (table 2), so firstly, all this Ca loss is attributed to precipitation of "CaSO₄" (table 3). Mg loss, therefore, must be due to a mixture of "MgSO₄" and "Mg(OH)₂" to account for ionizable hydrogen gain. The "Mg(OH)₂" fraction of the Mg loss is half the ionizable hydrogen gain, and the remainder, which represents "MgSO₄", should agree closely with the SO₄ loss in excess of Ca loss. The last two columns of table 2 are the results of these subtractions and indicate agreement within 1 and 1.5 millimolal and are within the stated analytical error of the fluid composition. These data then allow calculation of the composition and amount of the precipitates in terms of the components "CaSO₄", "MgSO₄", and "Mg(OH)₂" as shown on table 3.

The results for 300° and 350°C are similar, with "CaSO₄" making up approximately half the precipitate, "MgSO₄" 40 percent, and "Mg(OH)₂" 10 to 15 percent.

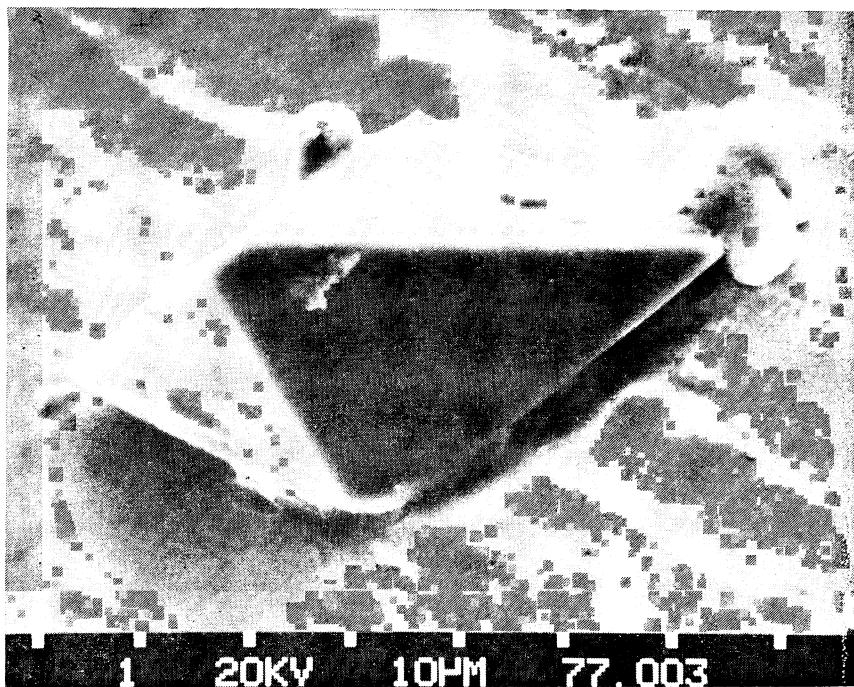
EXPERIMENTAL RECOVERY OF SOLIDS

Recovery of the precipitate requires quenching the entire pressure vessel, a process demanding several hours, by which time the solids would have completely redissolved. Thus, a separate experiment was performed for the recovery of the solids. Twenty-five ml of seawater was held at 325°C, 500 bars in a sample cell containing gold strips as substrates for the precipitate. After two weeks, most of the seawater was bled off at experimental conditions, the vessel quenched, and the strips recovered. Examination of the strips by optical microscope and SEM revealed the presence of a few milligrams of precipitate in two crystal phases. Laths of

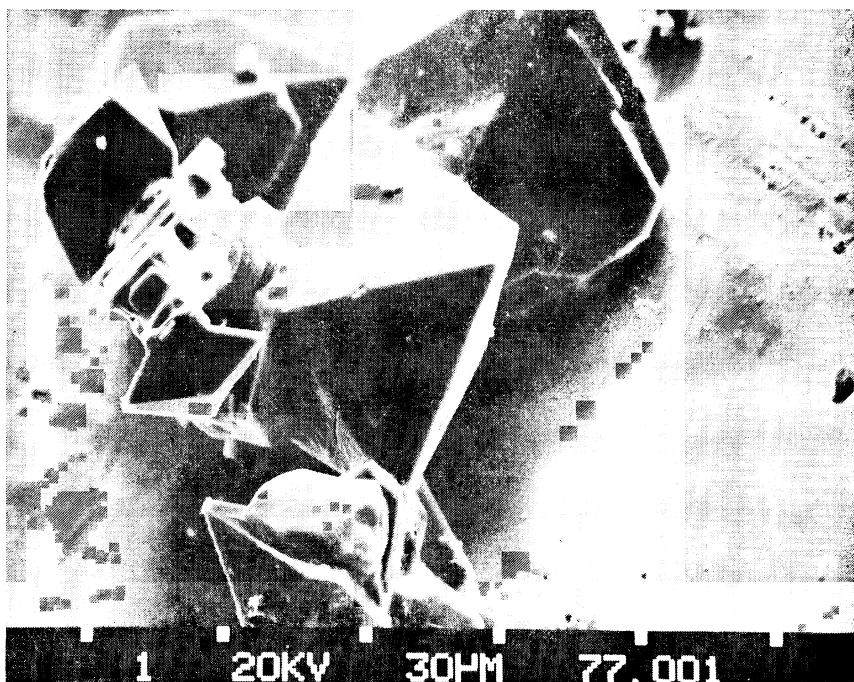
TABLE 3
Estimated composition of precipitate from heated
Point Hueneme seawater based on changes in dissolved components

T°C	Solid Component	Weight of Precipitate, g/kg	Mole percent of total solids
200	CaSO ₄	0.925	100
250	CaSO ₄	1.13	100
300	CaSO ₄	1.18	53
	"MgSO ₄ "	0.73	37
	"Mg(OH) ₂ "	$\frac{0.10}{2.01}$	10
350	CaSO ₄	1.2	43
	"MgSO ₄ "	1.05	42
	"Mg(OH) ₂ "	$\frac{0.18}{2.43}$	15

PLATE 1



A. SEM photomicrograph of magnesium oxysulfate phase precipitated from seawater at 325°C. Distance between white reference marks is 10 μ m.



B. SEM photomicrograph of magnesium oxysulfate phase precipitated from seawater at 325°C. Distance between white reference marks is 30 μ m.

anhydrite and transparent monoclinic or triclinic bipyramidal crystals of 30 to 100- μ size (pl. 1-A, -B) made up approximately equal portions of the precipitate. The unidentified crystals presumably are a single phase that represents the combined "MgSO₄" and "Mg(OH)₂" components inferred from the composition of the solution. The X-ray diffraction pattern obtained on a single crystal with a Gondolfi camera (table 4) does not correspond to any compound that we could find in the literature. Results of energy dispersive X-ray fluorescence analysis on the SEM revealed peaks only for Mg and S. No other elements were detected.

