

HYDROTHERMALLY ALTERED BASALTS
FROM THE MARIANA TROUGH

by

Jeffrey Allen Trembly

A Thesis Submitted to the Faculty of the
DEPARTMENT OF GEOSCIENCES
In Partial Fulfillment of the Requirements
For the Degree of
MASTER OF SCIENCE
In the Graduate College
THE UNIVERSITY OF ARIZONA

1982

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SIGNED: Jeffrey Allen Tremble

APPROVAL BY THESIS DIRECTOR

This thesis has been approved on the date shown below:

Arend Meijer
Arend Meijer
Assistant Professor

Nov. 30, 1982
Date

ACKNOWLEDGEMENTS

I would first like to thank Wes Bilodeau, Tom Teska, Mark Reagan, Bob Smith, and Karl Van Keuren for their invaluable assistance during the analytical portion of this thesis. S. R. Titley and M. J. Drake were kind enough to allow me access to the fluid inclusion and electron microprobe facilities. J. M. Guilbert provided many useful comments regarding the scientific content of this thesis along with some excellent editorial comments.

I owe a great debt to Richard April for sparking my original interest in geochemistry while I was an undergraduate and supporting me right through my Masters. He provided analytical, editorial, and scientific aid without which this thesis would have been impossible.

My greatest thanks go to Arend Meijer who conceived this project and then allowed me the freedom to pursue it in my own way while continuously providing support and constructive criticism. No more could be asked of any advisor. I deeply regret that this department has seen fit to deny future students the opportunity to work with Dr. Meijer.

My final thanks go to Jan Elliott who helped me do everything from cutting the first thin sections to touching up the final figures. Her aid and patience are greatly appreciated.

This work was funded in part by a National Science Foundation Graduate Fellowship.

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ABSTRACT

Mineralogical and chemical studies were conducted on fresh and altered basalts collected near the axis of spreading of the Mariana Trough, an actively spreading back-arc basin which is part of the Mariana Island Arc system. Alteration of the basalts occurred under seawater-dominant, followed by rock-dominant conditions. Fluid inclusion data indicate that temperatures may have increased during alteration, then retrogressed.

There do not appear to be significant differences between basalt alteration processes in back-arc environments and mid-ocean ridge environments. Although the samples analyzed here have no intrinsic economic value, their study leads to interpretations about processes forming massive sulfide deposits such as those on the island of Cyprus. It is tentatively concluded that massive sulfides are deposited under seawater-dominated conditions while the associated stockwork system is mineralized under rock-dominated conditions.

INTRODUCTION

Altered basalts comprise a considerable portion of the upper kilometer of the earth's crust. They have been recovered from many oceanic drill and dredge sites and extensively mapped in ophiolite complexes. These altered basalts are important for two major reasons. Because of their abundance, they play a significant role in the chemical mass balance between the ocean and the crust. Secondly, they serve as a host rock for valuable transition metal deposits, especially those containing copper. Several ophiolites, such as the Troodos Massif in Cyprus and the Oman Ophiolite, contain massive sulfide deposits that have been mined through most of recorded history.

Evidence recently acquired indicates that alteration of the oceanic crust begins soon after its formation. Heat flow profiles across spreading centers and in situ observations of ocean floor hot springs by submersibles have documented the existence of presently active geothermal systems along oceanic divergent plate boundaries (Corliss, et al., 1979). At these locations, cold seawater penetrates fractured oceanic crust, circulates downward, and is heated at depth. This water then rises and exits from the geothermal system as hot springs or "smokers". Chemical exchange between heated seawater

and basalt results in the alteration of the basalt and, under certain conditions, the deposition of metalliferous sediments or massive sulfides.

In this investigation, fresh and altered basalts dredged near the center of a back-arc basin, the Mariana Trough, were studied. The change in major element chemistry and mineralogy, from fresh to altered rock, was determined and is discussed in relation to similar studies from other oceanic sites and to experimental basalt-seawater interaction studies. The change in copper concentration as a result of alteration was also determined to provide data regarding transition metal mobility. Fluid inclusions were examined to determine the temperature of alteration. The results of this study help to further characterize the geothermal systems found at oceanic spreading centers.

SAMPLING

The samples used in this investigation are from Leg 8, Dredge 15 of the TASADAY Expedition conducted by Scripps Oceanographic Institute with the R. V. Thomas Washington in December 1973. Fifteen bags of fresh and altered basalt were collected near the axis of spreading in the Mariana Trough approximately 100 km west of the island of Almagren (Fig. 1). The dredge location relative to the proposed axis of spreading is shown in Figure 2, as is the location of Deep Sea Drilling Project (DSDP) Leg 60 drill sites 454 and 456. A NW-SE seismic reflection profile of the dredge site is given in Figure 3. The dredge haul was taken between 2737 and 3812 meters below the surface.

