

HYDROTHERMAL ALTERATION PROCESSES AT MID-OCEAN RIDGES: CONSTRAINTS FROM DIABASE ALTERATION EXPERIMENTS, HOT-SPRING FLUIDS AND COMPOSITION OF THE OCEANIC CRUST

WILLIAM E. SEYFRIED, JR., MICHAEL E. BERNDT AND JEFFREY S. SEEWALD

Department of Geology and Geophysics, University of Minnesota, Minneapolis, Minnesota 55455, U.S.A.

ABSTRACT

Results of diabase alteration experiments at elevated temperatures and pressures have been combined with theoretical calculations to define the metasomatic processes reflected by the chemistry of hot-spring fluids and the chemistry and mineralogy of metabasalts dredged from mid-ocean ridges and observed in ophiolite outcrops on land. These data demonstrate that Mg-, Ca- and Na-fixation reactions are affected differently by different alteration conditions, and thus it is likely that each dominates a specific region within the submarine geothermal system. Mg fixation characterizes the downwelling limbs of subseafloor convection cells, whereas Ca and Na fixation are related more fundamentally to hydrothermal upflow zones, Ca at depth and Na nearer the surface. Ca removal from solution and attendant H^+ production are enhanced greatly by decompression effects, which contribute as well to oxidation and stabilization of epidote relative to other calcic alteration phases. Epidote-rich rocks (epidosites) observed at the base of sheeted intrusive complexes of numerous ophiolites likely represent the effects of Ca fixation, decompression, and oxidation within deep-seated, permeable upflow zones. The local, integrated, fluid/rock mass ratio of epidosite reaction zones may be as high as 1000. Experimental models of ridge-crest hydrothermal processes suggest that epidote and plagioclase solid solutions control the chemistry and pH of hot-spring fluids. Temperatures and pressures of approximately 385–400°C and 300–400 bars characterize the reaction zone of fluids discharging from black-smoker vents at 21°N, East Pacific Rise. Reaction-zone conditions (T, P) can be estimated for virtually all hot-spring fluids provided that salinity effects and retrograde processes caused by conductive cooling and/or subseafloor mixing are unambiguously accounted for.

Keywords: hydrothermal alteration, diabase, ophiolite, metabasalt, epidosite, metasomatism, hot-spring fluids, mid-ocean ridges, experimental models, 21°N, East Pacific Rise.

SOMMAIRE

Les résultats expérimentaux sur l'altération d'une diabase à températures et pressions élevées, ainsi que des calculs théoriques, permettent de définir les processus métasomatiques que reflètent la composition chimique des eaux de sources thermales, ainsi que les compositions chimique et minéralogique de metabasalts, dragués le long des dorsales océaniques, ou bien observés dans les cortèges ophiolitiques. Les réactions responsables de la fixation du Mg, Ca et Na sont influencées différemment selon les conditions d'altération; il semble donc que chacune des réactions régit une région spécifique du système géothermal sous-

marin. La fixation du magnésium caractérise les portions descendantes de cellules de convection sous-marines, tandis que la fixation de Ca et de Na est plus étroitement liée aux zones de flux hydrothermal ascendant, le calcium en profondeur et le Na plus près de la surface. L'extraction de Ca d'une solution, et la production de H^+ qui s'ensuit, sont grandement favorisées par une décompression, qui contribue aussi à une oxydation et à la stabilisation de l'épidote par rapport aux autres minéraux calciques d'altération. Les roches à forte teneur en épidote (épidosites), qui se trouvent à la base de complexes stratiformes ophiolitiques, seraient l'expression à la fois de fixation du calcium, décompression, et oxydation au sein de zones perméables profondes de flux ascendant. Le rapport local et intégré de masse du fluide à celle de la roche dans les zones à épidosite pourrait atteindre 1000. Les modèles expérimentaux des processus hydrothermaux le long des dorsales font penser que les solutions solides dans l'épidote et le plagioclase régissent la chimie et le pH des fluides issus des sources thermales. Des températures de 385–400°C et des pressions de 300–400 bars sont typiques de la zone de réaction des fluides que déchargent les événements de type «fumeur noir» à 21°N, le long de la dorsale Est Pacifique. Nous pouvons évaluer les conditions (T et P) dans la zone de réaction pour presque toutes les eaux thermales, pourvu que les effets de la salinité et des réactions rétrogrades, dues au refroidissement par conduction ou au mélange de fluides au-dessous des fonds marins, soient pris en considération de façon non-équivoque.

(Traduit par la Rédaction)

Mots-clés: altération hydrothermale, diabase, ophiolite, metabasalte, épidosite, métasomatisme, fluides de sources thermales, dorsales océaniques, modèles expérimentaux, 21°N, dorsale Est Pacifique.

INTRODUCTION

High-temperature (350°C) hydrothermal fluids issuing from vents on the East Pacific Rise (EPR), Juan de Fuca Ridge, and Mid-Atlantic Ridge dramatically illustrate the effectiveness of heat- and mass-transfer processes associated with magmatism and subseafloor convective circulation at mid-ocean ridges (Von Damm *et al.* 1985, Von Damm & Bischoff 1988, Edmond *et al.* 1986). Relative to seawater chemistry, ridge-crest hydrothermal fluids are distinctly acid, depleted in Mg and SO_4 and enriched in SiO_2 , H_2S and a wide variety of other species, especially Fe, Mn, Zn, Cu (Von Damm *et al.* 1985) and dissolved gases, H_2 , CO_2 and CH_4

(Craig *et al.* 1980). Thus, these fluids are reducing and are probably buffered by pyrite-magnetite \pm pyrrhotite equilibria at appropriate subsurface conditions (Janecky & Seyfried 1984, Janecky *et al.* 1986).

Hot-spring fluids at 21°N, EPR are within $\pm 10\%$ of seawater chlorinity, although more recently discovered hot-spring fluids at 11–13°N (EPR) and southern Juan de Fuca Ridge have chlorinities ranging from 0.6 to 2 times seawater values (Michard *et al.* 1984, Bowers *et al.* 1988, Von Damm & Bischoff 1988). Furthermore, oxygen and strontium isotopic data for hot-spring fluids (Craig *et al.* 1980, Piepgras & Wasserberg 1985) reveal the effects of extensive reaction between seawater-derived hydrothermal fluid and newly crystallized oceanic igneous rocks, suggesting low fluid/rock mass ratios in subseafloor reaction zones.

To maximize our understanding of ridge-crest hydrothermal processes, studies of hot-spring fluids must be coupled with experimental and theoretical data. Laboratory data help to constrain the mechanism and responsiveness of alteration processes for a well-defined set of conditions, and therefore provide an ideal framework within which to interpret chemical and physical controls on the chemistry of hot-spring fluids. Bulk-rock alteration experiments have been performed at temperatures from 70–500°C, pressures from 400–1000 bars, and fluid/rock mass ratios of 0.5–125 (Bischoff & Dickson 1975, Hajash 1975, Mottl & Holland 1978, Mottl *et al.* 1979, Seyfried & Bischoff 1979, 1981, Seyfried & Mottl 1982, Rosenbauer & Bischoff 1983, Seyfried & Janecky 1985). These studies typically entail monitoring the change in fluid chemistry during reaction of seawater and seawater-type fluids with powdered basalt, and thus establish cause and effect relationships for basalt alteration processes as a function of temperature, pressure, rock and fluid chemistry, and fluid/rock mass ratio. However, owing to difficulties in determining equilibrium conditions and establishing, quantitatively, reaction relations between primary and secondary phases, mineral-solubility data have been difficult to retrieve from results of these experiments. Thus, theoretical data for end-member minerals and solid solutions have been used to supplement experimental data in terms of temperature, pressure, and fO_2 effects on mineral stability relations and hydrolysis equilibria (Seyfried 1987, Berndt 1987). This sort of approach can be usefully applied to identify unambiguously primary and likely secondary minerals in the subsurface at mid-ocean ridges from the chemistry of ridge-crest hydrothermal fluids. Similarly, the approach can be used to reconstruct the geological history of fossilized submarine hydrothermal systems based on the chemistry and mineralogy of metabasalts and metadiabase dredged from mid-

ocean ridges and outcropping in ophiolite complexes on land.

Seawater: physical constraints

The maximum conditions of temperature and pressure of seawater-derived hydrothermal fluids at mid-ocean ridges can be estimated from the maximum temperature of hot-spring fluids considering the *PVT* properties of the fluid and the inferred depth of sub-seafloor magma chambers, which Morton (1984) concludes occur at approximately 1–3 km beneath the seafloor, corresponding to pressures between 350 and 450 bars for seafloor depths of 2500 m. For example, applying the adiabat for seawater established by Bischoff & Rosenbauer (1984, 1985) to hot-spring fluids at 21°N, EPR, where measured temperatures are approximately 350°C (Von Damm *et al.* 1985), yields a temperature of approximately 365°C at a subseafloor depth of 2 km.

Delaney *et al.* (1984) reported fluid temperatures of approximately 400°C on the Endeavor segment, northern Juan de Fuca Ridge. At a seafloor pressure of, in this case only 230 bars, a temperature of 400°C places the fluid in the two-phase region, suggesting boiling on ascent to the seafloor. Bischoff & Pitzer (1985), for example, estimated boiling to have taken place under ideal closed-system conditions at approximately 2.9 km beneath the seafloor. However, considering the dynamics of high-temperature hydrothermal fluids, it is possible, perhaps probable, that equilibrium processes of phase separation may not be realized. Nevertheless, the existence of 400°C hot-spring fluids as well as hot-spring fluids with large salinity variations relative to seawater (Bowers *et al.* 1988) provides evidence for seawater circulation in the critical region near the seawater two-phase boundary. As virtually all transport properties and physical phenomena of hydrothermal fluids are characterized by extrema in the low-pressure supercritical region (Norton 1984), fluids in this pressure-temperature region of the crust will have maximum buoyancy and convective heat-transport capacity, and likely represent the dominant source region for high-temperature hot-spring fluids at mid-ocean ridges. Thus, recent basalt/diabase alteration and mineral solubility experiments have been performed under the *P-T* conditions which prevail there (Fig. 1 and Seyfried & Janecky 1985, Berndt 1987).

BASALT/DIABASE ALTERATION: EXPERIMENTAL AND THEORETICAL CONSTRAINTS

Seawater-basalt/diabase interaction

The most conspicuous feature of basalt-seawater interaction experiments at elevated temperatures and pressures is the nearly instantaneous removal of Mg from solution into hydrous alteration products such

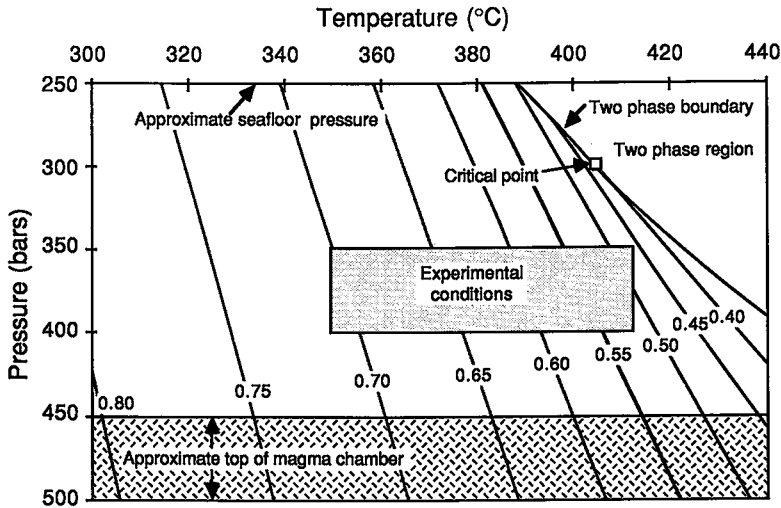


FIG. 1. Two-phase curve and density of seawater (3.2% NaCl fluid) as a function of temperature and pressure. Data and equations of Bischoff & Rosenbauer (1984, 1985) were used for the construction. Also shown are estimated pressures for the seafloor and the top of the axial magma chamber in the vicinity of the East Pacific Rise at 21°N (Morton 1984). The stippled region depicts pressure-temperature conditions investigated in recently performed bulk-rock alteration experiments. Temperature and pressures of 385–400°C and 300–400 bars are the most likely conditions for formation of fluids discharged at black smokers.

as smectite, smectite/chlorite, chlorite, tremolite-actinolite and talc (Bischoff & Dickson 1975, Hajash 1975, Mottl & Holland 1978, Mottl *et al.* 1979, Seyfried & Bischoff 1979, 1981). At 150°C, and probably lower temperatures, Mg removal from solution is complete even at seawater/rock mass ratios as high as 50 (Seyfried & Mottl 1982).