We attempted to determine the stoichiometry of the phase by measuring the peak ratio of Mg to S standardized against reagent MgSO₄. Replicate analyses on a single crystal face yielded good precision, but ratios varied significantly from face to face, owing to varying X-ray take-off angles and perhaps to varying Mg/S ratios. The averaged results using 16 analyses indicate that the ratio of MgSO₄ to Mg(OH)₂ in the solid is approx 5 to 1 with an uncertainty of ± 27 percent. Thus, the actual ratio is estimated to be between 3.65 and 6.35 to 1, compared with an estimate of 2.8 to 3.7 to 1 from the chemistry of the solution.

The compound is analagous to, but stoichiometrically different from, a magnesium oxysulfate studied by Marshall and Slusher (1965) with

TABLE 4
Gondolfi camera data for single crystal of magnesium oxysulfate
precipitated from Point Hueneme seawater at 325°C

d (Å)	Intensity
3.35	vs
3.219	vs
2.607	m
2.292	w
2.058	s (double reflection)
1.874	w
1.845	vw
1.744	w
1.667	s
1.606	s (double reflection)
1.462	m
1.385	w
1.317	m

the composition $\text{MgSO}_4 \cdot 5\text{MgO} \cdot \text{H}_2\text{O}$ which they synthesized at 135° to 200°C by incongruent dissolution of $\text{MgSO}_4 \cdot \text{H}_2\text{O}$. Our data, however, permit only the qualitative conclusion that our solid is a magnesium oxy-sulfate containing MgSO_4 in excess of $\text{Mg}(\text{OH})_2$ (or $\text{MgO} \cdot \text{H}_2\text{O}$) by a factor of from 3 to 5 and with an unknown water content. The precipitation process, therefore, must follow a reaction of the sort:

$(n + 1) \text{Mg}^{+2} + n\text{SO}_4^{=} + m \text{H}_2\text{O} \rightarrow \text{MgO} \cdot n\text{MgSO}_4 \cdot (n-2)\text{H}_2\text{O} + 2\text{H}^+$,
where $3 \leq n \leq 5$, and we have a mechanism for producing the observed acidity change.

DISTRIBUTION OF AQUEOUS SPECIES

In order to estimate such *in situ* parameters as mineral solubility, pH, and buffer capacity, we calculated the distribution of ionic species at each experimental temperature using analyzed (total) compositions. We used a technique and computer program developed by Reed (ms) for a seawater matrix that makes use of the methodology and latest thermodynamic data of Harold Helgeson and his coworkers at the University of California (Helgeson and Kirkham, 1974a and b, 1976, and in press; and Helgeson and others, 1978). Briefly, the total analyzed composition was distributed among 24 species (table 5), using simultaneous mass balances of the sort, $[\text{Mg}]$ (analyzed) = $[\text{Mg}^{++}] + [\text{MgHCO}_3^+] + [\text{MgCO}_3^0]$ where brackets refer to molal concentrations, in conjunction with simultaneous dissociation mass action expressions for each complex or ion pair. Distribution of species was first calculated for each experiment at 25°C , from which a total ionizable hydrogen content was determined. The distribution at the temperature of interest was then calculated employing the hydrogen mass balance. An advantage of this approach is that *in situ* pH can be calculated without recourse to a charge balance equation,

TABLE 5
Dissolved species used in distribution calculations for seawater
at temperatures and pressures of experiments

Primary ionic species	Complex ions	Neutral species
H^+	KSO_4^-	H_2CO_3^0
Cl^-	HSO_4^-	HCl^0
Ca^{++}	CaOH^+	NaCl^0
Mg^{++}	MgOH^+	KHSO_4^0
K^+	NaSO_4^-	CaCO_3^0
Na^+	NaCO_3^-	MgSO_4^0
$\text{SO}_4^=$	MgHCO_3^+	CaSO_4^0
HCO_3^-	CaHCO_3^+	
$\text{CO}_3^=$		
OH^-		

which produces a large uncertainty in *in situ* pH because of analytical error for Na and Cl. Activity coefficients were calculated from the expanded Debye-Hückel relation (Helgeson and Kirkham, 1974b).

The greatest uncertainty in these calculations results from errors in the dissociation constants of the complex ions and their projection to higher temperatures. These complexes apparently become increasingly stable with elevated temperature and thus increasingly important. Constants for H_2O , H_2CO_3 , HCO_3^- , HCl° , and KHSO_4° were taken from the compilation of Helgeson (1969), who lists values up to 300°C. Values at 350°C for these species were estimated by linear extrapolation. Constants for KSO_4^- , CaOH^+ , MgOH^+ , CaCO_3° , NaSO_4^- , NaCO_3^- , and CaHCO_3^+ were taken from the literature compilation and theoretical extrapolations by R. Siebert and C. Christ (written commun., May 1977). Constants for MgHCO_3^+ and MgCO_3° were taken from experimental work and projections to higher temperature of Siebert and Hostetler (1977a and b). Dissociation constants for HSO_4^- were taken from the experimental work to 350°C of Marshall and Jones (1966), for MgSO_4° from Marshall's (1967) experimental work to 200°C and linearly extrapolated to 350°C, and for CaSO_4° from Yeats and Marshall's (1969) experimental work to 350°C.

Extrapolations of dissociation constants are extremely uncertain at best, particularly above 200°C, not only because the trends are often non-linear and exponentially increasing, but also because they may go through unpredictable maxima and reversals in the range of extrapolation. Pressure provides an additional source of uncertainty.

Dissociation constants from the above sources are for the vapor pressure of water at the given temperature. The absence of partial molar volume data on the complexes precludes calculation of a pressure correction on the constants. Helgeson (1969) has pointed out that dissociation constants vary with changes in the dielectric constant of the fluid, which in turn is a function of T and P. The dielectric constant of water is little affected by pressure changes of 500 bars for the temperature range 0° to 300°C (Helgeson, 1969) indicating that dissociation constants measured at the vapor pressure will be little changed by the 500 bar pressure of our experimental conditions. Above 300°C, the dielectric constant varies rather strongly with pressure, and the validity of using the dissociation constants already projected to 350°C and vapor pressure at 500 bars is made even more uncertain.

Clearly much additional experimental work is needed on the stability of these complexes at elevated temperatures and pressures if polycomponent hydrothermal fluids are to be interpreted from the standpoint of thermochemistry and mineral equilibria.

In the present application, we cannot assess the degree of uncertainty in the calculated distribution of aqueous species, and we present the results of such calculations for our analyzed composition of seawater at each temperature with this restriction in mind. Our only test for the

accuracy of such calculations is the calculated degree of saturation of the fluid with respect to anhydrite (fig. 13) which precipitates at all temperatures above 150°C. The variations of activity with temperature of individual dissolved species were grouped in terms of H-bearing species (figs. 2 and 3), CO₂-bearing species (fig. 4), SO₄-bearing species (fig. 5), Ca-bearing species (fig. 6), and Mg-bearing species (fig. 7).