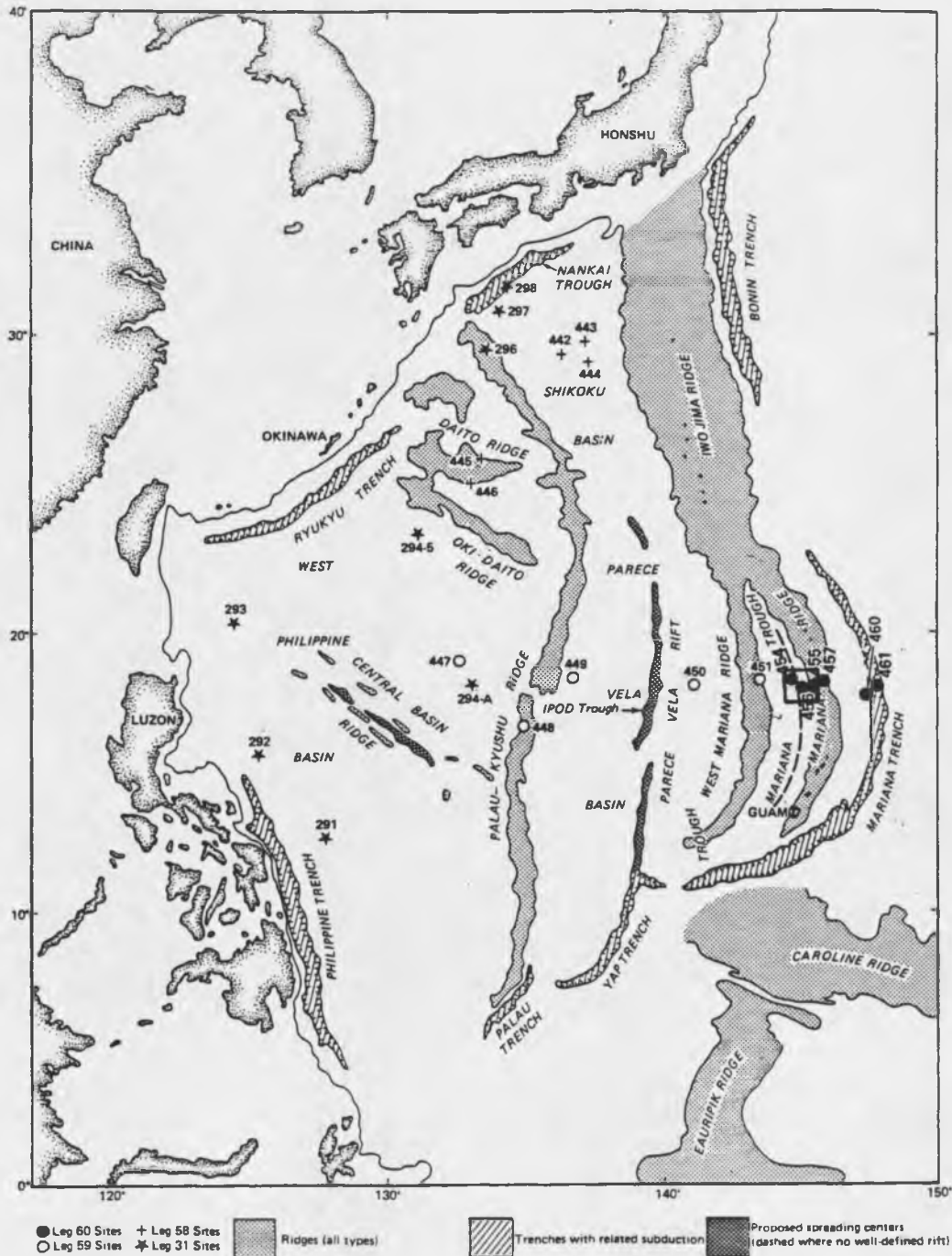


Figure 1. Map of the Western Pacific. The study area is shown in the box at right center which is enlarged in Figure 2 (Modified from Volume 60 of the Initial Reports of the Deep Sea Drilling Project (Hussong, Uyeda, et al., 1982)).

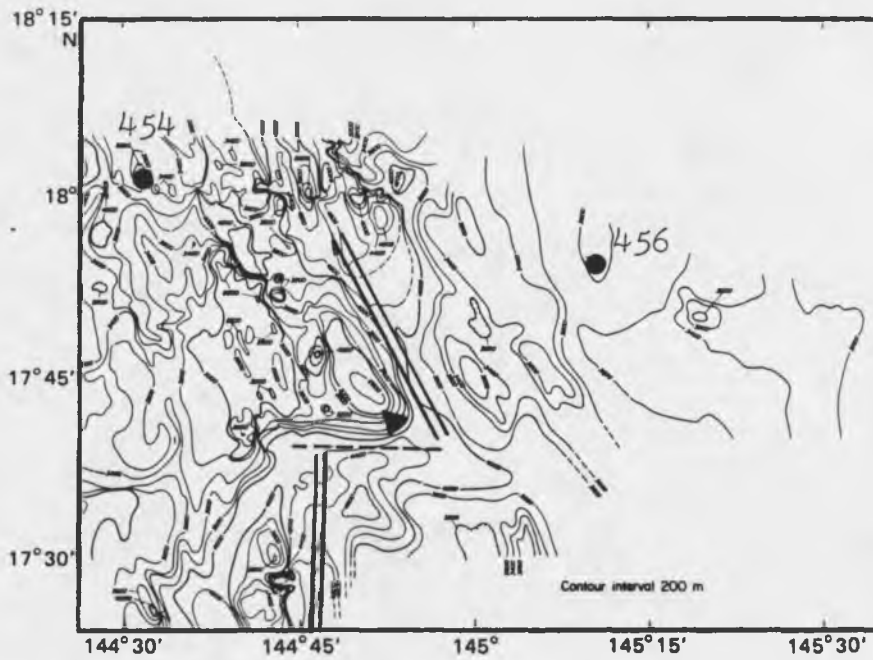


Figure 2. Bathymetry of the Mariana Trough. The dots denote the location of DSDP drilling sites 454 and 456 while the triangle shows the location of TASADAY Leg 8 Dredge 15. The twin solid lines represent the proposed spreading center for the Mariana Trough while the dashed line represents a proposed transform fault (Modified from Fryer and Hussong, 1982).