Removal of Mg from seawater to form Mg(OH)₂ components of secondary silicates releases H⁺ to solution, as indicated by reaction 1 (Table 1). Talc is used as an analog for compositionally more complex Mg silicates which form during experiments and in nature. As long as the fluid has a relatively high Mg concentration in solution, a potential exists for H⁺ generation (Seyfried & Mottl 1982). The extent of Mg removal from solution during seawater-basalt interaction has been used by Seyfried & Mottl (1982) to distinguish between basalt- and seawater-dominated systems. For basalt-dominated systems, seawater loses all of its Mg; H⁺ production is neutralized with respect to electrical charge by basalt dissolution involving release of K- and Ca-bearing components. The relative importance of these exchange reactions is a strict function of temperature and basalt chemistry and mineralogy. In contrast, seawater-dominated systems (fluid/rock mass ratios > 50) are characterized by incomplete removal of Mg from solution, and maintenance of acidic conditions (Mottl & Holland 1979, Mottl *et al.* 1979, Seyfried

& Bischoff 1981, Seyfried & Mottl 1982). Experiments have shown that in such systems, sufficient dissolved Mg exists to convert the basalt entirely to a Mg-rich assemblage of secondary phases (Seyfried & Mottl 1982).

TABLE 1. METASOMATIC REACTIONS FOR BASALT ALTERATION PROCESSES INVOLVING IDEALIZED MINERALS AT ELEVATED TEMPERATURES AND PRESSURES

Reaction	Conditions
<u>Mg-metasomatism (reaction 1*)</u>	
$3\text{Mg}^{2+} + 4\text{SiO}_2(\text{aq}) + 4\text{H}_2\text{O} = \text{Talc} \text{ Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2 + 6\text{H}^+$	Prograde at all P, T (Fig. 2)
<u>Ca-metasomatism (reaction 2)</u>	
$3\text{CaAl}_2\text{Si}_2\text{O}_8 + \text{Ca}^{2+} + 2\text{H}_2\text{O} = \text{Clnozoisite}^2 \text{ 2CaAl}_3\text{Si}_3\text{O}_{12}(\text{OH}) + 2\text{H}^+$	Prograde at all P when T > 350°C (Fig. 4)
<u>Na-metasomatism (reaction 3)</u>	
$2\text{Na}^+ + 4\text{SiO}_2(\text{aq}) + \text{CaAl}_2\text{Si}_2\text{O}_8 = \text{Albite}^3 \text{ 2NaAlSi}_3\text{O}_8 + \text{Ca}^{2+}$	Retrograde at all P, T (Fig. 5)
<u>Na-metasomatism and Ca-cycling (reaction 4)</u>	
$2\text{Na}^+ + 4\text{CaAl}_2\text{Si}_2\text{O}_8 + 4\text{SiO}_2(\text{aq}) + 2\text{H}_2\text{O} = \text{Clnozoisite} \text{ 2Ca}_2\text{Al}_3\text{Si}_3\text{O}_{12}(\text{OH}) + \text{Albite} \text{ 2NaAlSi}_3\text{O}_8 + 2\text{H}^+$	See text and Seyfried (1987)

* Reaction numbers in parentheses refer to reactions in text.

1 Anorthite refers to the anorthite component of plagioclase solid solution

2 Clnozoisite refers to the clinozoisite component of epidote solid solution

3 Albite refers to the albite component of plagioclase solid solution

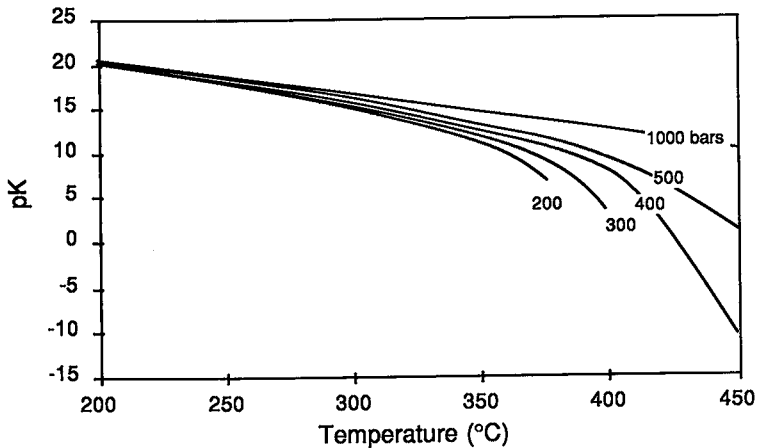


FIG. 2. pK ($-\log K$) for Mg-fixation reaction (Table 1, reaction 1) as a function of temperature and pressure. The continuously prograde nature of the reaction at all pressures makes it difficult for seawater-derived Mg to penetrate deeply into zones of high-grade hydrothermal metamorphism at mid-ocean ridges. Thermochemical data used in the diagram are from Helgeson *et al.* (1978).

Another way to illustrate the reactivity of Mg during hydrothermal alteration of basalt is to evaluate the change in the equilibrium constant for a reaction depicting Mg fixation as a function of temperature and pressure. We can accomplish this by using thermochemical data from Helgeson *et al.* (1978 and Fig. 2), where talc is used to represent Mg-rich alteration phases (Table 1, reaction 1). In these calculations, and others which follow, the standard state for H_2O and standard state for solids are consistent with unit activity of the pure components at any pressure and temperature. The standard state for aque-

ous species other than H_2O is one of unit activity in a hypothetical one molal solution referenced to infinite dilution at any pressure and temperature.

The continuous decrease in the pK ($-\log K$) value for reaction 1 (Table 1) indicates the likelihood for Mg fixation and production of acidity with increasing temperature (Fig. 2), precisely what was observed during the experiments. Thus, Mg uptake by secondary phases makes it unlikely that seawater-derived Mg will penetrate significantly into the high-temperature regions of submarine geothermal systems.

Na-Ca-K-Cl-basalt/diabase interaction

Seawater chemistry in the deep-seated portions of submarine geothermal systems is modified through earlier reactions in the recharge zone involving Mg fixation and homogeneous and heterogeneous precipitation of anhydrite (Bischoff & Seyfried 1978, Janecky & Seyfried 1982). Thus, recent basalt/diabase alteration experiments have utilized fluids which are chemically distinct from seawater (Seyfried & Janecky 1985, Rosenbauer & Bischoff 1983). These fluids are Mg- and SO_4 -free and are enriched in Ca to maintain the fluid at approximately 0.55 molal Cl. The experiments were performed at temperatures of 350–425°C, and a pressures of approximately 350–400 bars, utilizing flexible-cell hydrothermal equipment (Seyfried *et al.* 1987). The temperature-pressure conditions chosen include those thought most important for formation of ridge-crest hydrothermal fluids (Fig. 1), which, as noted previously, likely define a region of maximum convective

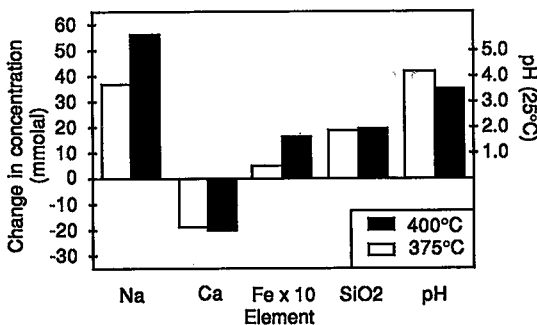


FIG. 3. Change in concentration of selected elements in solution during diabase alteration at 375 and 400°C, 400 bars pressure, and fluid/rock mass ratio of 2 (see Berndt 1987 for detailed experimental results). The composition (mmolal) of the starting fluid used for the experiment was as follows: Na (461); Ca (37.7); K (15.4); Cl (551).

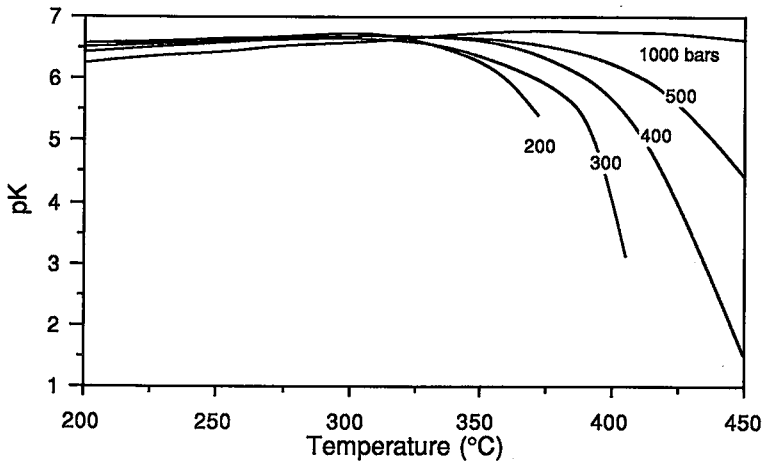


FIG. 4. pK ($-\log K$) for Ca-fixation reaction (Table 1, reaction 2) as a function of temperature and pressure. The decreasing pK value with decreasing pressure at temperatures greater than about 350°C illustrates the important role of pressure on the reaction at temperatures applicable to high-temperature hydrothermal activity at mid-ocean ridges. In the absence of dissolved Mg, Ca fixation plays a key role in the production of acidity and secondary mineral formation during basalt/diabase alteration. Thermochemical data used in the diagram are from Helgeson *et al.* (1978).

activity in the submarine geothermal system. The experiments were conducted at low fluid/rock mass ratios (0.5–5) to be consistent with the relatively high concentrations of so-called soluble elements in hot-spring fluids (B, Li, Rb and to a lesser degree K) (Von Damm *et al.* 1985, see also Seyfried *et al.* 1984).