At temperatures up to 200°C *in situ* pH (calculated) differs from pH_{25°} and is slightly on the alkaline side of neutrality (fig. 2). At 250°C and above, the *in situ* pH decreases to between 3 and 4, while the pH_{25°} drops precipitously to 2.52 at 350°C. Apparently, ionizable hydrogen produced by the magnesium oxysulfate precipitation is taken up by H⁺ bearing complexes. The increasing importance of these complexes with increasing temperature is apparent in figure 3. Thus HCl° and HSO₄⁻ account for the bulk of total ionizable hydrogen at temperatures above 250°C and provide a significant buffer reservoir of H⁺, while MgOH⁺, which also becomes quite concentrated, provides additional H⁺. At lower temperatures, particularly from 25° to 150°C, MgOH⁺, HCl, and HSO₄⁻ are virtually nonexistent, and the H⁺ system is dominated by HCO₃⁻, MgHCO₃⁺, and H₂CO₃.

Of the CO₂ bearing species (fig. 4), the familiar species of importance at 25°C, namely HCO₃⁻, CO₃⁼, CaHCO₃⁺, and CaCO₃[°], precipitously decrease with increasing temperature and are virtually gone by 150°C. CO₃⁼ and HCO₃⁻ are thus increasingly transferred to H₂CO₃ as temperature increases.

SO₄-bearing species also undergo significant change with temperature (fig. 5). Activity of free SO₄⁼ declines with temperature in favor of MgSO₄[°] and HSO₄⁻. Although MgSO₄[°] is also an important species at 25°C, HSO₄⁻ is not, and the increase of HSO₄⁻ with temperature through 5½ orders of magnitude is striking. Moreover, the distribution

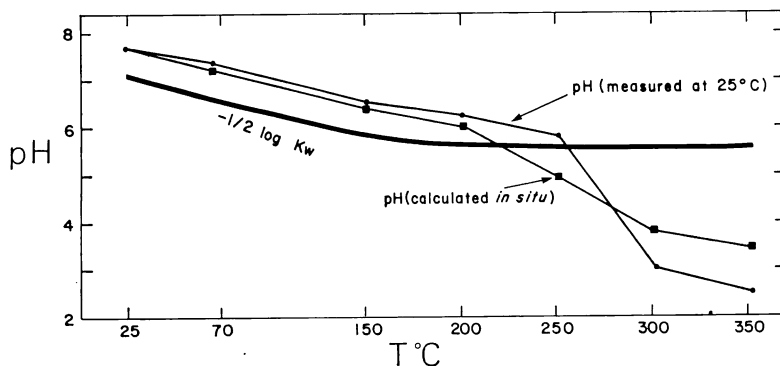


Fig. 2. Changes in pH measured at 25°C and in pH calculated from *in situ* conditions for seawater from 25° to 350°C relative to 1/2 log Kw (neutrality).

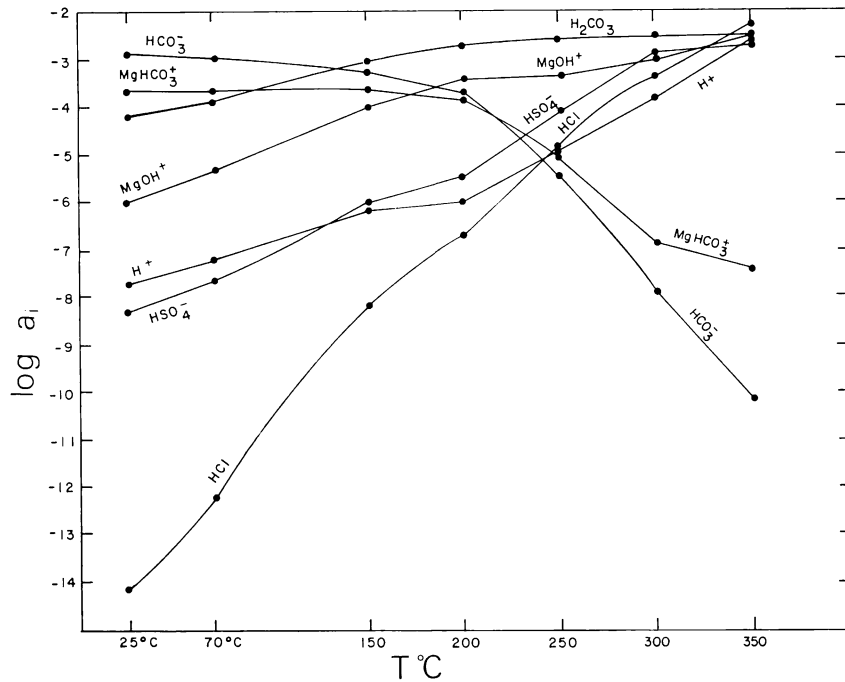


Fig. 3. Calculated activities of hydrogen-bearing species (H^+ , HCO_3^- , MgHCO_3^+ , HCl , HSO_4^- , H_2CO_3 , CaHCO_3^+ , and KHSO_4^0) in seawater from 25° to 350°C.

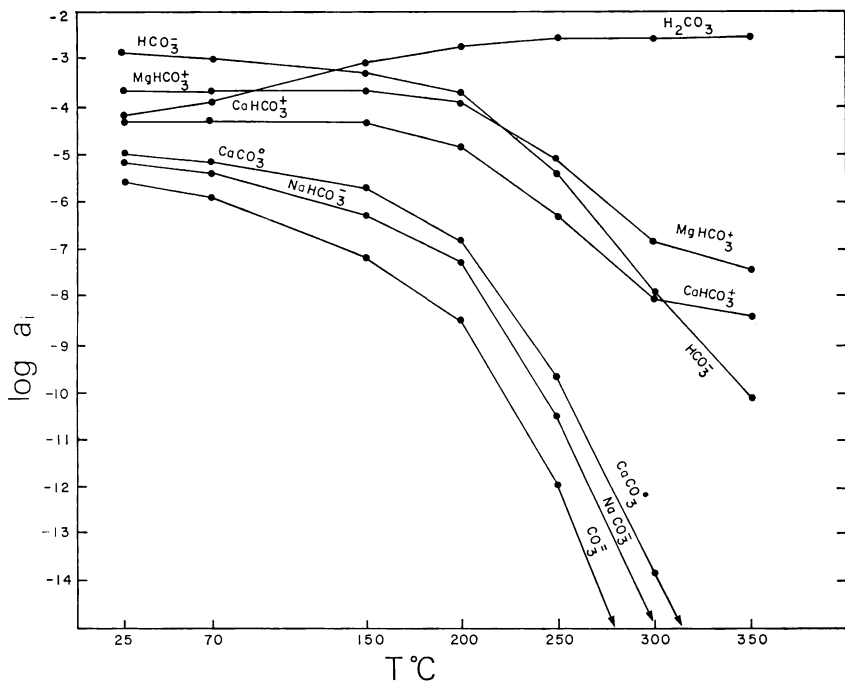


Fig. 4. Calculated activities of CO_3 -bearing species (HCO_3^- , MgHCO_3^+ , H_2CO_3 , NaCO_3^+ , CaHCO_3^+ , CaCO_3^0 , and CO_3^{2-}) in seawater from 25° to 350°C.

at 350°C demonstrates that free $\text{SO}_4=$ constitutes an insignificant fraction of total dissolved SO_4 .

Distribution of Ca species (fig. 6) reflects both the precipitation of anhydrite and the increasing acidity with temperature. Free Ca^{++} ion dominates the distribution at all temperatures up to 350°C.