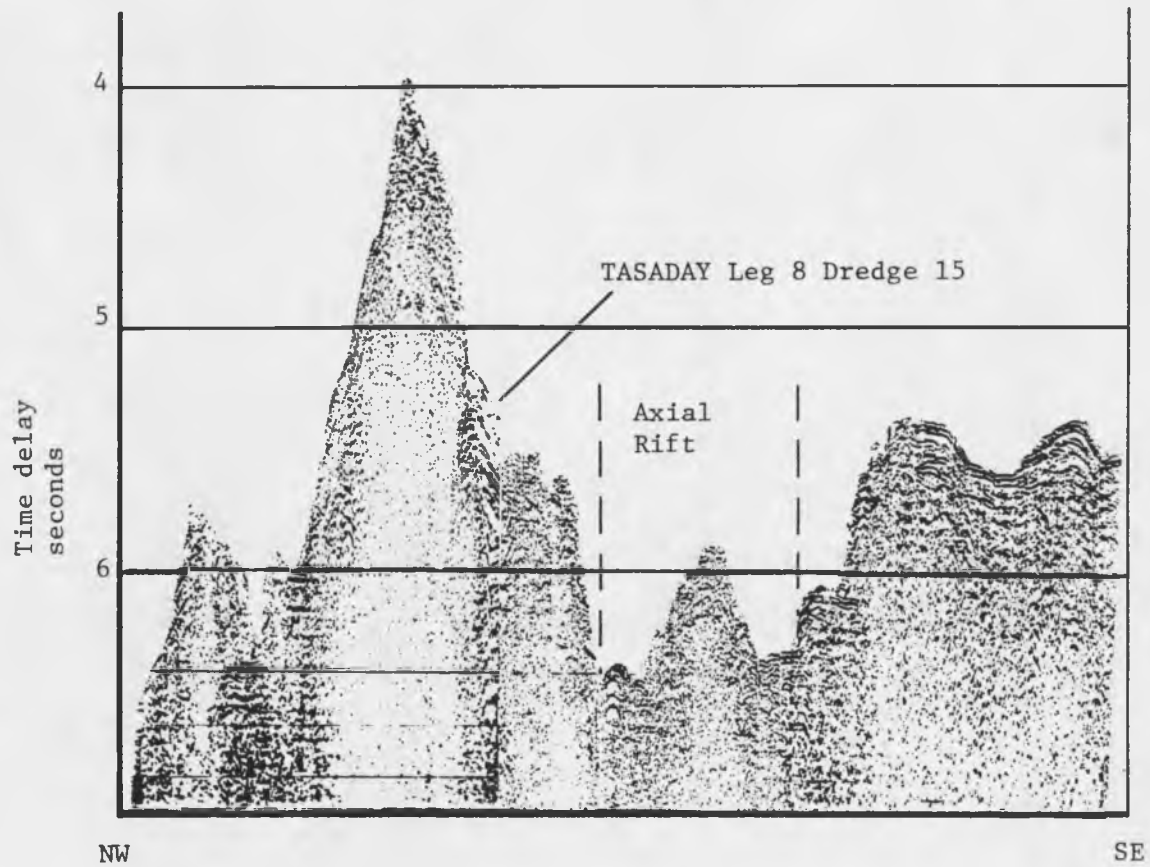


Figure 3. Seismic reflection profile from TASADAY Leg 8. Total relief is approximately 1200 meters.

GEOLOGIC SETTING

The Mariana Trough is an actively spreading back-arc basin associated with the Mariana Island Arc system. Karig's (1971) interpretation of the system's history has been corroborated by the results of DSDP Legs 31 and 59-60 (Karig, Ingle, et al., 1975; Kroenke, Scott, et al., 1980; Hussong, Uyeda, et al., 1982). According to Karig, an Eocene volcanic arc was longitudinally split in late Oligocene or early Miocene time by an extensional episode that produced a trough of new oceanic crust (Parece Vela Basin) bounded by an inactive remnant arc to the west (Palau-Kyushu Ridge) and an active volcanic arc (proto-West Mariana Ridge) to the east (Fig. 1). The process repeated itself in the Pliocene forming the inactive West Mariana Ridge and the currently active Mariana Ridge and Mariana Trough.

Geophysical and geological surveys indicate that the spreading mechanism within the Mariana Trough is similar to that at slow spreading, mid-oceanic ridges such as the Mid-Atlantic Ridge (Fryer and Hussong, 1982). The spreading center of the trough is a north-south ridge with an axial graben cross-cut by at least one ridge-ridge transform fault (Karig, 1971; Karig, Anderson and Bibee, 1978; Fryer and Hussong, 1982) (Fig. 2). Spreading is believed to be symmetric at rates estimated at 1.5 cm/yr (Bibee, Shor, and Lu, 1980) to 1.65 cm/yr

(Hussong and Fryer, 1980). Heat flow studies demonstrate that hydrothermal systems are presently active near the axis of spreading (Anderson, 1975).

ANALYTICAL METHODS

Samples of both fresh and altered basalts were chosen from among several bags of rocks brought up by the TASADAY dredge. Basalts were considered fresh if they were grey in color, lacked veins or other evidence of alteration, and had lustrous black glass along one or more surfaces. The altered basalts chosen for this study are olive green in color with dark green clay veins 1-5 mm in width and scattered sulfide grains < 1 mm in size. Some altered samples also contain quartz veins 1-2 mm wide. The presence of sulfides was considered important as an indication of the behavior of the transition metals in hydrothermal systems associated with back-arc spreading centers.

The samples were cut into slabs and examined with a binocular microscope to determine which would be used to make polished thin sections. Fresh samples were chosen if they contained both crystalline basalt and glass while altered samples were chosen if they contained abundant sulfides and clay or quartz veins. Polished thin sections were then examined with a petrographic microscope with transmitted light to determine silicate mineralogy and textures. Reflected light was used to determine sulfide mineralogy.

Carbon-coated polished sections were analyzed with an electron microprobe to yield the chemical compositions of the minerals in the

fresh and altered basalt. Small chips of the samples were fused to glass and examined with the microprobe to determine their major element chemistry (Brown, 1976). X-ray fluorescence techniques (Meijer, Anthony, and Reagan, 1982) were used to evaluate the copper content of the rocks.

Doubly polished thick sections were made of altered samples containing quartz veins. These sections were carefully inspected for fluid inclusions in the quartz. When found, inclusions were heated and frozen using the analytical methods of Roedder (1976) and a Mark III gas-flow fluid inclusion stage manufactured by SGE Inc..