An important objective of these so-called evolved-fluid experiments was to evaluate the effectiveness of H^+ production in the absence of dissolved Mg. Ridge-crest hydrothermal fluids are variably acidic and, in the absence of Mg, only Ca is capable of forming hydrous alteration phases and generating the requisite acidity. The absence of dissolved Mg had a profound effect on hydrothermal alteration processes. In particular, chlorite/smectite minerals did not dominate the alteration assemblage, but were found only as replacement products of olivine and orthopyroxene. Clinozoisitic epidote and plagioclase (see Berndt 1987) were the most prominent secondary phases produced during the recent experiments. Saussuritized plagioclase feldspar is associated with minor amounts of sulfide and oxide phases (Seyfried & Janecky 1985, Berndt 1987). Thus, Mg-metasomatic reactions (*e.g.*, reaction 1, Table 1) which are required for H^+ production during seawater–basalt interaction (Seyfried & Bischoff 1981), are superceded by other H^+ -producing metasomatic reactions. These reactions are manifested by formation of Ca-rich secondary phases and account for a pH trend which decreases with increasing reaction progress until a steady-state value

is achieved (Seyfried & Janecky 1985). This value is dependent on temperature, pressure, and basalt chemistry.

To illustrate the reactivity of diabase in a 0.55 molal Na–Ca–K–Cl fluid at elevated temperatures and pressures, we report the results of two experiments at 375 and 400°C , 400 bars, and a fluid/rock mass ratio of 2. The diabase used for these experiments was dredged from the Mid-Atlantic Ridge (see Seyfried & Janecky 1985), and is holocrystalline and olivine-normative. As discussed by Berndt (1987) and Berndt *et al.* (1988), the fluid composition and experimental P - T conditions, together with the use of non-glassy basalt, were chosen specifically to model deep-formation of hydrothermal fluids at 21°N , EPR (see Von Damm *et al.* 1985).

Both experiments showed significant decreases in dissolved Ca, although the magnitude of the decrease is greater at 400 than 375°C (Fig. 3). Accompanying the decrease in dissolved Ca is a pH decrease resulting from replacement of plagioclase by clinozoisitic epidote (Table 1, reaction 2). In this reaction, anorthite represents the anorthite component of plagioclase solid solution, and clinozoisite indicates the clinozoisite component of epidote solid solution. The greater Ca-uptake with increasing temperature (Fig. 3) is significant and likely results from the effects of temperature and pressure on the mass-action expression of reaction 2 (Table 1). For example, data from Helgeson *et al.* (1978) indicate that pK for reaction 2 ($\log a_{\text{Ca}^{++}}/a_{\text{H}^+}^2$) decreases with

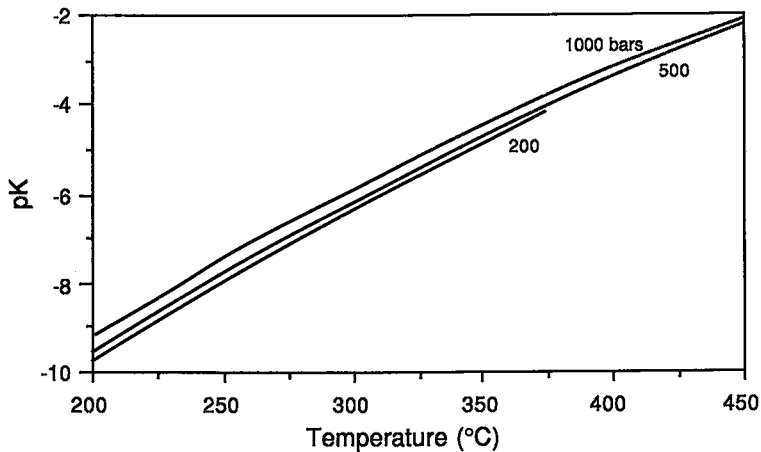


FIG. 5. pK ($-\log K$) for plagioclase solid solutions (Table 1, reaction 3) as a function of temperature and pressure. Thermochemical data used in the diagram are from Helgeson *et al.* (1978).

increasing temperature from 375 to 400°C at 400 bars (Fig. 4). At this pressure, pK values actually increase slightly with increasing temperature over the 200–350°C range. Thus, Ca fixation can result in significant H^+ production provided that temperatures are greater than about 350°C. Above this value, temperature and pressure play an increasingly important role in the extent of Ca fixation because of their effects on water properties, especially density. At these relatively high temperatures, lowering of pressure and fluid densities generally results in lower pH values and dissolved Ca concentrations (Seyfried & Janecky 1985).

The relatively high dissolved Ca concentration of the fluid used for the diabase experiments (37.7 mmolal), coupled with relatively high temperatures and dissolved SiO_2 concentrations at or below quartz saturation (Fig. 3), also results in the development of more calcic plagioclase. Na is released to solution, presumably from dissolution of the albite component of plagioclase solid solution (Fig. 3). Thus, Na and Ca concentrations in solution are influenced by plagioclase solid solution (Table 1, reaction 3). Indeed, Berndt (1987) and Berndt *et al.* (1988) present compelling evidence for formation of hydrothermal calcic plagioclase and clinozoisite (epidote solid solution) during high-temperature diabase-alteration experiments. Other experiments utilizing SiO_2 -rich crystalline basalt (Seyfried & Janecky 1985) are characterized by early-stage albitization and Na removal from solution (Berndt 1987). The stoichiometry of reaction 3 (Table 1) clearly illustrates the significant role played by SiO_2 in albitization and anorthitization of plagioclase.

Reaction 3 (Table 1) is strongly temperature-dependent, although not greatly pressure-dependent

(Fig. 5). The continuously positive pK slopes for reaction (3) indicate that Ca fixation will be favored at elevated temperatures. Low-temperature basalt alteration will result in Ca-rich fluids due to the greater stability of albite, whereas high-temperature alteration produces Ca-depleted fluids. For a fixed plagioclase composition, temperature and pressure, dissolved Na and Ca concentrations are also fixed assuming plagioclase can be treated as a continuous solid-solution series and quartz is present (Berndt 1987, Seewald 1987). Since hydrothermal alteration processes at mid-ocean ridges are rock-dominated, as is evidenced by the "soluble"-element chemistry of hot-spring fluids (Von Damm *et al.* 1985), it is likely that a specific plagioclase composition + quartz buffers the major-element chemistry in solution (*e.g.*, Na, Ca, SiO_2). Thus, the major-element chemistry of ridge-crest hydrothermal fluids may be used to estimate reaction-zone conditions in terms of temperature and pressure (see below and Berndt 1987).

The various metasomatic processes discussed so far have demonstrated little interdependence. We can show this, however, by coupling reactions 2 and 3 (Table 1) to give an overall reaction depicting more complex precipitation and recrystallization reactions for idealized (Fe-free) basaltic systems (Table 1, reaction 4). In effect, Na fixation permits Ca cycling to occur between the anorthite component of plagioclase solid solution and the clinozoisite component of epidote solid solution, thereby generating acidity in amounts greater than that possible by reaction 2 alone. The P , T dependency of reaction 4 reveals the combined effects of reactions 2 and 3 (Seyfried 1987, Seewald 1987).

Results of theoretical and experimental models of

basalt (diabase) alteration reveal the importance of Mg-, Ca- and Na-fixation reactions and the effects of pressure (depth of circulation) on changes in fluid chemistry and formation of secondary phases. Near the critical temperature of the fluid, pressure plays an extremely important and heretofore chiefly overlooked role in basalt alteration, while Ca fixation and hydrous Ca-silicate formation represent the primary acid-producing processes (Table 1, reactions 2 and 4).

BASALT/DIABASE ALTERATION: CONSTRAINTS FROM NATURAL SYSTEMS

Seawater-dominated systems: Mg metasomatism

As described previously, seawater Mg is unlikely to penetrate to the deepest levels of the submarine geothermal system. This is consistent with the chemistry (Mg-rich, Ca-poor) and mineralogy (chlorite-quartz) of ridge metabasalts which are thought to record the products of alteration within downwelling limbs of seafloor convection cells (Mottl 1983). This same scenario has been recognized in hydrothermally altered basalts at Deep Sea Drilling Site 504B (Alt *et al.* 1986) where early-stage seawater penetration and alteration of lower pillow lavas and upper dyke rocks are characterized by abundant chlorite and Mg-rich clay minerals. These rocks also display a general increase in bulk rock $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (Friedrichsen 1985). Seawater/rock mass ratios estimated from the extent of Mg enrichment of pillow-basalt rims and along fractures at 504B (Alt *et al.* 1986) and from the chlorite-quartz-rich greenstones from the Mid-Atlantic Ridge (Mottl 1983) yield values as high as 30–60; this assumes, of course, quantitative removal of Mg from solution (see Mottl 1983).

A subsequent stage of hydrothermal alteration at 504B is characterized by anhydrite formation (Alt *et al.* 1986). Anhydrite is located exclusively in veins and provides evidence of seawater recharge, since seawater contains SO_4 for anhydrite formation and anhydrite solubility decreases with increasing temperature (Bischoff & Seyfried 1978). Basalt-seawater experiments (Seyfried & Mottl 1982) suggest that Ca in anhydrite is most likely basalt-derived, though it may return to solution either by dissolution at lower temperatures (retrograde solubility) or by dissolution accompanying reduction of sulfate to sulfide. The former process is more likely in recharge zones because the abundance of anhydrite exceeds the capacity of the rock to reduce it (Mottl *et al.* 1979, Mottl 1983), and reduction of seawater SO_4 is kinetically sluggish below 350°C (Mottl *et al.* 1979, Shanks *et al.* 1981).

Anhydrite and Mg-rich chlorite are the typical products of seawater-basalt interaction within the recharge zones of seafloor hydrothermal systems; this constrains greatly the composition of fluids

involved in higher grade metasomatic processes.

Rock- and fluid-dominated systems: Ca and Na metasomatism

Mottl (1983) recognized an inverse correlation between Mg enrichment and the degree of Na and Ca enrichment in metabasalts and metadiabases from the Mid-Atlantic Ridge. Alt *et al.* (1986) identified an epidote-quartz-sulfide \pm albite alteration assemblage in dyke rocks at hole 504B which, based on fluid inclusion and oxygen isotopic data, was thought to have formed at temperatures between 200 and 380°C. In both cases, the altered rocks were interpreted as fossilized remnants of deep-seated portions of seafloor convective systems, and were thought to be related closely to the environment of formation of ridge-crest hot-spring fluids, such as those at 21°N on the East Pacific Rise. The albitic composition of the plagioclase from both localities suggests temperatures less than those of the two diabase-alteration experiments discussed above (where the primary igneous plagioclase was recrystallized but not albitized). Field and experimental data indicate that the anorthite content of plagioclase solid solutions in the presence of epidote generally increases with increasing temperature (*e.g.*, Rimbaldi 1973, Goldsmith 1982, Maruyama *et al.* 1982). Extensively albitized basalts from the ophiolite-hosted Turner-Albright sulfide deposit indicate formation temperatures in the range of 140–200°C based on oxygen isotope geothermometry (Zierenberg *et al.* 1988). In contrast, secondary plagioclase in metagabbros dredged from the Mid-Cayman Rise, altered under upper greenschist- to lower amphibolite-facies conditions show more calcic compositions ranging from An_{20} to primary igneous values (Ito & Clayton 1982). Thus, it is highly unlikely that the albite-rich alteration assemblage in greenstones dredged from the Mid-Atlantic Ridge or recovered from hole 504B could have formed at temperatures much greater than 300°C.