Distribution of Mg species (fig. 7) is affected relatively little by increasing temperature up to 300°C. At 25°C free Mg^{++} ion predominates but is exceeded by MgSO_4° at 150°C and above. Between 300° and 350°C, MgOH^+ becomes the dominant species displacing MgSO_4° .

It is apparent that Mg plays a central role in seawater chemistry at elevated temperature. Not only does its precipitation as an oxysulfate produce strong acidity above 250°C, its strong tendency to form complex ions makes it dominate the distribution of SO_4 and CO_2 and thereby buffer the system. Clearly, large changes in the total Mg content will greatly affect the distribution of species and acidity. Thus, for rock-dominated seawater geothermal systems in which Mg is quickly and quantitatively removed from solution, the distribution of species and the pH must be quite different than for water-dominated systems (Seyfried and Bischoff, 1977).

BUFFER CAPACITY

The question arises as to what capacity heated seawater has to maintain its acidity. Buffer capacity, β , is defined as

$$\beta = \frac{dC_B}{dpH} = - \frac{dC_A}{dpH}$$

where dC_B and dC_A are the molal changes of strong base or strong acid required to produce a change in pH of dpH . It can be shown (Stumm

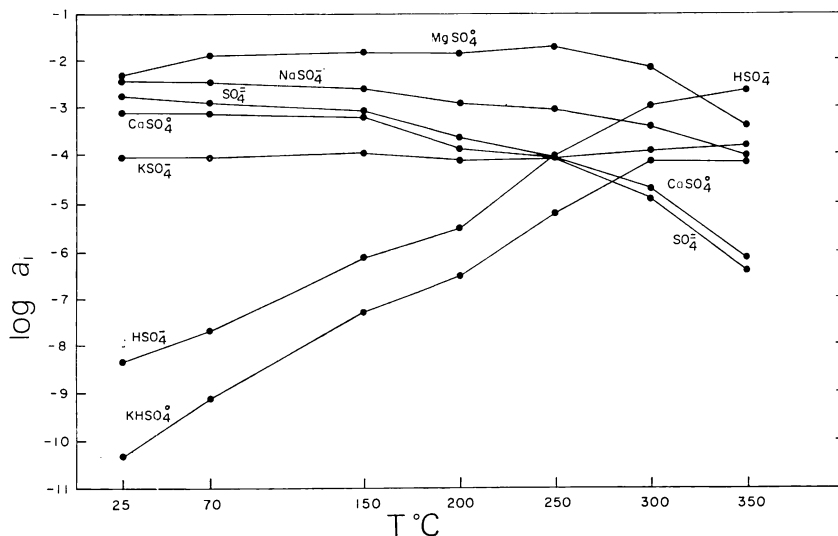


Fig. 5. Calculated activities of sulfate-bearing species ($\text{SO}_4=$, NaSO_4^- , MgSO_4° , HSO_4^- , KHSO_4° , KSO_4^- , and CaSO_4°) in seawater from 25° to 350°C.

and Morgan, 1970, p. 110) that for a solution containing various acid-base pairs HA, A; HB, B; et cetera

$$\beta = 2.3 \left[[\text{H}^+] + [\text{OH}^-] + \frac{[\text{HA}][\text{A}]}{[\text{HA}] + [\text{A}]} + \frac{[\text{HB}][\text{B}]}{[\text{HB}] + [\text{B}]} + \dots \right]$$

where brackets refer to molalities.

From the foregoing, seawater at the various temperatures can be considered to contain four weak acid systems, $\text{H}_2\text{CO}_3\text{--HCO}_3^-$, $\text{HCO}_3^-\text{--CO}_3^{=}$, $\text{HSO}_4^-\text{--SO}_4^{=}$, and HCl--Cl^- .

Thus, buffer capacity is given by

$$\beta = 2.3 \left[[\text{H}^+] + [\text{OH}^-]_t + \frac{[\text{H}_2\text{CO}_3][\text{HCO}_3^-]_t}{[\text{H}_2\text{CO}_3] + [\text{HCO}_3^-]_t} + \frac{[\text{HCO}_3^-]_t[\text{CO}_3^{=}]_t}{[\text{HCO}_3^-]_t + [\text{CO}_3^{=}]_t} + \frac{[\text{HSO}_4^-]_t[\text{SO}_4^{=}]_t}{[\text{HSO}_4^-]_t + [\text{SO}_4^{=}]_t} + \frac{[\text{HCl}][\text{Cl}^-]}{[\text{HCl}] + [\text{Cl}^-]} \right]$$

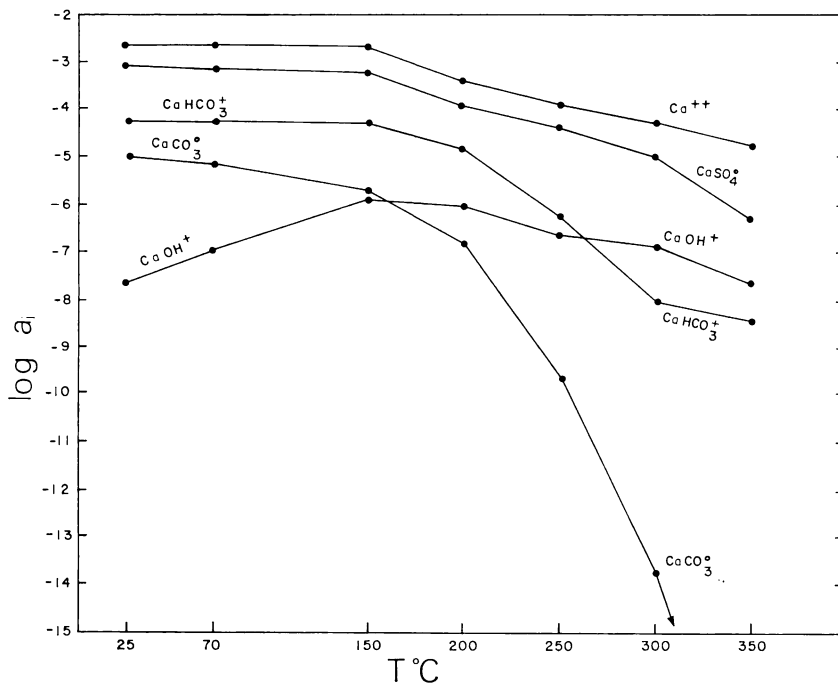


Fig. 6. Calculated activities of Ca-bearing species (Ca^{2+} , CaSO_4° , CaOH^+ , CaHCO_3^+ , and CaCO_3°) in seawater from 25° to 350°C.