Small portions of representative samples were powdered in a titanium carbide crusher and analyzed on a Siemens X-ray Diffractometer from $65-5^\circ 2\theta$. The resulting x-ray diffraction pattern was used in conjunction with petrography to characterize the mineralogy of the fresh and altered basalts.

Chips of the altered rocks were sonified in water and the resulting suspension centrifuged to isolate the $< 2\text{-}\mu\text{m}$ fraction. This fraction was slurried on to glass slides and dried to produce oriented clay mounts. These oriented sections were analyzed with a Diano 8535 X-ray diffractometer from $32-2^\circ 2\theta$ after being first air dried, then glycol saturated, and then heated to 350°C and 530°C for one hour. XRD analysis was also done on three samples, mounted on unglazed porcelain tiles, that had been saturated in MgCl_2 , dried, and coated with glycerol. The X-ray diffraction patterns acquired after these five treatments, along with the diffraction pattern of a randomly

oriented clay mount, were used to characterize the clay mineralogy of the altered basalt.

ANALYTICAL RESULTS

Fresh Basalt

The fresh pillow basalts recovered in TASADAY Dredge 15 are very similar to basalts cored in hole 454A of DSDP Leg 60 described by Sharaskin (1982), Wood et al. (1982), and Bougault et al. (1982). In hand specimen these rocks are grey, fine-grained, and olivine phyric. Vesicles up to 1 mm in diameter comprise 1-7% of the sample with the percentage increasing away from the glassy rind.

Olivine phenocrysts with an analyzed composition of Fo₈₇₋₈₈ (see Appendix A, Table 2) make up 5% of the fresh sample in thin section. Olivines are fresh and range from 0.3-1 mm in size. Chromite occurs as small inclusions within the olivine phenocrysts while small Fe-Ti oxides occur both within the phenocrysts and groundmass. The groundmass consists of very fine-grained plagioclase and augite laths and up to 30% glass. X-ray diffraction data indicate that the plagioclase is labradorite.

The major element chemistry of the basalt is given in Appendix A, Table 1. The chemistry is similar to N-type ocean ridge basalt as described by Sun, Nesbitt, and Sharaskin (1979) but it is slightly lower in Mg, possibly the result of olivine fractionation before the eruption of these particular pillow basalts.

Altered Basalt

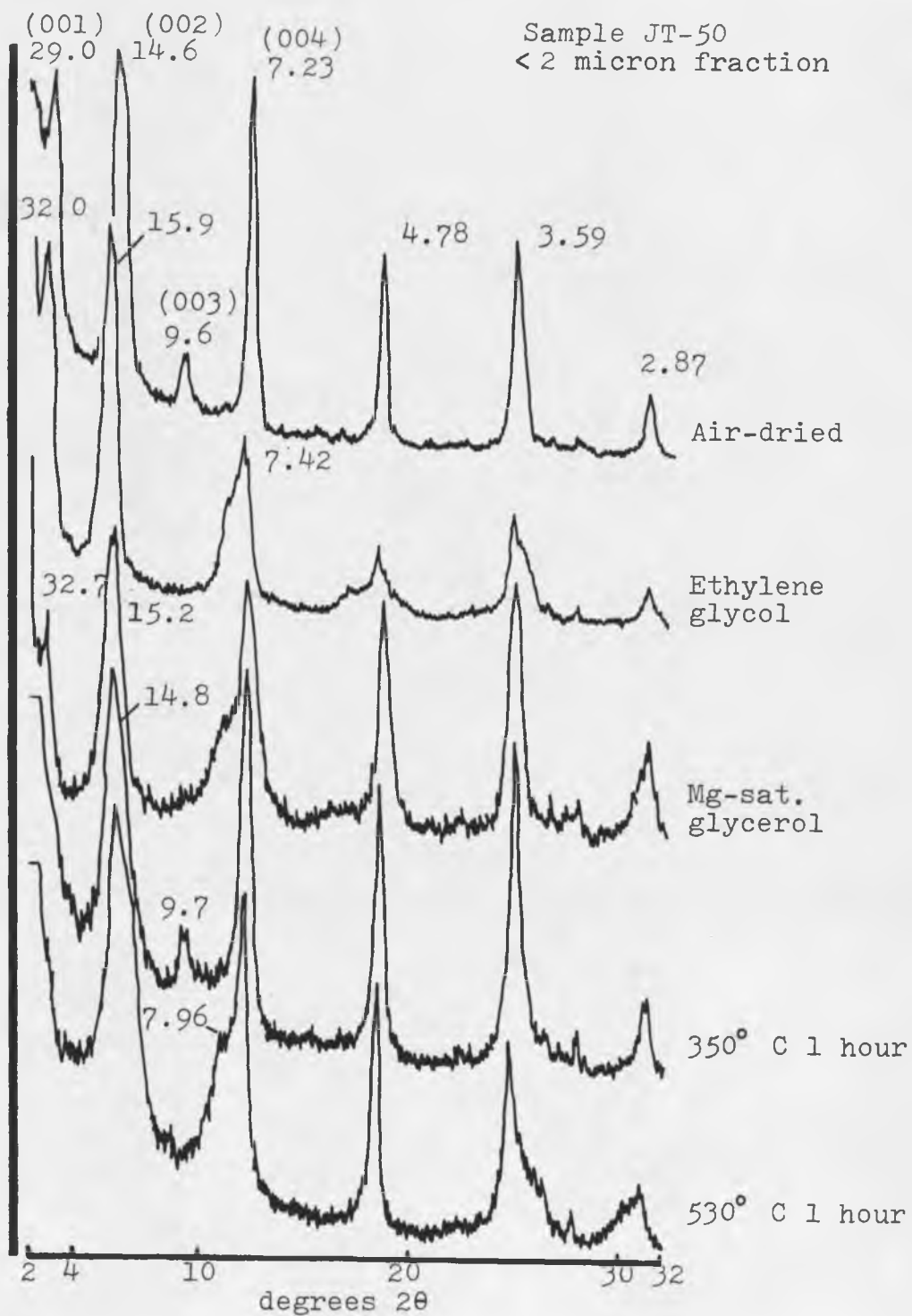
As described in the previous section, altered basalts are olive green with thin, dark green clay veins occasionally cross-cut by later, equally thin quartz veins. Quartz also replaces the clay within several of the dark green veins. Sulfides, generally less than 0.5 mm in size, are scattered within the groundmass of the rock and along the centers of the clay veins. Many sulfide grains are partially oxidized.