The modal abundance of albitic plagioclase, and consequently the degree of Na enrichment in the rock, is directly limited if the fluids contain high contents of dissolved Mg. In effect, Na fixation occurs only for fluids characterized by sufficiently high Na/Mg ratios (Seewald 1987). It is not surprising, therefore, that Mottl (1983) observed the inverse correlation between Na and Mg enrichment. The slight degree of Mg enrichment indicates low seawater/rock mass ratios. However, it is important to recognize that the seawater/rock mass ratio calculated from metabasalt chemistry reveals the amount of Mg exposed to the rock; this may significantly underestimate the actual fluid/rock mass ratio if the fluid is depleted in Mg relative to normal seawater. A continuous supply of a Mg-depleted, Si-rich fluid

high in Na/Ca molal ratio would tend to albitize basalt. This is precisely the situation within the upflow zones of active hydrothermal systems where Si-rich, Mg-free, and Ca-depleted fluids which form during high-temperature processes at depth are cooled both adiabatically and conductively during ascent (Von Damm *et al.* 1985). Reaction of these fluids with fresh or previously altered basalt likely results in extensive albitization. Na enrichment of basalt in recharge (downwelling) zones of sub-seafloor hydrothermal systems is also possible provided a local or regional mechanism exists to increase sufficiently the Na/Mg ratio of the fluid. Seyfried *et al.* (1978) and Seewald (1987) showed this on the scale of individual basalt pillows where the removal of Mg from seawater at the pillow exterior (owing to chlorite formation) may provide high Na/Mg ratio fluids for pillow-core alteration and albitization. A characteristic feature of hydrothermally altered pillow basalts is the replacement of the once glassy and relatively permeable pillow exterior by a chlorite-quartz assemblage, whereas the crystalline and less permeable pillow interior contains albite and epidote.

*Evolved-fluid-dominated systems:
the epidosite problem*

Seismic data from modern ridges (Morton 1984), coupled with the chemistry of hot-spring fluids (Von Damm *et al.* 1985), suggest that seawater penetration into the crust is limited by the existence of shallow (1–3 km beneath the seafloor) magma chambers. Thus, if the ophiolite model is correct, seawater-derived, compositionally evolved fluids react with diabasic dykes and gabbros before buoyantly rising to the seafloor as a result of expansion caused by close proximity of the magmatic heat source. Oxygen isotopic data from the Samail Ophiolite (Gregory & Taylor 1981, Stakes *et al.* 1983) show that very small amounts of fluid reach the base of the layered gabbro sequence. Diabase alteration under such conditions (*e.g.*, 400°C and 400 bars pressure) will almost certainly result in Ca removal from solution (Figs. 3, 4, 5), formation of epidote solid solutions, and stabilization of plagioclase compositions close to values of their igneous precursors. Fluids more saline than seawater will likely fix Na in plagioclase, whereas Ca will cycle between anorthite, epidote, and the aqueous phase (see below, and Shanks & Seyfried 1987). In either case, formation of epidote solid solutions is of primary importance to the chemistry of the fluid and solid alteration phases.

Field studies of ophiolites (Stakes *et al.* 1983, Richardson *et al.* 1987, Schiffman *et al.* 1987, Schiffman & Smith 1988, Harper *et al.* 1988) indicate that epidote-rich zones (so-called epidosites) occur mainly at the base of the sheeted intrusive complex and in

the vicinity of high-level gabbros (the inferred top of fossilized magma chambers). As noted by Richardson *et al.* (1987), the epidosite zones usually appear as relatively narrow subvertical bands of pale green rock set in blue-grey diabase, suggesting that they developed in subvertical fracture systems.

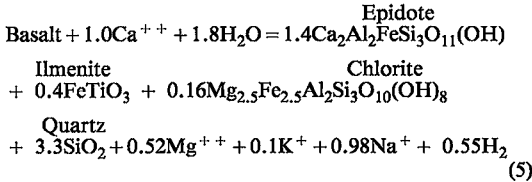
In addition to their abundant epidote, epidosites contain quartz \pm chlorite; they are entirely lacking in any relict igneous texture (Richardson *et al.* 1987). Relative to fresh basalt or diabase, these rocks are enriched in Ca, Sr, H₂O and Fe³⁺ and are depleted in alkalis, ¹⁸O, Zr, Cu, Zn, and in extreme cases, Al and Mg (Richardson *et al.* 1987, Schiffman & Smith 1988, Harper *et al.* 1988). Oxygen isotopic systematics and fluid-inclusion data from epidosite zones strongly suggest temperatures of formation as high as 400°C and salinities similar to normal seawater. Although some debate exists as to whether or not the epidosite zones were axis-parallel or axis-subparallel features, and therefore respectively related to on-axis and off-axis hydrothermal activity (*e.g.*, Richardson *et al.* 1987, Schiffman *et al.* 1987), there is no disagreement as to the intensity of hydrothermal activity and metasomatic effects required to produce the observed alteration assemblage.

The reasons for the extreme Ca fixation in epidosite zones likely involve a combination of factors. The fluid is certainly not seawater, but probably is a seawater-derived Na–Ca–K–Cl fluid which has reacted extensively with diabase and gabbro at elevated temperatures and pressures prior to the epidosite formation process. We believe that the fluid which caused epidosite formation was rich in Ca and very acidic, *i.e.*, not unlike that which resulted from our diabase-alteration experiment at 400°C, 400 bars (Fig. 3), or the end-member hydrothermal fluid at 21°N on the East Pacific Rise (Von Damm *et al.* 1985).

High fluid flow-rates are required to account for the extreme chemical modification necessary to convert basalt or diabase to epidosite. Chemical and physical observations from numerous hydrothermal systems indicate that the particular alteration assemblage that forms is ultimately determined by the composition of the fluid and the permeability of the rock, in addition to temperature and pressure. The fluid which penetrated epidosite zones was presumably near equilibrium with respect to epidote, and the permeability must have been sufficiently high to permit the fluid to determine alteration processes and not allow minerals other than epidote to crystallize. Epidosite zones may be related to tectonic or thermally induced fracturing which provides conduits for up-flowing hydrothermal fluid.

The chemical changes necessary to convert 1 kg of a typical mid-ocean ridge basalt (Carmichael *et al.* 1974) to epidote, quartz, ilmenite, and minor

chlorite can be calculated using the following reaction:



where stoichiometric factors are in moles and rounded to the nearest 0.01 (which is responsible for the slight imbalance for some elements). We have arbitrarily conserved Al_2O_3 , SiO_2 , FeO , Fe_2O_3 , TiO_2 , and a small amount of MgO (chlorite) in solid phases, whereas the alkalis and most of the MgO are partitioned into the fluid as ionic species. To accomplish this, H^+ is necessary to break the cation-oxygen bonds. H^+ is provided by Ca fixation and basalt hydrolysis reactions (Table 1, reaction 2). Thus, addition of Ca and H_2O to basalt yields an "epidosite" composed of about 75% epidote and 25% quartz by mass, while releasing Mg, K, Na and H_2 to solution. The production of significant H_2 in reaction 5 is a consequence of the (oxidative) formation of an Fe^{3+} -bearing phase (epidote) from basalts characterized by a relatively low $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio.

We can estimate the integrated fluid/rock mass ratio for "epidosite" formation by fixing the concentration of one or more of the components released to solution. For example, results of basalt- and diabase-alteration experiments (Mottl & Holland 1978, Seyfried 1987) reveal equilibrium Mg concentrations on the order of 0.5 mmol/kg H_2O . These low values are consistent with the chemistry of ridge-crest hydrothermal fluid (Von Damm *et al.* 1985), and reflect the tendency of Mg to remain in solid phases, underscoring the significance of the Mg-depleted epidotes from ophiolites (Richardson *et al.* 1987, Schiffman & Smith 1988). In order to remove 0.52 mol Mg from one kg of basalt using a solution which can transport only 0.5 mmol Mg/kg H_2O , about 1040 kg of hydrothermal fluid are required. Epidotes with greater amounts of Mg (so-called chlorite-rich epidote) require proportionally lower fluid/rock mass ratios.

Redox processes. As indicated by reaction (5), release of considerable H_2 to solution results from the epidotization process. However, the H_2 content of fluids involved in basalt alteration processes at elevated temperatures and pressures is appreciable (Craig *et al.* 1980), approximately equivalent to that in equilibrium with the assemblage pyrite-pyrrhotite-magnetite (Janecky *et al.* 1986). Thus, it is difficult to envisage a process wherein reaction of a reducing fluid with a reducing rock (basalt) results in the formation of an epidote-rich (Fe^{3+}) alteration assemblage.

Adiabatic decompression may provide the mechanism to account for the requisite flux of H_2 to solution for epidotization of basalt. In the near-supercritical region, changes in pressure can dramatically affect the physical and chemical nature of the fluid. For example, for a high-temperature hydrothermal fluid undergoing decompression, total dissolved H^+ increases because of changes in pressure-dependent dissociation equilibria (Hemley *et al.* 1986) and cation-fixation reactions (Seyfried & Janecky 1985, Seyfried 1987). Pressure-sensitive equilibria at near-supercritical temperatures may also affect redox processes.

To test this, we conducted a decompression experiment at 410°C utilizing mid-ocean-ridge crystalline basalt dredged from the Juan de Fuca Ridge (J. Delaney, pers. comm.) and 0.55 molal Na-Ca-K-Cl fluid. The fluid/rock mass ratio for the experiment was unity. At 400 bars, changes in fluid chemistry were similar to those in the diabase experiments reported earlier (Fig. 3), that is, dissolved Ca and pH decreased from values prior to reaction, whereas Fe increased (Fig. 6). The lower pH and higher Fe concentrations in solution relative to the diabase experiments are almost certainly a result of the 10°C higher temperature. Decompression, first to 375 bars and then to 350 bars, caused further Ca fixation (epidote-clinozoisite formation), and pH decreased and Fe increased. The effects of decompression are entirely consistent with theoretical constraints discussed earlier (Table 1, reaction 2), and in effect render plagioclase unstable relative to epidote solid solutions. Furthermore, the increase in dissolved H_2 reflects Fe oxidation and water dissociation with

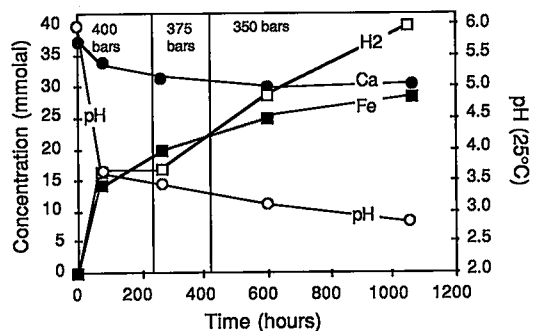
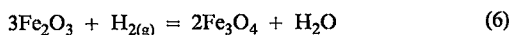


FIG. 6. Change in concentration of selected aqueous species during interaction of crystalline basalt with a Na-Ca-K-Cl (0.55 m, see Fig. 3) fluid at 410°C and decreasing pressure. The pressure decrease from 400 bars to 350 bars causes dissolved Ca and pH (measured at laboratory conditions) to decrease, and Fe and H_2 to increase. The conspicuous increase in H_2 indicates oxidation of the basalt by H_2O . Decompression effects may be important in the formation of epidotes at the base of many sheeted intrusive complexes in ophiolites.

reaction progress and decompression (Fig. 6), which is consistent with epidote formation (high $\text{Fe}^{3+}/\text{Fe}^{2+}$) from basalt/diabase (low $\text{Fe}^{3+}/\text{Fe}^{2+}$).