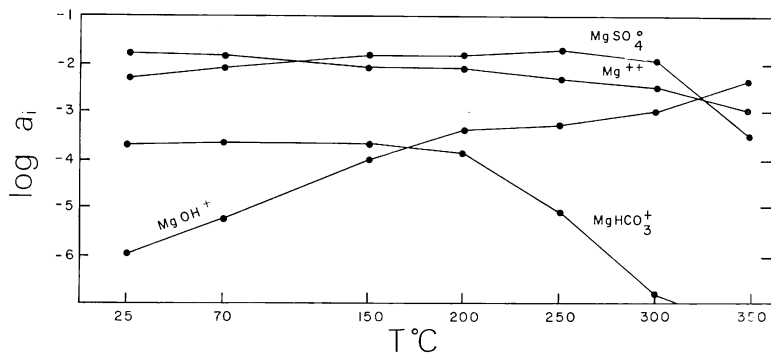


Fig. 7. Calculated activities of Mg-bearing species (Mg^{2+} , $MgSO_4^0$, $MgHCO_3^+$, and $MgOH^+$) in seawater from 25° to 350°C.

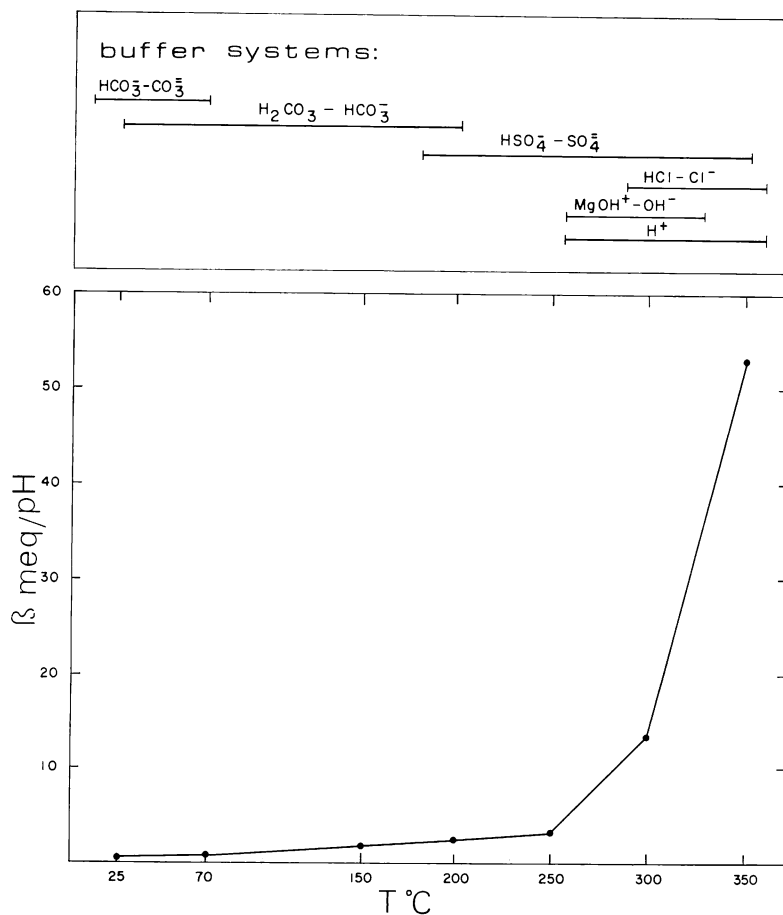


Fig. 8. Buffer intensity, β , and dominant buffer systems in seawater from 25° to 350°C.

where

$$[\text{HCO}_3^-]_t = [\text{HCO}_3^-] + [\text{CaHCO}_3^+] + [\text{MgHCO}_3^+]$$

$$[\text{CO}_3^{=}]_t = [\text{CO}_3^{=}] + [\text{CaCO}_3] + [\text{NaCO}_3^-]$$

$$[\text{HSO}_4^-]_t = [\text{HSO}_4^-] + [\text{KHSO}_4^\circ]$$

$$[\text{SO}_4^{=}]_t = [\text{SO}_4^{=}] + [\text{KSO}_4^-] + [\text{MgSO}_4^\circ] + [\text{CaSO}_4^\circ] + [\text{NaSO}_4^-]$$

and

$$[\text{OH}^-]_t = [\text{OH}^-] + [\text{CaOH}^-] + [\text{MgOH}^+]$$

Substituting molalities from the distribution of species at each temperature (fig. 8) shows that buffer capacity increases dramatically with temperature, particularly in the range above 250°C. At 350°C, buffer capacity is 54 meq/pH compared to 0.24 meq/pH at 25°C.

Buffering is caused primarily by H_2CO_3 , and HCO_3^- to 200°C and by HSO_4^- , HCl° , and MgOH^+ above 200°C. The buffer capacity of seawater at 300° (13 meq/pH) and 350° (54 meq/pH) is very large indeed and can be compared to a 0.56N acetic acid solution (generally considered to be a highly buffered acid) that has a pH of 2.5 and a buffer capacity of 7.27 meq/pH! Clearly, seawater at 300° to 350°C is not only very acidic, it is highly buffered.

Another way to view the acidity increase is by summing the molality of all H^+ bearing species, a quantity equal to total ionizable hydrogen, $[\text{H}^+]_t$. This sum is

$$\begin{aligned} [\text{H}^+]_t = & [\text{H}^+] + [\text{HCO}_3^-] + [\text{HCl}] + [\text{HSO}_4^-] + 2[\text{H}_2\text{CO}_3] \\ & + [\text{KHSO}_4^\circ] + [\text{MgHCO}_3^+] + [\text{CaHCO}_3^+] \\ & - [\text{OH}^-] - [\text{CaOH}^+] - [\text{MgOH}^+]. \end{aligned}$$

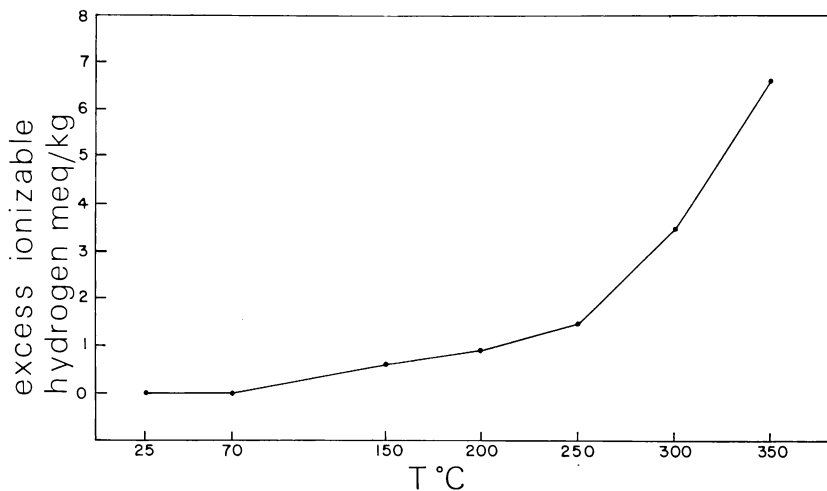


Fig. 9. Excess ionizable hydrogen (sum of equivalents of all hydrogen-bearing species at temperature minus that for 25°C) in seawater from 25° to 350°C.

Total ionizable hydrogen in seawater increases from 2.16 meq/kg at 25°C to 8.65 at 350°C. Thus, excess $[H^+]_t$, the total amount of hydrogen ion available for reaction with rock, can be considered to be the difference between these two concentrations, or 6.49 meq/kg (fig. 9). This number corresponds to and agrees well with that of 6.07 meq/kg in table 2, which was independently estimated by summing C_T and hydrogen ion molality at 25°C.