The dominant minerals seen in thin section are plagioclase and light yellow to green clay minerals. Plagioclase laths appear to be extensively altered and indeed have been nearly totally albitized (see Appendix A, Table 3).

Clay minerals occur in these samples as fracture and vesicle fillings and as a major portion of the groundmass, replacing glass and ferro-magnesian minerals. X-ray diffraction analysis indicates that the dominant clay mineral in these hydrothermally altered basalts is corrensite, a mixed-layer chlorite/smectite clay named for Professor C. W. Correns of Göttingen (Carroll, 1970). Minor chlorite is generally found in association with the corrensite whereas smectite is found in less altered samples.

The reflection at 29\AA in the air-dried diffractogram of Figure 4 is a superlattice peak (001) resulting from the regular interlayering of 14\AA chlorite and 15\AA smectite. When the clay is

Figure 4. X-ray powder diffraction patterns of the < 2 micron fraction of sample JT-50, a hydrothermally altered basalt (Cu K α radiation).



saturated in an ethylene glycol atmosphere, the smectite layers swell to 18\AA moving the superlattice peak to 32\AA . The Mg-saturation-glycerol treatment produces similar results. Heating to 530°C for 1 hour collapses the structure to approximately 24\AA .

Chemical compositions of clay minerals found in the altered samples are given in Appendix A, Table 4. The analyses having the highest totals from 4 different samples are shown. Weight percent totals are significantly less than 100 due to the presence of approximately 12 weight percent water and the presence of Fe_2O_3 , rather than strictly FeO as analyzed. Similar concentrations of water were found in clay minerals from altered oceanic basalts studied by Scheidegger and Stakes (1977) and Melson and Thompson (1973). Fe_2O_3 will be discussed in more detail below.

Note that the compositions are strikingly consistent though the analyses are from vesicle and fracture fillings and the groundmass from four different samples taken from the dredge haul. This consistency could be biased by two factors. One is the plucking of less resistant clays during polishing. Many rough areas were seen under high magnification on the microprobe and these areas produced unsatisfactory totals when analyzed. However, even in these areas element ratios were similar to the superior analyses. The second factor is the necessary use of a defocused electron beam to analyze the clay minerals by microprobe. This procedure can produce an average composition from finely intergrown mixtures of different clays.

A structural formula for the mixed-layer chlorite/smectite was calculated using the analysis of clay in sample JT-50 normalized to 100% (see Appendix B). The formula is based on 1/2 unit cell of chlorite and 1/2 unit cell of smectite and has 20 oxygens plus 10 (OH) or 50 equivalents. Formula A of Appendix B is the direct result of the calculations. The octahedral cation population of 9.05 is slightly higher than the ideal population of 9.00 that would occur if both the chlorite and smectite layers were perfectly trioctahedral. This discrepancy may be due to errors in the analyses or the unaccounted presence of one of the octahedral cations, such as Mg^{2+} , in the interlayer sites. The redistribution of some octahedral cations into the interlayer sites would not place the total interlayer charge outside of the 0.20-0.40 equivalents normal for these types of clays (April, 1981). Formula A is not electrically neutral because no allowances have been made for ferric iron. Oxidation of 65% of the total iron in the octahedral site will achieve electrical neutrality as shown in Formula B. This results in an Fe^{3+}/Fe^{2+} ratio of 1.89, within the range of 1.11-10.93 reported by other workers for various clays from oceanic altered basalts (Thompson, 1973; Bass, 1976). The totals of the oxide analyses reported in Appendix A, Table 4 will be increased slightly more than 1% if Fe as Fe_2O_3 is taken into consideration rather than expressing all iron as FeO.

Fine-grained quartz is present both in the groundmass and the veins of the altered basalts. The results of a fluid inclusion study of vein quartz are shown in Appendix C. Inclusions were very rare and

when found, were usually small enough to make analysis difficult. Though there were not enough temperature determinations to provide a definitive temperature history for the quartz veins, the results suggest that vein filling occurred at temperatures between 150°C and 225°C. These temperatures are corroborated by the presence of the mixed-layer clay which is also abundant in the seawater-basalt geothermal systems of Reykjanes, Iceland, at temperatures of 200-230°C (Tomasson and Kristmannsdottir, 1972).

Sulfide grains were examined in reflected light and with an electron microprobe using energy dispersive scanning. They were determined to be pyrite containing no detectable copper or zinc. No other sulfide minerals were found. Pyrite was more common and better preserved when found in association with the corrensite veins. When found in quartz veins, pyrite usually showed textural evidence of dissolution. As mentioned above, nearly all the sulfides found within the samples showed evidence of oxidation.

The major element chemistry of an altered specimen is given in Appendix A, Table 1 where it is compared to the chemistry of the fresh basalt. The most notable changes are in the abundance of Mg and Ca. The Mg/Ca ratio changes nearly two orders of magnitude from 0.56 for fresh basalt to 44 for altered basalt. The alkali metals increase slightly while the transition metals Mn, Fe, and Cu were decreased as a result of alteration. There is also a slight drop in the SiO₂

percentage with an accompanying relative increase in the amount of Al_2O_3 . An explanation for these changes is discussed in the next section.