The increase in dissolved H_2 results from the effect of decreasing pressure (at a constant temperature) on the Henry's law constant for H_2 (HH_2). Thus, $\text{HH}_2 = f\text{H}_{2(\text{g})}/X\text{H}_2$, where $X\text{H}_2$ is the H_2 concentration in solution and $f\text{H}_{2(\text{g})}$ is the fugacity of $\text{H}_{2(\text{g})}$. At a constant temperature, a change in pressure has an insignificant effect on the equilibrium $f\text{H}_{2(\text{g})}$ for redox reactions involving Fe^{2+} and Fe^{3+} -bearing oxide minerals and H_2O , but has a substantial effect on the Henry's law constant (Kashima & Sakai 1984). For example, for the Fe_2O_3 - Fe_3O_4 - H_2O system at 416°C (data from Kashima & Sakai 1984), a pressure change from about 1 kbar to 365 bars results in less than 10% change in $f\text{H}_{2(\text{g})}$, or pK for the reaction:



(Helgeson *et al.* 1978), whereas the Henry's law constant decreases five fold over this pressure range (Kashima & Sakai 1984). Thus, a fluid in equilibrium with any redox assemblage at high pressures becomes an oxidizing fluid if decompressed, and results in a re-adjustment of the relative abundances of the reduced and oxidized minerals; that is, the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio of the assemblage must increase with adiabatic decompression.

These data indicate that hot hydrothermal fluids flowing up through a deep-seated and permeable reaction zone can cause oxidation of wallrock alteration in amounts proportional to the expansivity of the fluid and the local, integrated fluid/rock mass ratio. In effect, a rapidly ascending hydrothermal fluid models an isothermal decompression, and although the magnitude of the decompression process in nature is small compared to that of our experiment (50 bars at 410°C), the result is the same, namely, oxidation. As long as fluid expands, even slightly, a finite oxidative capacity exists for the fluid, which could cause a corresponding increase in $\text{Fe}_2\text{O}_3/\text{FeO}$ ratio in the basalt. Since the expansion-oxidation process is repeated with each parcel of fluid which passes through the reaction zone, substantial oxidative effects are likely.

Epidosites, therefore, seem to reflect the fossilized residue of basalt/diabase exposed repeatedly to discharging hydrothermal fluids at conditions near the critical point of seawater. The conspicuous depletion in so many elements relative to fresh basalt or diabase, including the trace elements Cu, Zn and even Zr (Schiffman *et al.* 1987), is more a function of the locally high and in some cases extreme fluid/rock mass ratios, than it is of fluid chemistry. Because the fluid/rock mass ratio of epidosite zones is necessarily large, their abundance is necessarily

small if one is to reconcile the chemistry of these rocks with the chemistry of fluids discharging from black smokers.

Chemistry of ridge-crest hydrothermal fluids

End-member hydrothermal fluids issuing from vents at sites on the East Pacific Rise and Mid-Atlantic Ridge show significant departures from seawater chemistry (Von Damm *et al.* 1985, Edmond *et al.* 1986). Plagioclase recrystallization reactions, and epidote and chlorite formation, likely control dissolved concentrations of Ca, Sr, Na, Mg and fluid pH (Von Damm *et al.* 1985, Bowers *et al.* 1988, Seyfried 1987, Seewald 1987, Berndt *et al.* 1988). Under rock-dominated conditions, a relatively small amount of rock alteration results in large changes in fluid chemistry, and the inventory of primary igneous minerals is never entirely eliminated (although olivine and orthopyroxene are more affected by alteration than are plagioclase and clinopyroxene: Ito & Anderson 1983). Rock-dominated conditions are required for the relatively high concentrations of K, Li, Rb and B in hot-spring fluids. These elements are present in trace amounts in mafic igneous rocks, but partition effectively and in some cases completely into the fluid during rock alteration (Seyfried *et al.* 1984, Von Damm *et al.* 1985, Bowers *et al.* 1988). Heavy and base metals, which are present in hot-spring fluids in relatively high concentrations, are constrained by temperature-, pressure-, and pH-dependent solubility of various oxide and sulfide phases (Von Damm *et al.* 1985, Seyfried & Janecky 1985, Von Damm & Bischoff 1988), and dissolved- SiO_2 concentrations may be controlled by quartz (Von Damm *et al.* 1985).

Temperature and pressure effects. The chemical composition of a fluid may be used to determine alteration conditions provided that the relative solubilities of minerals are well known under an appropriate range of conditions, or temperature- and pressure-dependent empirical trends can be determined from results of experiments which model the natural rock - fluid interaction process.

Dissolved concentrations of SiO_2 are often used to estimate temperatures and pressures of geothermal fluids by assuming quartz - fluid equilibria. The dissolved concentration of SiO_2 in equilibrium with quartz can be predicted for a wide range of conditions utilizing equations and data in Fournier (1983). However, to estimate both temperature and pressure from SiO_2 concentration in solution, the effective density of the fluid is required (Fournier 1983, Bischoff & Rosenbauer 1985).

The pH of fluids involved in basalt or diabase alteration processes is also sensitive to changes in temperature and pressure owing to fluid speciation effects (Hemley *et al.* 1986), and changes in the relative solubilities of primary and secondary basalt/dia-

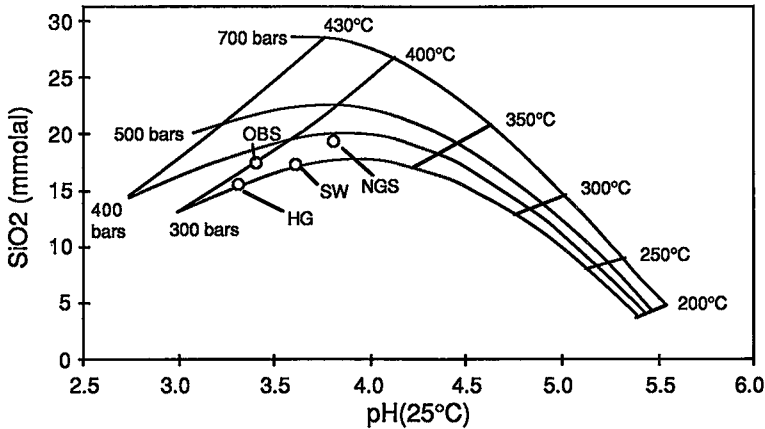


Fig. 7. SiO_2 (mmolal) versus pH (measured) for 21°N , EPR hot-spring fluids in terms of back-calculated temperature and pressure at sites of formation. Temperature-pressure grid constructed by assuming quartz saturation (Fournier 1983) and applying results of bulk-rock basalt alteration experiments (Seyfried & Janecky 1985). Since quartz solubility and pH can be related to fluid density using data from these experiments, temperature and pressure can then be calculated from the density-temperature-pressure relations of Bischoff & Rosenbauer (1985).

base alteration phases. Based on results of numerous bulk-rock alteration experiments, Seyfried (1987) developed the following relationship between density and pH as measured under laboratory conditions:

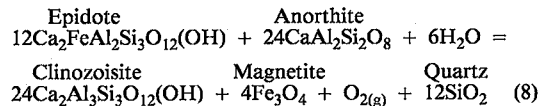
$$\text{pH} = 0.31 + 5.67 (\rho_{\text{sw}}) \quad (7)$$

where ρ_{sw} is the density of the fluid at the T and P of the reaction as determined by Bischoff & Rosenbauer (1985).

Dissolved SiO_2 and pH therefore are related empirically to fluid density (under experimental conditions). The fluid density in turn can be used to define temperature and pressure conditions for a fluid of known composition. Thus, the temperature and pressure of a seafloor reaction zone can be estimated from the pH and dissolved SiO_2 concentration of ridge-crest hydrothermal fluid. For example, hot-spring fluids at 21°N , EPR, indicate temperatures and pressures of 385–400°C and 300–400 bars, respectively (Fig. 7). Even the minimum temperatures are significantly higher than those measured at the seafloor, suggesting that conductive cooling of the ascending hydrothermal fluids may be more common than initially expected (see Von Damm *et al.* 1985), or temperature-probe measurements may not be as accurate as has been thought. The approach used here, however, assumes that the minerals that control the pH of the fluids in the experiments are the same as those that control the pH of the hot-spring fluids at EPR, 21°N , and that the fluids are saturated with respect to quartz. The

accuracy of these assumptions cannot be tested as we do not have access to the reaction zone at EPR, 21°N . Theoretical data and field observations from ophiolites may help to constrain some of the uncertainty, as discussed in the following sections.

The composition of epidote solid solutions in equilibrium with plagioclase, magnetite and quartz is a function of $f\text{O}_2$, as follows:



for which the equilibrium constant can be described by the law of mass action, thus:

$$K = (a_{\text{cz}}^{24} a_{\text{mt}}^4 f_{\text{O}_{2(\text{g})}} a_{\text{qtz}}^{12}) / (a_{\text{H}_2\text{O}}^6 a_{\text{ep}}^{12} a_{\text{an}}^{24}) \quad (9)$$

Rearranging and substituting values of unity for $a_{\text{H}_2\text{O}}$, a_{mt} , and a_{qtz} results in the following relationship:

$$a_{\text{cz}}^{24} / a_{\text{ep}}^{12} = K (a_{\text{an}}^{24} / f_{\text{O}_{2(\text{g})}}) \quad (10)$$

where K for reactions 8 and 9 can be calculated utilizing data from Helgeson *et al.* (1978) and Bird & Helgeson (1981). At $f_{\text{O}_{2(\text{g})}}$ values above quartz-fayalite-magnetite equilibrium and at 400°C and 400 bars, epidote as opposed to clinozoisite is predicted to be the primary component of epidote solid solution in equilibrium with typical igneous plagioclase (Fig. 8). The $P_{\text{fluid}}-T-X$ stabilities of epidote and clinozoisite obtained from experimental studies (*e.g.*,

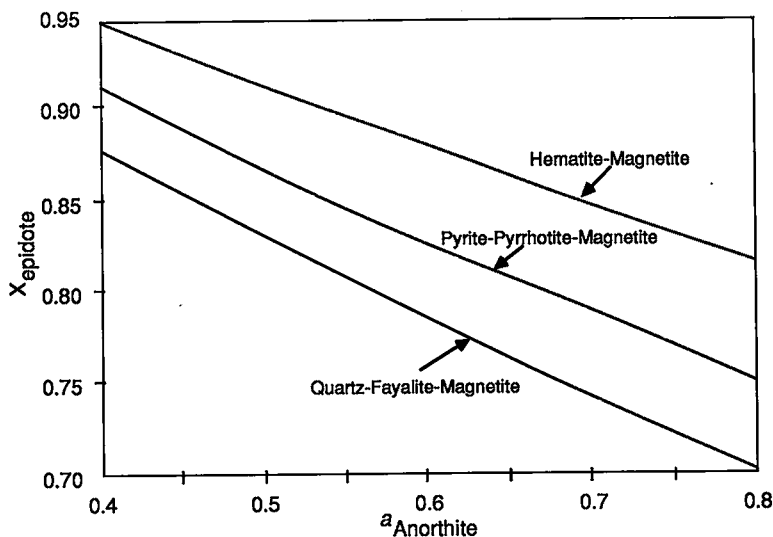


FIG. 8. Composition of epidote in the $\text{Na}_2\text{O}-\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{FeO}-\text{Fe}_2\text{O}_3-\text{H}_2\text{O}$ system at three different $f\text{O}_2$ buffers, and at 400°C and 400 bars. Epidote solid solutions were calculated using equations and data of Bird & Helgeson (1980, 1981). Plagioclase solid solutions are not assumed to be ideal; therefore, anorthite activity is shown. Thermochemical data used for the construction are from Helgeson *et al.* (1978). At a typical igneous anorthite activity (in plagioclase) of 0.7, epidote solid solutions contain significant X_{ep} at low $f\text{O}_2$ values determined by the Q-F-M redox buffer.