Now, we see that acidity and buffer capacity are created by Mg precipitation, which in these experiments is limited by the solubility of the magnesium oxysulfate. During interaction with rock, the analogous reaction is that Mg precipitates as a "sepiolite"-type molecule ($2Mg(OH)_2 \cdot 5SiO_2$) as part of the smectite or chlorite alteration phase in response to silica release from the rock. This process also creates ionizable hydrogen in an analogous manner but with two H^+ released for each Mg removed. Thus, the capacity of seawater to alter a rock by hydrogen "metasomatism" is essentially equal to the total equivalents of Mg in seawater or 100 meq/kg. This is equivalent to an acid with a pH of 1. During such interaction, this total amount of H^+ is never present in solution at one time because H^+ is continuously removed from solution by the rock in exchange for Ca and K as well as the transition metals Fe, Mn, and Cu.

MINERAL SOLUBILITIES

The distribution of species in heated seawater allows us to assess the degree of saturation with respect to various minerals. Because Al and Si are essentially absent from the system, minerals bearing these elements are, of course, infinitely under-saturated. Thus, our attention is directed to those minerals whose components are contained in seawater, namely those that contain carbonate (calcite, magnesite, and dolomite), sulfate (anhydrite), and hydroxide (brucite). Additionally, if we knew the stoichiometry of the magnesium oxysulfate, we could assess its solubility and hence its standard free energy at 300° and 350°C. The calculation, however, must await a more definitive chemical analysis of the solid.

Hydrolysis constants for the minerals calcite, dolomite, magnesite, anhydrite, and brucite for 25° and 350°C and 1 to 500 bars were provided by H. Helgeson (written commun., 1976), from equations and data of Helgeson and Kirkham (1974a and b, 1976, and in press) and Helgeson and others (1978).

These constants and their respective ion-activity products (IAP's) are plotted in relation to temperature in figures 10 through 13. Hydrolysis constants at 25° are for 1 bar total pressure, and those from 70° to 350°C for 500 bars, corresponding to the experimental conditions. The increase in pressure accounts for the slope changes in some of the solubility curves.

As one would infer from the observed decline of *in situ* pH with increasing temperature, the carbonate minerals become increasingly

undersaturated (figs. 10-12). Calcite, magnesite, and dolomite all display increasing thermodynamic stability with temperature, but these trends are overshadowed by even stronger decline of IAP's. The carbonate minerals are slightly supersaturated at 25°C, barely saturated at 70°C, and become progressively undersaturated by 6 to 14 orders of magnitude at 350°C. Clearly, circulating seawater under water-dominated conditions will not deposit carbonates during descent into rock bodies. Thus, carbonates that are commonly found coexisting with other alteration minerals in sea-floor basalts (Seyfried, Shanks, and Bischoff, 1976; Jehl, Poty, and Weisbrod, 1976) must reflect low temperatures of alteration, as their stable isotopes commonly imply.

Brucite precipitation was one of the processes first postulated as the cause of the observed Mg loss and ionizable hydrogen gain at 300° and 350°C. Brucite was not found among the precipitates, however, but its solubility trend compared to its IAP (fig. 13) indicates that brucite would have become saturated at about 250°C had not the precipitation of the magnesium oxysulfate precipitously decreased Mg^{++} activity. Experimental observation indicated anhydrite reached saturation at between 150° and 200°C during the experiments. Calculated solubility is consistent with observed results (fig. 13). Ideally the IAP points should fall exactly on the solubility curve for all temperatures above 150°C. These points, however, are consistently 0.4 log units (that is, apparent undersaturation by a factor of 0.38) below the solubility curve but follow the curve very closely. This discrepancy probably reflects unassessed pressure effects and thermochemical stability uncertainties in the sulfate complexes discussed above.

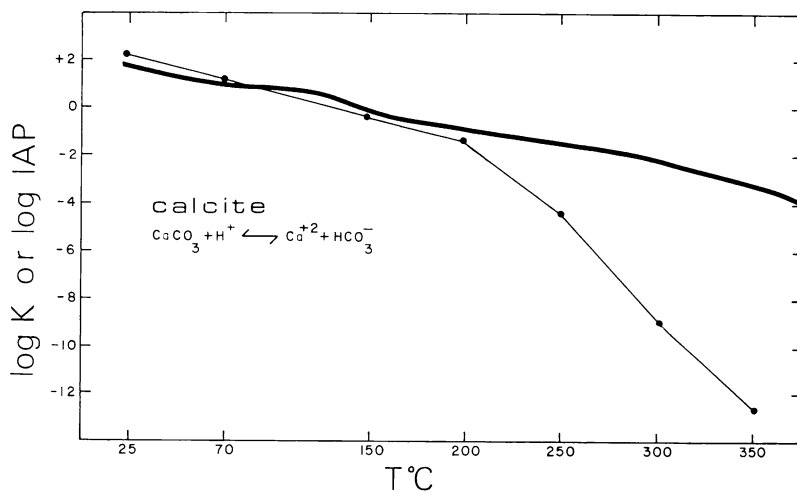


Fig. 10. Calculated IAP of calcite in seawater experiments from 25° to 350°C (dots). Solid line, theoretical log K for dissolution equilibrium of calcite at 500 bars pressure.

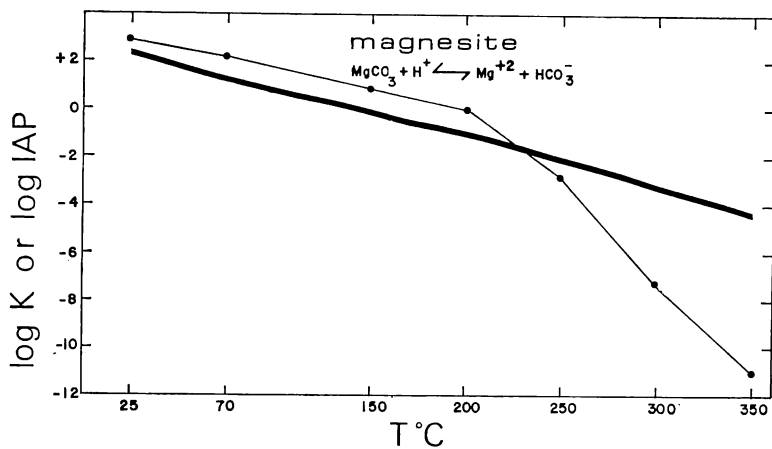


Fig. 11. Calculated IAP of magnesite in seawater from 25° to 350°C (dots). The solid line is the theoretical log K for dissolution equilibrium of magnesite at 500 bars pressure.