DISCUSSION

Experimental basalt-seawater interaction studies undertaken by various workers have demonstrated that the water/rock mass ratio is the most important factor in determining the stable mineral assemblage and coexisting solution composition resulting from the hydrothermal alteration of basalts by seawater. Mottl and Seyfried (1980) have made important distinctions between seawater-dominated and rock-dominated conditions within oceanic hydrothermal systems. Seawater-dominated conditions produce an acidic solution rich in transition metals, Mg^{2+} , and $SiO_2(aq)$ and in equilibrium with smectite, mixed-layer clay, or chlorite (depending on the temperature) and usually minor amounts of quartz, hematite, and anhydrite. Rock-dominated conditions produce a neutral or slightly alkaline solution that is depleted in metals and in equilibrium with a more complicated assemblage of minerals including zeolites, albite, epidote, prehnite, tremolite-actinolite, sphene, pyrite, and the previously mentioned clays (Mottl and Seyfried, 1980).

In their study of the mineralogic and stable isotope composition of altered oceanic rocks, Stakes and O'Neil (1982) make the following distinctions between saponite-rich pillow breccias (SPB), which form under seawater-dominant conditions, and greenstones, which form under rock-dominant conditions.

- (1) The only layered silicate found in greenstones is chlorite while Fe-rich saponite is found in the SPB.
- (2) Plagioclase is albitized in the greenstones but not in the SPB.
- (3) Pyroxene is unaltered in greenstones but generally replaced by saponite in the SPB.

Because the specimens examined in this study contain mixed-layer chlorite/smectite, albite, and altered pyroxene, I believe that they have experienced both styles of alteration. I will show below how low temperature, seawater-dominated conditions followed by higher temperature, rock-dominated conditions can produce the alteration assemblage found in these samples.

Seawater-dominated conditions are those having water/rock mass ratios greater than 50±5:1 (Mottl and Seyfried, 1980). In experimental studies, basalt glass quickly reacts with seawater to produce smectite at temperatures lower than 200°C and mixed-layer chlorite/smectite at higher temperatures (Bischoff and Dickson, 1975; Seyfried and Bischoff, 1979; Mottl and Seyfried, 1980). As part of the reaction, Mg^{2+} and OH^- are taken from seawater into the clay structure resulting in a rise in the H^+ concentration in seawater. If excess Mg^{2+} is present, as it would be at high water/rock ratios, H^+ is produced faster than it is consumed by silicate hydrolysis reactions and the pH of the reacting solution quickly decreases (Bischoff and Dickson, 1975).

At low water/rock ratios, Mg^{2+} becomes depleted in the solution by reaction with basalt glass to produce clay. Silicate hydrolysis consumes H^+ faster than it is being produced and the pH rises after an initial drop. The pH then levels off at near neutrality (Bischoff and Dickson, 1975). The same reactions occur when diabase is used in place of glass, except that the process is slower, especially at lower temperatures (Seyfried and Bischoff, 1979).

Wolery and Sleep (1976) compared the seawater flux estimated from convective heat loss at spreading centers to the amount of new crust produced there and arrived at water to rock mass ratios for the global system of up to 20:1. Thus it seems likely that localized water/rock ratios of 50:1 or higher are possible in basalt having open fractures and vesicles. In the case of the TASADAY samples, at least 50 grams of seawater are necessary to provide the magnesium added to one gram of fresh basalt during alteration.

The first phase of alteration of the basalts studied here occurred in seawater-dominant conditions. A preliminary XRD analysis of less altered samples collected from the same location, but which contain no sulfides or quartz, indicates that Mg-rich smectite (saponite) is the major alteration phase replacing olivine and glass. Plagioclase remains unaltered as does pyroxene. The persistence of pyroxene in seawater-dominant conditions, contrary to the findings of Stakes and O'Neil (1982), may be due to the coarser crystallinity of these rocks as compared to the breccias with which

they worked or to a difference in water/rock ratios between the samples.

The acidic solution produced under these conditions leached Na^+ , K^+ , Ca^{2+} , and transition metals from the rock while mobilizing Al^{3+} so it was available to the clays filling fractures and vesicles. Alteration took place under essentially non-oxidative conditions (Bass, 1976; Stakes and O'Neil, 1982) though Bass (1976) points out that this terminology is somewhat misleading since some oxidation of iron has occurred.

Light stable isotope study results show that saponite-rich pillow breccias form at temperatures of 130-170°C (Stakes and O'Neil, 1982). Saponites from the Mariana Trough probably formed in this temperature range. They certainly formed at temperatures below 200°C, the highest temperature at which smectite is stable in experimental studies and in the Reykjanes geothermal system (Tomasson and Kristmannsdottir, 1972). These moderate temperatures are partly responsible for the persistence of plagioclase and in some cases, pyroxene, in the less altered samples.

As smectite filled fractures and vesicles, permeability, and consequently the water/rock ratio, decreased and the alteration conditions became rock-dominant. Albite, pyrite, mixed-layer chlorite/smectite, and finally quartz became the stable secondary phases. This assemblage is discussed below.

The samples containing quartz veins cross-cutting clay veins have fluid inclusion temperatures in the quartz that are generally

higher than the upper stability limit of smectite. The dominant mineral in the clay veins is mixed-layer chlorite/smectite. This observation seems to indicate that temperatures rose prior to or as a result of the introduction of the quartz veins producing chlorite/smectite from the aggradation of smectite in a Mg-rich environment. If the clay veins had formed initially at a higher temperature than the subsequent fluid inclusions, chlorite would likely have been the original stable layered silicate. Also, chlorite would have had to degrade by loss of alternate $Mg(OH)_2$ interlayers to form corrensite. Chlorite can degrade under weathering or oxidizing conditions to form mixed-layer minerals, but this process apparently results in the production of interlayered chlorite/vermiculite rather than chlorite/smectite (April, 1980 and references cited). Thus, temperature likely did increase from the 130-170°C range up to 200-230°C. Possible causes for this temperature increase will be discussed further in the following section.