Liou 1973) indicate that $f\text{O}_2$ values in excess of Q-F-M cause a drastic expansion in the stability range of epidote at virtually all temperatures and pressures. The composition of epidotes at the base of the sheeted intrusive complex of the Troodos ophiolite (Richardson *et al.* 1987, Schiffman & Smith 1988) and epidote from Del Puerto (Evarts & Schiffman 1983) and Betts Cove (Coish 1977) ophiolites seem to corroborate this. At Del Puerto and Betts Cove, however, there is a correlation between epidote chemistry and stratigraphic position in that most of the more clinozoisitic epidotes are from the plutonic member, where they occur within saussuritized plagioclase and have compositions of approximately P_{820} . Clinozoisitic epidote was observed in the diabase alteration experiments as well (Seyfried & Janecky 1985), where it also occurred as saussuritized plagioclase. At the $f\text{O}_2$ of these experiments, which was calculated from measured H_2 concentrations in solution (Janecky *et al.* 1986) to be in the vicinity of that buffered by pyrite-pyrrhotite-magnetite, P_{825} is the stable epidote composition (Fig. 8). However, owing to the fine grain size, very limited abundance, and intimate association with other phases including plagioclase (anorthite) and magnetite, it is not possible at this time to confirm the composition of epidote predicted by data in Figure 8 with the composition of epidote derived

experimentally. That the experiments generate an alteration phase similar to that from appropriate regions in ophiolites is reassuring, but it remains to be determined that the experimental alteration products are entirely consistent with theoretical and compositional constraints. Since the pH-controlling reactions during basalt alteration processes are as much a function of a_{O_2} in the mass-action expression of reaction 2 (Table 1) as they are on temperature and pressure, models of the physical-chemical conditions of formation of ridge-crest hydrothermal alteration based entirely on results of bulk-rock alteration experiments, must be applied with caution.

Conductive cooling. When initially sampled in 1979, the NGS vent at 21°N EPR had a measured temperature of 350°C (Von Damm *et al.* 1985). A subsequent visit in 1981 found the vent sealed, but after the chimney was broken open, hydrothermal fluid flowed from it at a reduced rate and a temperature of only 273°C (Von Damm *et al.* 1985). Venting at this temperature and a reduced rate was still occurring during a third visit in 1985 (Campbell *et al.* 1988). Despite an 80°C drop in the measured temperature, there was little or no change in the major-element chemistry of the fluid, although dissolved Fe was approximately half what it was in 1979 (Campbell *et al.* 1988). It is important for a full understanding of axial hydrothermal systems to

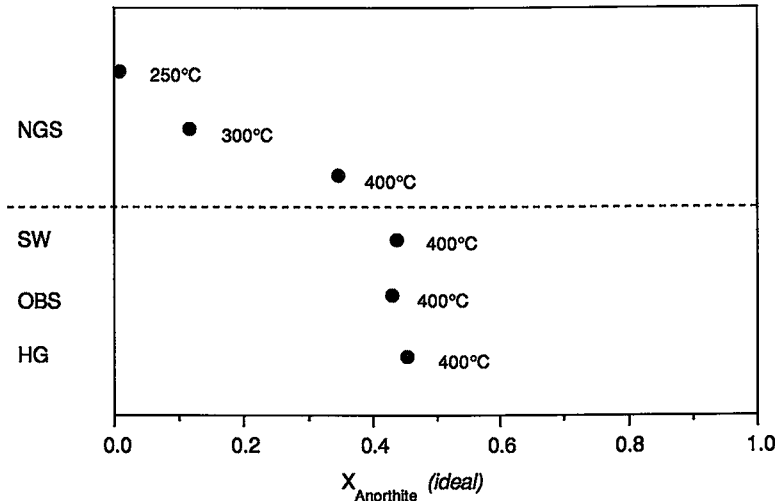


FIG. 9. Plagioclase compositions calculated from activity-concentration relations (assuming ideal solid solution) for 21°N, EPR fluids. Calculations performed for 400 bars and 250, 300, and 400°C. For assumed temperatures of 400°C, similar idealized plagioclase compositions are predicted from OBS, SW, and HG vent fluid. If the sub-seafloor plagioclase compositions beneath each of the vent sites are similar, the calculations suggest the source zone for NGS vent fluids is at a temperature and pressure higher than 400°C and 400 bars. Plagioclase compositions predicted for NGS vent fluids at 250°C and 300°C (400 bars) yield values which depart further from idealized plagioclase compositions based on data from the other vent sites. Clearly, NGS vent fluid must be derived at temperatures significantly above the 273°C measured temperature.

determine whether the temperature drop reflects a real change at depth.

Fluid/rock ratios calculated from the concentrations of mobile elements such as Li, B, and K indicate low values ranging from 3.0 to 0.28 at 21°N EPR (Von Damm *et al.* 1985, Spivack & Edmond 1987). The constant concentration of these elements at the NGS vent between 1979 and 1981 strongly indicates that the amount of fresh rock encountered by the hydrothermal fluid did not change greatly, if at all. Mass transfer between a fluid and a set of reactants will occur until the fluid becomes saturated with respect to a thermodynamically stable assemblage which may include primary igneous minerals. The vent fluids from 21°N, EPR should tend toward equilibrium with primary plagioclase of composition near An_{60} , typical of oceanic basalts from the EPR (Pearce *et al.* 1986).

In low-fluid/rock systems, fluid - plagioclase equilibria can be used as a *relative* geothermometer since both fluid chemistry and plagioclase composition are known. The composition of plagioclase in equilibrium with the sampled fluids from 21°N EPR was calculated at 400°C and 400 bars pressure from reaction (3) by computing the aqueous activities of Na, Ca, and SiO_2 using the computer code of Berndt (1987) for speciating aqueous fluids in the

low-pressure supercritical region and by assuming ideal plagioclase solid solution (Fig. 9). Plagioclase compositions were calculated at 400 bars for the NGS vent at 250°C and 300°C using SOLVEQ (Reed 1982) for the aqueous speciation (Fig. 9), to determine if the measured temperature of 273°C could possibly represent the maximum temperature in the reaction zone at depth. (The SOLVEQ code has an upper temperature limit of 350°C, and therefore could not be used for speciation calculations at 400°C; the high-temperature code of Berndt (1987) and SOLVEQ are entirely compatible and give similar results at conditions within their mutual working ranges.) These calculations are strongly dependent on temperature, the assumption of ideal plagioclase solid solution, and the accuracy of the thermodynamic data used. However, this is of minor significance for the present discussion, as any inaccuracies would affect all the calculations similarly, and it is only the *relative* plagioclase compositions that are of interest. At 400°C and 400 bars, the calculated plagioclase compositions range from An_{35} at NGS to about An_{43} at HG, OBS, and SW. The slightly more sodic value at NGS may be due to spatial variations in primary basalt composition. Alternatively, the temperature of interaction may be still higher at NGS assuming 400 bars pressure, and per-

forming the speciation calculations at the higher temperature would bring the NGS vent fluid into equilibrium with more calcic plagioclase.

The calculated plagioclase compositions for the NGS vent at 300 and 250°C, temperatures that bracket the measured value of 273°C, are $An_{12.5}$ and $An_{1.0}$, respectively (Fig. 9). However, albitic plagioclase is not a primary phase in oceanic basalts, and the mobile trace-elements indicate reaction with abundant fresh basalt. Thus, peak temperatures of reaction for NGS vent fluid were clearly higher than 273°C, and likely similar to, if not higher than other vent fluids at 21°N. This conclusion is consistent with temperatures inferred from the low pH and high metal content of the fluids (see above, and Seyfried 1987) and arguments based on quartz geothermometry (see above, and Von Damm *et al.* 1985).

Dissolved Cl effects. Hot-spring fluids at mid-ocean ridges are characterized by important salinity variations. For example, vent fluids from the southern Juan de Fuca Ridge have elevated Cl contents relative to seawater, ranging from 896 to 1087 mmolal (Von Damm & Bischoff 1988). Fluids from 11 and 13°N EPR show both Cl depletions and enrichments varying from 338 to 718 mmolal, although the majority are enriched (Bowers *et al.* 1988). Fluids from 21°N, EPR are slightly depleted

in Cl with respect to seawater except for NGS which is slightly enriched (Von Damm *et al.* 1985). At least three mechanisms can influence the salinity of submarine hydrothermal fluids: (1) hydration reactions, (2) precipitation and dissolution of Cl-rich alteration minerals (Seyfried *et al.* 1986), and (3) two-phase separation or boiling of seawater-derived hydrothermal fluids (Delaney 1982, Bischoff & Rosenbauer 1984). Each of these mechanisms has merit, but none seems to be applicable to all hot-spring systems (Delaney *et al.* 1987, Von Damm & Bischoff 1988). Variations in salinity, however, affect significantly mineral solubility relations and cause non-linear, but systematic changes in the major- and trace-element chemistry of hot-spring fluids. For example, owing to the squared term in the denominator of the mass-action expression of reaction 3 (Table 1), changes in total dissolved chloride can affect Ca and Na concentrations in solution and the relative stability of albite and anorthite components of plagioclase (Orville 1972). For plagioclase equilibrium at quartz saturation, charge-balance and mass-action relations require a_{Na^+} and $a_{Ca^{++}}$ to increase with increasing chlorinity while $a_{Ca^{++}}/a_{Na^+}^2$ remains constant. If so, then for a constant plagioclase composition, temperature, and pressure, the Na/Ca ratio (molal) in solution decreases exponentially with increasing

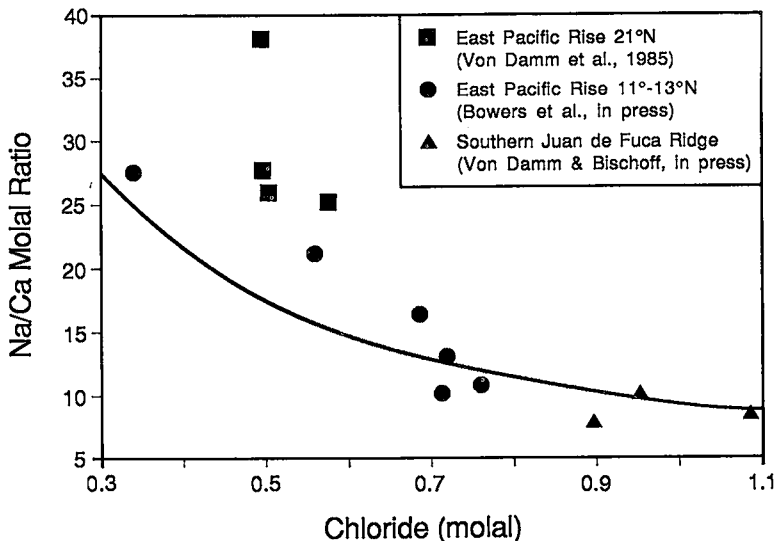


FIG. 10. Na/Ca molal ratio versus dissolved chloride for active hydrothermal vent fluids at mid-ocean ridges. The solid line connects points of equivalent mCa^{2+}/m^2Na^+ ratio. The exponential increase in Na/Ca with decreasing chloride results from the stoichiometry of the plagioclase solubility expression, in particular, the squared term of Na in the mass action expression (Table 1, reaction 3). The relatively high Na/Ca molal ratios of vent fluids at 21°N, EPR suggest that they formed under conditions different from those at other vent sites. Silica-geobarometry results suggest that a significant cause of the difference may involve pressure effects (Von Damm *et al.* 1985, Seyfried 1987, Von Damm & Bischoff 1988).

salinity. This is precisely the trend observed for hot-spring fluids.