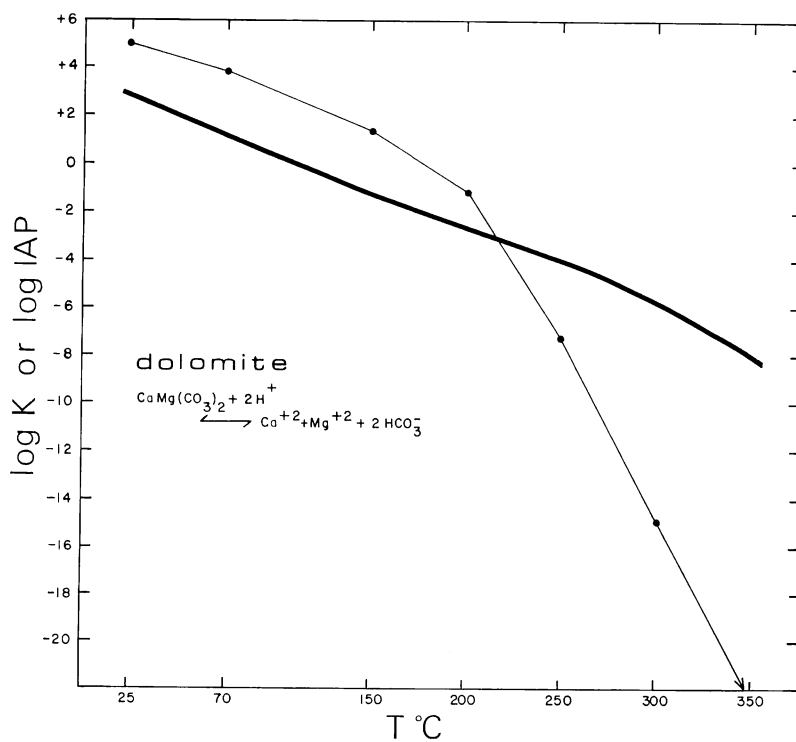


Fig. 12. Calculated IAP of dolomite in seawater experiments from 25° to 350°C (dots). The solid line is the theoretical log K for dissolution equilibrium of dolomite at 500 bars pressure.

The mass of anhydrite precipitate is significant and depletes the seawater of 67 percent of its initial SO_4 and 90 percent of its initial Ca. The process is even more pronounced in the presence of rock, where abundant Ca is leached from the rock, such that even at 200°C, SO_4 is essentially quantitatively removed from solution (Bischoff and Dickson, 1975). Thus, even in water-dominated systems of sub-sea floor circulation, abundant anhydrite, or textural evidence of dissolved anhydrite should be found in altered rocks on the sea floor.

Although anhydrite is found in the upper parts of the Reykjanes system (Tomasson and Kristmannsdottir, 1972), its absence from dredged and cored rocks from the sea floor is difficult to reconcile with popularly accepted models of subsurface seawater circulation and must be considered a major problem. Proposals that SO_4 is quantitatively reduced by basalt to form sulfides are also inadequate, because each mole of sulfide requires oxidation of 7 moles of ferrous iron if pyrite is formed and

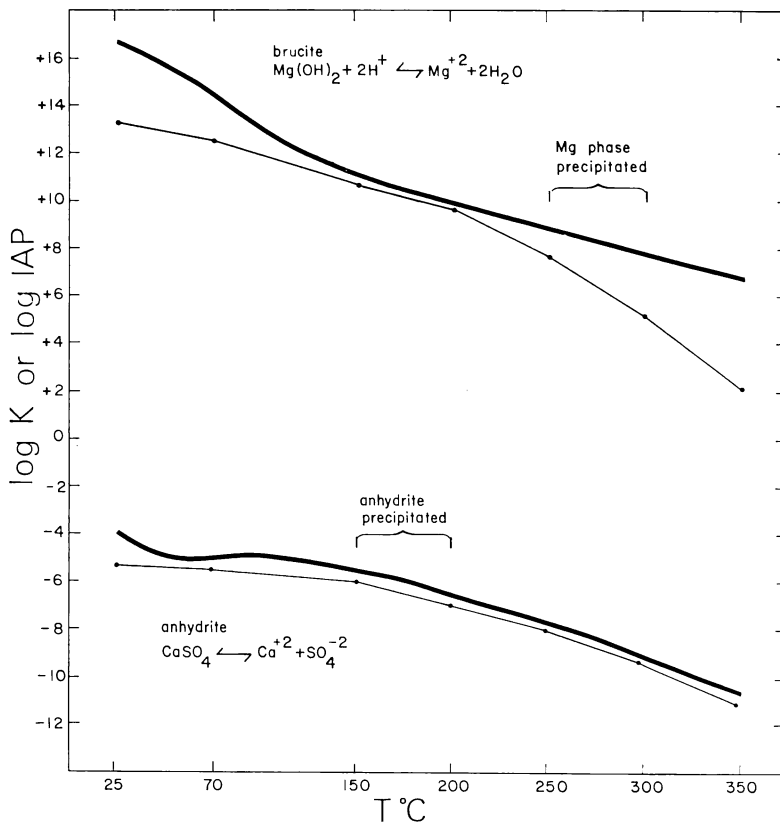


Fig. 13. Calculated IAP of brucite (upper) and anhydrite (lower) in seawater from 25° to 350°C (dots). Solid line, theoretical log K for dissolution equilibrium at 500 bars pressure.

8 moles if a monosulfide is formed (Mottl, ms). At seawater/rock ratios of six or greater, the total mass of ferrous ion in basalt is insufficient to reduce all seawater SO_4 . Thus, if this process were important, we should find abundant highly oxidized basalts containing pyrite on the sea floor. Examples of basalts from the Mid-Atlantic Ridge altered to the greenschist facies, however, (Miyashiro, Shido, and Ewing, 1971; Melson and van Andel, 1966) are commonly no more oxidized than their unaltered counterparts. More data from deep ocean drilling programs are needed to solve the anhydrite problem. Until adequate samples of the ocean crust are obtained from beneath actively spreading ridge systems and seawater at elevated temperatures is sampled, the models proposed to explain the absence of anhydrite must remain speculative.

SUMMARY AND CONCLUSIONS

We believe that our experimental results warrant the following conclusions:

1. During closed system heating to 350°C , seawater displays progressive depletion in Ca, Mg, and SO_4 , owing to precipitation of anhydrite and a previously undescribed magnesium oxysulfate.
2. Seawater becomes progressively acid with increasing temperature, primarily because a magnesium oxysulfate is precipitated above 250°C and secondarily because a few parts per million of dissolved organic matter are oxidized.
3. Seawater becomes progressively buffered with increasing temperature owing to increased association of H^+ -bearing complexes such as HCl° and HSO_4^- . The pH and buffer capacity of seawater above 250°C are comparable to a 0.5N acetic acid solution.
4. Seawater is slightly supersaturated with respect to calcite, dolomite, and magnesite at 25°C but becomes progressively undersaturated with increasing temperature. Anhydrite, however, first precipitates between 150° to 200°C in agreement with its calculated solubility.
5. The acidity and buffer capacity at elevated temperatures make seawater an aggressive leaching medium for heavy metals under conditions of water-dominated seawater-basalt interaction.

ACKNOWLEDGMENTS

This work was supported in part by NSF grant ID 074-12880. We are indebted to R. Rosenbauer for assistance with the laboratory work, to M. Reed for making available the computer program for the distribution of species calculation, and to H. Helgeson for providing summaries of mineral thermochemistry in advance of publication. B. de Jung kindly performed X-ray analysis of the magnesium oxysulfate with the Gonda camera. We are grateful to F. Dickson who made the Stanford hydrothermal laboratory available for the experimental work. Finally, we thank C. Christ, A. J. Ellis, M. Mottl, and W. Shanks for many helpful ideas and critical reviews of the manuscript.