Experimental evidence indicates that Na is leached from basalts at high water/rock ratios but enriched at low water/rock ratios (Seyfried and Bischoff, 1979; 1981; Mottl and Holland, 1978). Mottl and Holland (1978) believe that Na absorption occurs through slow Na^+ for Ca^{2+} exchange in plagioclase and some crystallization of albite from the fluid phase. This explains the nearly total conversion of labradorite to albite in most of the highly altered samples. The addition of Na^+ in this phase of the alteration results

in a net Na^+ gain of approximately 10% over the original amount in the basalt (see Appendix A, Table 1).

Low water/rock mass ratios also make conditions favorable for the precipitation of sulfides (Mottl and Seyfried, 1980; Seyfried and Bischoff, 1981). Sulfides are found in the interiors of the TASADAY samples and as late fillings in the centers of the chlorite/smectite veins. These are areas where rock-dominated conditions are likely to have existed. Only pyrite is found in these samples since the temperature was too low for the formation of chalcopyrite, another sulfide commonly found in altered basalts. Chalcopyrite is found in experimental seawater-basalt studies at 300°C (Mottl, Holland, and Corr, 1979) and 400°C (Hajash, 1975) and in quartz-pyrite-chalcopyrite veins in the Troodos Massif at temperatures of 300°C and up (Spooner and Bray, 1977). Mark Reagan (Univ. of Arizona, Dept. of Geosciences, personal communication, 1982) found chalcopyrite in quartz-epidote veins in rocks dredged from the Mariana Trough that had fluid inclusion homogenization temperatures of 300-312°C.

Reduced sulfur for the sulfides can be obtained directly from the basalt or from the reduction of seawater sulfate. Mottl et al (1979) found that the amount of sulfate reduced would only have to be 5-10% of the total at 300°C and that interaction of basalt with a sulfate free solution at 300°C would also produce sulfides, but less of them. A seawater solution could indeed be sulfate-free at temperatures over 150°C because of the precipitation of anhydrite (Bischoff and Seyfried, 1978). These findings seem to indicate that

reduced sulfur in the sulfides of these samples was provided mainly by the basalt.

Anhydrite, or rather the lack of it, in altered oceanic basalts has been a mystery for several years. All experimental studies indicate that anhydrite should form as soon as the temperature of the seawater exceeds 150°C. Yet, until recently, no trace of anhydrite was found in naturally occurring hydrothermally altered basalts. Anhydrite was recovered in DSDP Leg 83 cores but only from rocks whose temperature is presently 150°C or above. Apparently, anhydrite is forming in oceanic hydrothermal systems but is being redissolved upon cooling of the rocks.

Quartz is the last major alteration phase to have formed in the TASADAY dredge samples. Other workers have found that quartz is rare in smectite-rich altered basalts but common in chlorite- and epidote-rich greenstones where it occurs as a late phase (Bass, 1976; Humphris and Thompson, 1978; Stakes and O'Neil, 1982). Experimental studies at 200°C show that aqueous silica levels exceed quartz and approach amorphous silica saturation during interaction between seawater and basalt but no quartz is formed (Bischoff and Dickson, 1975; Mottl and Holland, 1978). $\text{SiO}_2(\text{aq})$ concentration may be controlled by another silicate, such as corrensite, or kinetic barriers may prohibit the crystallization of quartz.

In the Mariana Trough samples, quartz appears mainly in veins which cross-cut, intrude, and sometimes replace clay veins. The rock was apparently fractured and some of the clay veins were reopened by a

later tectonic event. These fractures allowed the introduction of a highly-reacted silica-rich fluid. Judging from its higher temperature, this fluid probably originated deeper within the system. By this stage, the rock was extensively altered so nearly all the available Al was tied up in stable phases. No new aluminosilicates crystallized and quartz became the stable silica phase. Cations within this secondary fluid were likely absorbed into the clay interlayers already present.

The changes in whole rock chemistry from fresh to altered basalt, shown in Appendix A, Table 1 and described briefly in Chapter 5, are a result of alteration under both seawater- and rock-dominated conditions. Though the fresh basalt analyzed here is not necessarily the exact precursor of the altered basalt, it has a chemistry similar to many other basalts dredged and cored from the Mariana Trough and is certainly representative of fresh oceanic crustal material.

Seawater-dominant conditions altered the basalt at moderate temperatures and low pH. The transition metals Mn and Cu were moderately depleted while Fe abundances remained nearly stable due to inclusion of Fe in stable clay minerals. Ca was extensively leached from basalt glass and replaced by Mg in the formation of Mg-rich clays. Al was locally mobilized such that it was available to clays that were filling fractures and vesicles. Na, K, and Si were probably depleted during this alteration phase but were replaced later as discussed below.

Higher temperatures and more alkaline conditions prevailed during the rock-dominated alteration phase. Na and Si were resorbed and more Ca lost from the original basalt as albite replaced labradorite. More Mg was absorbed into clay minerals as chlorite, the stable layered silicate at higher temperatures, began to replace smectite. K was absorbed into clay interlayers and may have become concentrated in small amounts of other silicate phases. One poorly crystallized aluminosilicate was analyzed from sample JT-50 that contained 8-10 weight percent K. Titanium abundances remained stable throughout the alteration process. Ti occurs in oxides in the fresh basalt and in very small grains of sphene in the altered basalt.

GEOLOGIC IMPLICATIONS

The mineralogical and chemical changes that occurred during alteration of basalt from the Mariana Trough have been interpreted as having evolved from seawater-dominated followed by rock-dominated conditions with increasing temperature and a secondary fracturing episode. Now the geological events necessary to produce these conditions must be evaluated with respect to the geology normally associated with a slow-spreading center.