Na/Ca versus Cl for the hot-spring fluids is demonstrated in Figure 10 where the solid curve connects points of equal mCa^{++}/m^2Na^+ ratio (see reaction 3 and above discussion). That the vent fluids from 11°–13°N, EPR and the southern Juan de Fuca Ridge all plot close to a single curve suggests that the conditions of chemical interaction (temperature, pressure, and plagioclase composition) were similar for these vent fluids. It must be realized that changes in temperature or pressure (or both) too small to be detected by plagioclase–fluid equilibria (Fig. 10) may be sufficient to cause salinity changes by boiling if the T, P condition is close to the two-phase boundary of the fluid. As noted previously, so little is known about mechanisms of salinity change in hot-spring fluids that it is difficult to couple the two processes.

Quartz geothermometry places the maximum temperature of interaction for the southern Juan de Fuca Ridge vent fluids between 370 and 390°C (Von Damm & Bischoff 1988). Measured temperatures are decidedly lower, however, (approximately 284°C), suggesting heat loss by conduction or technical difficulties which may have prevented accurate temperature measurements (Von Damm & Bischoff 1988). A similar scenario can be developed for the 11–13°N, EPR vent fluids where measured vent temperatures range from 330–380°C (Bowers *et al.* 1988).

Vent fluids from 21°N, EPR plot above the calculated curve for plagioclase–fluid equilibria (Fig. 10), indicating that the conditions of chemical interaction are different from those at the other hot-spring sites. Pressure estimates based on quartz geobarometry are lower at 21°N than at 11–13°N EPR and the southern Juan de Fuca Ridge (Von Damm *et al.* 1985, Bowers *et al.* 1988, Von Damm & Bischoff 1988). Thus, at 21°N, EPR, lower silica activities due to quartz equilibration at lower pressures result in a reduced thermodynamic tendency towards albitization and higher Na/Ca molal ratios. The vent fluid with the highest Na/Ca ratio is HG, which based on quartz geobarometry/geothermometry (Fig. 7) is derived from a relatively shallow reaction zone and has a conspicuously low pressure (approximately 300 bars, see Fig. 7). By contrast, NGS vent fluid may be from greater depths and pressures more closely related to those of vent fluids at 11–13°N, EPR, and southern Juan de Fuca Ridge, assuming similar plagioclase compositions and reaction-zone temperatures.

CONCLUSIONS

Results of alteration experiments at elevated temperatures and pressures have been combined with theoretical calculations and field observations,

including the chemistry of hot-spring fluids and the chemistry and mineralogy of metabasalt and metadiabase, to develop a better understanding of sub-seafloor hydrothermal alteration processes. Experimental data from basalt–seawater and diabase–fluid (Na–Ca–K–Cl = 0.55 *m*) interaction encompassing a wide range of temperatures, pressures, and fluid/rock mass ratios, define the metasomatic processes which are revealed by the chemistry of hot-spring fluids, and of metabasalts dredged from mid-ocean ridges and observed in ophiolites on land. These data, supplemented by theoretical constraints, demonstrate that Mg-, Ca- and Na-fixation reactions are affected differently under different alteration conditions. It is likely, therefore, that each characterizes a specific region within the submarine geothermal system.

Mg fixation is entirely prograde and is probably restricted to downwelling limbs of subseafloor convection cells, giving rise to chlorite–quartz-rich alteration assemblages. Ca fixation, in contrast, increases with increasing temperature, provided that pressure is sufficiently low. Shallow emplacement of sub-seafloor magma chambers at mid-ocean ridges creates conditions (temperatures $\geq 350^\circ\text{C}$ and relatively low pressures) favorable for Ca removal from solution, attendant H^+ production, heavy-metal solubility, formation of clinzoisite–epidote solid solutions, and in some cases, plagioclase solid solutions more calcic than typical igneous values. Adiabatic decompressive effects, which provide a previously overlooked mechanism to oxidize Fe in basalt/diabase, enhance Ca fixation and further stabilize epidote. Epidote-rich rocks, such as the so-called epidotes located mainly at the base of sheeted intrusive complexes of ophiolites, most likely represent the fossilized residue of a once-permeable reaction zone dominated by hot, ascending (decompressing) hydrothermal fluids. Local fluid/rock mass ratios as high as 1000 may characterize epidote zones. In contrast with the generally prograde nature of Mg- and Ca-fixation reactions, Na fixation exhibits retrograde tendencies and thus may dominate reaction zones affected by ascending hydrothermal fluids which may cool by conduction. Na fixation is also enhanced by increased Cl concentrations in solution, owing to charge-balance constraints and the stoichiometry of the exchange reaction for plagioclase equilibria in terms of anorthite and albite components (reaction 3). It is for this reason that the Na/Ca ratio of hot-spring fluids generally decreases with increasing dissolved Cl.

Experimental models of ridge-crest hydrothermal processes require temperatures and pressures in the vicinity of 385–400°C and 300–400 bars to duplicate the composition of hot-spring fluids at 21°N, EPR. The accuracy of these estimates, however, depends on whether the alteration phases in the experimen-

tal reactions are chemically and mineralogically similar to those phases in seafloor reaction zones. Whatever variation exists in this regard, the uncertainty in alteration conditions estimated for the hot-springs is small compared with the actual variations observed. For example, NGS vent fluid at 21°N, EPR has a measured temperature approximately 80°C cooler than other hot-spring fluids at 21°N, yet it is similar in chemistry. Clearly, hydrothermal fluids ascending through the NGS vent system lose heat in amounts greater than that possible by adiabatic decompression. Based on relatively low vent temperatures of hydrothermal fluids at 11–13°N, EPR and southern Juan de Fuca Ridge, conductive cooling affects are likely here too. Reaction-zone pressures for these hydrothermal vent systems, however, seem to be greater than for 21°N, EPR as revealed by systematic differences in Na/Ca versus Cl trends (plagioclase – fluid equilibria) and quartz geothermometry/geobarometry.

ACKNOWLEDGEMENTS

We wish to thank Dr. Theresa S. Bowers, Dr. M. K. Tivey and the editors for their numerous constructive comments which greatly improved the manuscript. Comments by Dr. Dave Janecky are gratefully acknowledged. Research funds were provided by NSF grants OCE-8510517 and OCE-8700762.

REFERENCES

- ALT, J.C., HONNOREZ, J., LAVERNE, C. & EMMERMANN, R. (1986): Hydrothermal alteration of a 1 km section through the upper oceanic crust, Deep Sea Drilling Project hole 504B: Mineralogy, chemistry, and evolution of seawater–basalt interactions. *J. Geophys. Res.* **91**, 10,309–10,335.
- BERNDT, M.E. (1987): *Experimental and Theoretical Constraints on the Origin of Mid-Ocean Ridge Geothermal Fluids*. Ph.D thesis, University of Minnesota, Minneapolis, Minnesota.
- _____, SEYFRIED, W.E., JR. & BECK, J.W. (1988): Hydrothermal alteration processes at mid-ocean ridges: experimental constraints from Ca and Sr exchange reactions and Sr isotopic ratios. *J. Geophys. Res.* **93**, 4573–4585.
- BIRD, D.K. & HELGESON, H.C. (1980): Chemical interactions of aqueous solutions with epidote-feldspar mineral assemblages in geologic systems. I. Thermodynamic analysis of phase relations in the system CaO–FeO–Fe₂O₃–Al₂O₃–SiO₂–H₂O–CO₂. *Amer. J. Sci.* **280**, 907–941.
- _____ & _____ (1981): Chemical interaction of aqueous solutions with epidote-feldspar mineral assemblages in geologic systems. II. Equilibrium constraints in metamorphic/geothermal processes. *Amer. J. Sci.* **281**, 576–614.
- BISCHOFF, J.L. & DICKSON, F.W. (1975): Seawater–basalt interaction at 200°C and 500 bars: implications for origin of sea-floor heavy metal deposits and regulation of seawater chemistry. *Earth Planet. Sci. Lett.* **25**, 385–397.
- _____ & PITZER, K.S. (1985): Phase relations and adiabats in boiling seafloor hydrothermal systems. *Earth Planet. Sci. Lett.* **75**, 327–338.
- _____ & ROSENBAUER, R.J. (1984): The critical point and two-phase boundary of seawater, 200–500°C. *Earth Planet. Sci. Lett.* **68**, 173–189.
- _____ & _____ (1985): An empirical equation of state for hydrothermal seawater (3.2 percent NaCl). *Amer. J. Sci.* **285**, 725–763.
- _____ & SEYFRIED, W.E., JR. (1978): Hydrothermal chemistry of seawater from 25°C to 350°C. *Amer. J. Sci.* **278**, 838–860.
- BOWERS, T.S., CAMPBELL, A.C., MEASURES, A.J., SPIVACK, A.J. & EDMOND, J.M. (1988): Chemical controls on the composition of vent fluids at 13–11°N and 21°N, East Pacific Rise. *J. Geophys. Res.* **93**, 4522–4537.
- CAMPBELL, A.C., BOWERS, T.S. & EDMOND, J.M. (1988): A time-series of vent fluid compositions from 21°N EPR (1979, 1981, 1985) and the Guaymas Basin, Gulf of California (1982, 1985). *J. Geophys. Res.* **93**, 4537–4551.
- CARMICHAEL, I.S., TURNER, F.J. & VERHOOGEN, J. (1974): *Igneous Petrology*. McGraw-Hill, New York.
- COISH, R.A. (1977): Ocean floor metamorphism in the Betts Cove ophiolite, Newfoundland, Canada. *Contr. Mineral. Petrology* **60**, 255–270.
- CRAIG, H., WELHAN, J.A., KIM, K., POREDA, R. & LUP- TON, J.E. (1980): Geochemical studies of the 21°N EPR hydrothermal fluids. *EOS, Trans. Amer. Geophys. Union* **61**, 922.
- DELANEY, J.R. (1982): Generation of high salinity fluids from seawater by two-phase separation. *EOS, Trans. Amer. Geophys. Union* **63**, 1135.
- _____, MCDUFF, R.E. & LUP- TON, J.E. (1984): Hydrothermal fluid temperatures of 400°C on the Endeavour Segment, northern Juan de Fuca. *EOS, Trans. Amer. Geophys. Union* **65**, 973.
- _____, MOGK, D.W. & MOTTI, M.J. (1987): Quartz cemented breccias from the Mid-Atlantic Ridge: Samples of a high salinity hydrothermal upflow zone. *J. Geophys. Res.* **92**, 9175–9192.
- EDMOND, J.M., CAMPBELL, A.C., PALMER, M.R. & KLINKHAMMER, G.P. (1986): Preliminary report on the chemistry of hydrothermal fluids from the Mid- Atlantic Ridge. *EOS, Trans. Amer. Geophys. Union* **67**, 1021.