REFERENCES

- Bischoff, J. L., and Dickson, F. W., 1975, Seawater-basalt interaction at 200°C and 500 bars: implications for the origins of sea-floor heavy metal deposits and regulation of seawater chemistry: *Earth and Planetary Sci. Letters*, v. 25, p. 385-397.
- Dickson, F. W., Blount, C., and Tunell, G., 1963, Use of hydrothermal solution equipment to determine the solubility of anhydrite in water from 100° to 275°C and from 1 bar to 1000 bars pressure: *Am. Jour. Sci.*, v. 261, p. 711-724.
- Duursma, E. K., 1960, Dissolved organic carbon, nitrogen, and phosphorus in the sea: *Meth. Jour. Marine Research*, v. 1, p. 1-148.
- Helgeson, H. C., 1969, Thermodynamics of hydrothermal systems at elevated temperatures and pressures: *Am. Jour. Sci.*, v. 267, p. 729-804.
- Helgeson, H. C., Delaney, J. M., Nesbitt, H. W., and Bird, D. K., 1978, Summary and critique of thermodynamic properties of the rock forming minerals: *Am. Jour. Sci.*, v. 278-A, in press.
- Helgeson, H. C., and Kirkham, D. H., 1974a, Theoretical prediction of the thermodynamic behavior of aqueous electrolytes at high pressures and temperatures: I. Summary of the thermodynamic/electrostatic properties of the solvent: *Am. Jour. Sci.*, v. 274, p. 1089-1198.
- 1974b, Theoretical prediction of the thermodynamic behavior of aqueous electrolytes at high pressures and temperatures: II. Debye Hückel parameters for activity coefficients and relative partial molal properties: *Am. Jour. Sci.*, v. 274, p. 1199-1261.
- 1976, Theoretical prediction of the thermodynamic properties of aqueous electrolytes at high pressures and temperatures: III. Equation of state for aqueous species at infinite dilution: *Am. Jour. Sci.*, v. 276, p. 97-240.
- in press, Theoretical prediction of the thermodynamic properties of aqueous electrolytes at high pressures and temperatures: IV. Calculations of activity coefficients osmotic coefficients and apparent molality, and standard and relative partial molal properties to 5 kb and 600°C and >6 m: *Am. Jour. Sci.*, in press.
- Jehl, V., Poty, B., and Weisbrod, A., 1976, Hydrothermal metamorphism of the oceanic crust in the North Atlantic Ocean: *Am. Geophys. Union Trans.*, v. 57, p. 597.
- Lister, C. R. B., 1972, On the thermal balance of a mid-ocean ridge: *Royal Astron. Soc. Geophys. Jour.*, v. 26, p. 515-535.
- Marshall, W. L., 1967, The dissociation constant and thermodynamic functions of magnesium sulfate to 200°C: *Jour. Phys. Chemistry*, v. 71, p. 3584.
- Marshall, W. L., and Jones, E. V., 1966, Second dissociation constant of sulfuric acid from 25° to 350°C evaluated from solubilities of calcium sulphuric acid in sulfuric acid solutions: *Jour. Phys. Chemistry*, v. 70, p. 4028-4040.
- Marshall, W. L., and Slusher, R., 1965, Solubility and hydrolytic instability of magnesium sulfate in sulfuric acid—Water and deuteriosulfuric acid—Deuterium oxide solutions, 200° to 350°C: *Jour. Chem. and Eng. Data*, v. 10, p. 353-358.
- Melson, W. G., and van Andel, Tj. H., 1966, Metamorphism in the Mid-Atlantic Ridge, 22°N: *Marine Geology*, v. 4, p. 165-186.
- Miyashiro, A., Shido, F., and Ewing, M., 1971, Metamorphism in the Mid-Atlantic Ridge near 24° and 30°N: *Royal Soc. London Philos. Trans.*, ser. A, v. 268, p. 589-603.
- Mottl, M. J., ms, 1976, Chemical exchange between seawater and basalt during hydrothermal alteration of the oceanic crust: Ph.D. thesis, Harvard Univ., Cambridge, Mass., 107 p.
- Mottl, M. J., Corr, R., and Holland, H., 1975, Trace element content, Reykjanes-Svartsengi thermal brines, Iceland: *Geol. Soc. America Abs. with Programs*, v. 7, p. 1206.
- Reed, M. H., ms, 1977, Geology and geochemistry of the West Shasta massive sulfide ore deposits: Ph.D. thesis, California Univ., Berkeley, 107 p.
- Seyfried, W. E., ms, 1977, Seawater-basalt interaction from 25°-300°C and 1-500 bars: Implications for the origin of submarine metal-bearing hydrothermal solutions and regulation of ocean chemistry: Ph.D. thesis, Univ. Southern California, Los Angeles, 216 p.
- Seyfried, W. E., and Bischoff, J. L., 1977, Hydrothermal transport of heavy metals by seawater: the role of seawater/basalt ratio: *Earth and Planetary Sci. Letters*, v. 34, p. 71-77.
- Seyfried, W. E., Shanks, W. C., and Bischoff, J. L., 1976, Alteration and vein formation in Site 321 basalts, in Yeats, R. S., Hart, S. R., and others, Initial reports of the Deep Sea Drilling Project: Washington, D.C., U.S. Govt. Printing Office, v. 34, p. 385-393.

- Siebert, R. M., and Hostetler, P. B., 1977a, Stability of magnesium bicarbonate ion-pair from 10 degrees to 90 degrees C: *Am. Jour. Sci.*, v. 277, p. 697-715.
- 1977b, Stability of magnesium carbonate ion-pair from 10 degrees C to 90 degrees C: *Am. Jour. Sci.*, v. 277, p. 716-734.
- Stumm, W., and Morgan, J., 1970, *Aquatic chemistry*: New York, Wiley Intersci., 583 p.
- Tomasson, J., and Kristmannsdottir, H., 1972, High temperature alteration minerals and thermal brines, Reykjanes, Iceland: *Contr. Mineralogy Petrology*, v. 36, p. 123-134.
- Williams, D. L., Von Herzen, R. P., Sclater, J. G., and Anderson, R. N., 1974, The Galapagos spreading center: lithospheric cooling and hydrothermal circulation: *Royal Astron. Soc. Geophys. Jour.*, v. 38, p. 587-608.
- Wolery, T. J., and Sleep, N. D., 1976, Hydrothermal circulation and geochemical flux at mid-ocean ridges: *Jour. Geology*, v. 84, p. 249-275.
- Yeats, L. B., and Marshall, W. L., 1969, Apparent invariance of activity coefficients of calcium sulfate at constant ionic strength and temperature in the system $\text{CaSO}_4\text{-Na}_2\text{SO}_4\text{-NaNO}_3\text{-H}_2\text{O}$ to the critical temperature of water association equilibria: *Jour. Phys. Chemistry*, v. 73, p. 81.