- EVARTS, R.C. & SCHIFFMAN, P. (1983): Submarine hydrothermal metamorphism of the Del Puerto ophiolite, California. *Amer. J. Sci.* **283**, 289-340.
- FOURNIER, R.O. (1983): A method of calculating quartz solubilities in aqueous sodium chloride solutions. *Geochim. Cosmochim. Acta* **47**, 579-586.
- FRIEDRICHSEN, H. (1985): Strontium, oxygen and hydrogen isotope studies on primary and secondary minerals in basalts from the Leg 83 section of DSDP hole 504B, Costa Rica Rift. *Initial Reports Deep Sea Drilling Project 83*, 289-296. U.S. Gov. Printing Office, Washington, D.C.
- GOLDSMITH J.R. (1982): Review of the behavior of plagioclase under metamorphic conditions. *Amer. Mineral.* **67**, 643-652.
- GREGORY, R.T. & TAYLOR, H.P., JR. (1981): An oxygen isotope profile in a section of Cretaceous oceanic crust, Samail ophiolite, Oman: Evidence for $\delta^{18}\text{O}$ -buffering of the oceans by deep (> 5 km) seawater-hydrothermal circulation at mid-ocean ridges. *J. Geophys. Res.* **86**, 2737-2755.
- HAJASH, A. (1975): Hydrothermal processes along mid-ocean ridges: an experimental investigation. *Contr. Mineral. Petrology* **53**, 205-226.
- HARPER, G.D., BOWMAN, J.R. & KUHN, R. (1988): Field, chemical, and isotopic aspects of submarine hydrothermal metamorphism of the Josephine ophiolite, northwestern California. *J. Geophys. Res.* **93**, 4625-4657.
- HELGESON, H.C., DELANEY, J.M., NESBITT, H.W. & BIRD, D.K. (1978): Summary and critique of the thermodynamic properties of rock-forming minerals. *Amer. J. Sci.* **278-A**, 1-229.
- HEMLEY, G.L., CYGAN, G.L. & D'ANGELO, W.M. (1986): Effect of pressure on ore mineral solubilities under hydrothermal condition. *Geology* **14**, 377-379.
- ITO, E. & ANDERSON, A.T., JR. (1983): Submarine metamorphism of gabbros from the Mid-Cayman Rise: Petrographic and mineralogic constraints on hydrothermal processes at slow-spreading ridges. *Contr. Mineral. Petrology* **82**, 37-388.
- _____, & CLAYTON, R.N. (1982): Submarine metamorphism of gabbros from the Mid-Cayman Rise: An oxygen isotopic study. *Geochim. Cosmochim. Acta* **47**, 535-546.
- JANECKY, D.R. & SEYFRIED, W.E., JR. (1982): The solubility of magnesium-hydroxide-sulfate-hydrate in seawater at elevated temperatures and pressures. *Amer. J. Sci.* **283**, 831-860.
- _____, & _____ (1984): Formation of massive sulfide deposits on oceanic ridge crests: Incremental reaction models for mixing between hydrothermal solutions and seawater. *Geochim. Cosmochim. Acta* **48**, 2723-2738.
- _____, _____ & BERNDT, M.E. (1986): Fe-O-S redox reactions and kinetics in hydrothermal systems. *Fifth Int. Symp. Water-Rock Interaction*, 282-285.
- KASHIMA, N. & SAKAI, H. (1984): A simple gas analytical technique for the Dickson-type hydrothermal apparatus and its application to the calibration of MH, NNO and FMQ oxygen buffers. *Geochemical J.* **18**, 19-29.
- LIU, L.G. (1973): Synthesis and stability relations of epidote, $\text{Ca}_2\text{Al}_2\text{FeSi}_3\text{O}_{12}(\text{OH})$. *J. Petrology* **14**, 381-413.
- MARUYAMA, S.K., LIU, J.G. & SUZUKI, K. (1982): The peristerite gap in low-grade metamorphic rocks. *Contr. Mineral. Petrology* **81**, 268-276.
- MICHARD, G., ALBAREDE, F., MICHARD, A., MINSTER, J.-F., CHARLOU, J.-L. & TAN, N. (1984): Chemistry of solutions from the 13°N East Pacific Rise site. *Earth Planet. Sci. Lett.* **67**, 297-308.
- MORTON, J.L. (1984): *Oceanic Spreading Centers: Axial Magma Chambers, Thermal Structure and Small Scale Ridge Jumps*. Ph.D. thesis, Stanford University, Stanford, CA.
- MOTTL, M.J. (1983): Metabasalts, axial hot-springs and the structure of hydrothermal systems at mid-ocean ridges. *Geol. Soc. Amer. Bull.* **94**, 161-180.
- _____, & HOLLAND, H.D. (1978): Chemical exchange during hydrothermal alteration of basalt by seawater. *Geochim. Cosmochim. Acta* **43**, 1103-1115.
- _____, _____ & CORR, R.F. (1979): Chemical exchange during hydrothermal alteration of basalt by seawater - II. Experimental results for Fe, Mn, and sulfur species. *Geochim. Cosmochim. Acta* **43**, 869-884.
- NORTON, D. (1984): Theory of hydrothermal system. *Ann. Rev. Earth Planet. Sci.* **12**, 155-177, (G.W. Wetherill, A.L. Albee & F.G. Stehli, eds.). Annual Reviews, Inc., Palo Alto, CA.
- ORVILLE, P.M. (1972): Plagioclase cation exchange equilibria with aqueous chloride solution: Results at 700°C and 2000 bars in the presence of quartz. *Amer. J. Sci.* **272**, 234-272.
- PEARCE, J.A., ROGERS, N., TINDLE, A.J. & WATSON, J.S. (1986): Geochemistry and petrogenesis of basalts from Deep Sea Drilling Project Leg 92, Eastern Pacific. *Initial Reports Deep Sea Drilling Project* (M. Leinen, D.K. Rea et al., eds.), 435-457, U.S. Gov. Printing Office, Washington, D.C.
- PIEPGRAS, D.J. & WASSERBURG, G.J. (1985): Strontium and neodymium isotopes in hot-springs on the East Pacific Rise and Guaymas Basin. *Earth Planet. Sci. Lett.* **72**, 341-356.

- REED, M.H. (1982): Calculation of multicomponent chemical equilibria and reaction processes involving minerals, gases and an aqueous phase. *Geochim. Cosmochim. Acta* **46**, 513-528.
- RICHARDSON, C.J., CANN, J.R., RICHARDS, H.G. & COWAN, J.G. (1987): Metal-depleted root zones of the Troodos ore-forming hydrothermal systems, Cyprus. *Earth Planet. Sci. Lett.* **84**, 243-254.
- RIMBALDI, E.R. (1973): Variation in the composition of plagioclase and epidote in some metamorphic rocks near Bancroft, Ontario. *Can. J. Earth Sci.* **10**, 852-868.
- ROSENBAUER, R.J. & BISCHOFF, J.L. (1983): Uptake and transport of heavy metals by heated seawater: a summary of the experimental results. In *Hydrothermal Processes at Seafloor Spreading Centers* (P.A. Rona, K. Bostrom, L. Laubier & K.L. Smith, Jr., eds.) Plenum, New York.
- SCHIFFMAN, P. & SMITH, B.M. (1988): Petrology and O-isotope geochemistry of a fossil seawater hydrothermal system within the Solea graben, northern Troodos Ophiolite, Cyprus. *J. Geophys. Res.* **93**, 4612-4625.
- _____, SMITH, B.M., VARGA, R.J. & MOORES, E.M. (1987): Geometry, conditions and timing of off-axis hydrothermal metamorphism and ore deposition in the Solea graben, N. Troodos ophiolite, Cyprus. *Nature* **325**, 423-425.
- SEEWALD, J.S. (1987): *Na and Ca Metasomatism During Hydrothermal Basalt Alteration: An Experimental and Theoretical Study*. M.Sc. thesis, University of Minnesota, Minneapolis, Minnesota.
- SEYFRIED, W.E., JR. (1987): Experimental and theoretical constraints on hydrothermal alteration processes at mid-ocean ridges. *Ann. Rev. Earth and Planet. Sci.* **15**, 317-335. (G.W. Wetherill, A.L. Albee & F.G. Stehli, eds.), Annual Reviews, Inc., Palto Alto, California.
- _____, BERNDT, M.E. & JANECKY, D.R. (1986): Chloride mobility during hydrothermal alteration of basalt in the low-pressure supercritical region. *Geochim. Cosmochim. Acta* **50**, 469-475.
- _____ & BISCHOFF, J.L. (1979): Low temperature basalt alteration by seawater: An experimental study at 70°C and 150°C. *Geochim. Cosmochim. Acta* **43**, 1937-1947.
- _____ & _____ (1981): Experimental seawater-basalt interaction at 300°C, 500 bars: Chemical exchange, secondary mineral formation and implications for the transport of heavy metals. *Geochim. Cosmochim. Acta* **45**, 135-149.
- _____ & JANECKY, D.R. (1985): Heavy metal and sulfur transport during subcritical and supercritical hydrothermal alteration of basalt: Influence of fluid pressure and basalt composition and crystallinity. *Geochim. Cosmochim. Acta* **49**, 2545-2560.
- _____, _____ & BERNDT, M.E. (1987): Rocking autoclaves for hydrothermal experiments. II. The flexible reaction cell system. In: *Experimental Hydrothermal Techniques* (G. Ulmer & H. Barnes, eds.), Wiley, N.Y., 216-240.
- _____, _____ & MOTTI, M.J. (1984): Alteration of the oceanic crust: Implications for the geochemical cycles of lithium and boron. *Geochim. Cosmochim. Acta* **48**, 557-569.
- _____ & MOTTI, M.J. (1982): Hydrothermal alteration of basalt by seawater under seawater-dominated conditions. *Geochim. Cosmochim. Acta* **46**, 985-1002.
- _____, _____ & BISCHOFF, J.L. (1978): Seawater/basalt ratio effects on the chemistry and mineralogy of spilites from the ocean floor. *Nature* **275**, 211-213.
- SHANKS, W.C. III & SEYFRIED, W.E., JR. (1987): Stable isotope studies of vent fluids and chimney minerals, southern Juan de Fuca Ridge: Sodium metasomatism and seawater sulfate reduction. *J. Geophys. Res.* **92**, 11,387-11,399.
- _____, BISCHOFF, J.L. & ROSENBAUER, R.J. (1981): Seawater sulfate reduction and sulfur isotope fractionation in basaltic systems: Interaction of seawater with fayalite and magnetite at 200-350°C. *Geochim. Cosmochim. Acta* **45**, 1977-1995.
- SPIVACK, A.J. & EDMOND, J.M. (1987): Boron isotope exchange between seawater and the oceanic crust. *Geochim. Cosmochim. Acta* **51**, 1033-1043.
- STAKES, D.S., TAYLOR, H.P., JR. & FISHER, R.L. (1983): Oxygen-isotope and geochemical characterization of hydrothermal alteration in ophiolite complexes and modern oceanic crust. In *Ophiolite and Oceanic Lithosphere* (I.G. Gass, S.J. Lippard & A.W. Shelton, eds.), Blackwell Scientific Publications, Oxford, England.
- VON DAMM, K.L. & BISCHOFF, J.L. (1988): Chemistry of hydrothermal solutions from the Southern Juan de Fuca Ridge. *J. Geophys. Res.* **92**, 11334-11346.
- _____, EDMOND, J.M., GRANT, B., MEASURES, C.I., WALDEN, B. & WEISS, R.F. (1985): Submarine hydrothermal solutions at 21°N, East Pacific Rise. *Geochim. Cosmochim. Acta* **49**, 2197-2220.
- ZIERENBERG, R.A., SHANKS, W.C. III, SEYFRIED, W.E., JR., KOSKI, R.A. & STRICKLER, M.D. (1988): Mineralization, alteration and hydrothermal metamorphism of the ophiolite-hosted Turner-Albright sulfide deposit, southwestern Oregon. *J. Geophys. Res.* **93**, 4657-4675.

Received July 9, 1987; revised manuscript accepted December 27, 1987.