As mentioned in the Discussion section, water/rock mass ratios approaching seawater-dominant conditions are possible in fresh basalt having extensive open fractures. Overall ratios up to 20:1 have been calculated (Wolery and Sleep, 1976; Humphris and Thompson, 1978), so an effective ratio of 50:1 or higher is not unlikely along a fracture boundary. Fracturing should be especially prevalent in a region characterized by extensive normal faulting such as a slow-spreading center. A decrease in water/rock ratios down to rock-dominated conditions is to be expected when fracture filling by alteration phases is taken into account.

The increase in temperature which occurred during the alteration of these samples could be the result of several different processes. One interpretation relies entirely on the decreased seawater circulation resulting from the filling of fractures by

smectite. In the region of high heat flow near a spreading center, seawater circulation generally cools the crust and depresses the geothermal gradient. Decreased circulation would then allow an increase in temperature. Following the temperature increase, the rock was fractured, probably by a tectonic event and the fractures filled by quartz crystallizing from locally derived, highly-reacted fluids at very low water/rock ratios.

Another interpretation is that the secondary fracturing allowed the introduction of higher temperature fluids from deeper in the system. The quartz then crystallized from these fluids and filled the fractures. A combination of these two processes is a third possibility.

A final possibility for the late temperature increase is the capping of the system by sedimentation and the consequent trapping of heat within the crust. This event is unlikely for these samples because of the relief of the study area and its proximity to the axis of spreading, but such a situation is found elsewhere in the Mariana Trough (Natland and Hekinian, 1982). A higher sedimentation rate is one of the few factors that distinguish back-arc from mid-ocean spreading centers.

ECONOMIC IMPLICATIONS

The rocks examined in this study have no current intrinsic economic value because they contain no conventional ore minerals. However, the study of these samples and relevant literature provides information which leads to significant conclusions regarding the processes which may have produced economically viable ore deposits.

Ophiolitic massive sulfide deposits are believed to have been formed directly on the ocean bottom by mixing of metal-rich fluids derived from basalt alteration with cold oceanic waters (Edmond et al, 1979). Extensive leaching of basalt is necessary as is rapid transport of the metals to the water-rock interface to minimize precipitation within the geothermal system.

Leaching of transition metals from basalt is most efficient at moderate temperatures and high water/rock mass ratios or high temperatures ($\geq 400^{\circ}\text{C}$) and low water/rock ratios (Seyfried and Bischoff, 1981). Only the former conditions would allow for rapid transport of the minerals out of the crust, because of higher fluid flow rates. Thus the most extensive leaching probably occurs after the solidification of the basalt while fractures are still open and permeability is high.

Associated with the massive sulfide deposits of Troodos are mineralized stockworks (Contantinou and Govett, 1973). The stockwork

vein mineral assemblage is dominantly quartz-pyrite with lesser amounts of chalcopyrite, chlorite, and hematite. Fluid inclusions within the vein quartz have homogenization temperatures generally between 300 and 325° C (Spooner and Bray, 1977). This assemblage was produced at this temperature in experimental studies at low water/rock ratios (Mottl et al, 1979). A similar assemblage was also produced at high water/rock ratios, but precipitation of sulfides did not become significant until the temperature of the fluid dropped below 200°C (Seyfried, Mottl, and Janecky, 1979). Thus it seems that while the massive ore most likely formed under seawater-dominant conditions, the associated stockwork was mineralized during rock-dominant conditions. The stockwork probably served as a feeder for the massive sulfide deposits forming on the ocean floor but only became mineralized itself as circulation slowed within the system and water/rock ratios decreased.

The TASADAY samples would correlate best with the stockwork portion of a massive sulfide system. Copper was leached from the samples during the seawater-dominant alteration phase but temperatures were not high enough during the rock-dominated phase for chalcopyrite to be stable. Quartz was the last mineral phase to form in both the Troodos and TASADAY samples and in both cases it frequently corroded earlier formed sulfides.

CONCLUSIONS

(1) The TASADAY Leg 8 Dredge 15 basalt samples were altered in seawater-dominant followed by rock-dominant conditions.

(2) Temperature increased during alteration.

(3) There appear to be no significant mineralogical or chemical differences between these back-arc samples and altered basalts collected from other oceanic sites.

(4) Mixed-layer chlorite/smectite appears to form by the aggradation of smectite in a Mg-rich environment.

(5) The samples analyzed here have no economic potential but rather were a source of copper which was apparently distributed elsewhere in the system.

(6) Massive sulfide deposits may be formed under seawater-dominant conditions while their stockworks are formed under rock-dominant conditions.

APPENDIX A: Electron Microprobe Analyses

Table 1. Major Element Chemistry of Fresh and Altered Basalt

oxides	weight%	weight%	Gains and losses	
			weight%	percentage of original
SiO ₂	50.41	46.48	-3.93	-7.80%
TiO ₂	1.08	0.99	-0.09	-8.3%
Al ₂ O ₃	15.28	19.11	+3.83	+25.07%
FeO*	9.47	9.22	-0.25	-2.6%
MnO	0.25	0.10	-0.15	-60.0%
MgO	6.53	17.40	+10.87	+166.0%
CaO	11.59	0.40	-11.19	-97.0%
Na ₂ O	2.84	3.11	+0.27	+9.5%
K ₂ O	0.52	0.65	+0.13	+25.0%
P ₂ O ₅	0.06	0.08	+0.02	+33.0%
Total of microprobe analyses	98.03	97.54		
%weight lost during fusion	2.84	9.31		
Cu(ppm)	69.4	40.3	-29.1ppm	42.0%

*Total Fe reported as FeO.

Table 2. Olivine Analyses from Fresh Basalt (Sample JT-1)

Oxide	weight %	weight %
SiO ₂	39.55	39.98
TiO ₂	-	0.07
Al ₂ O ₃	0.07	0.07
Cr ₂ O ₃	-	0.06
FeO*	11.66	12.06
MnO	0.18	0.22
MgO	47.57	47.44
CaO	0.26	0.25
Na ₂ O	0.02	-
K ₂ O	0.02	-
Total	99.33	100.15
Composition	Fe ₈₈	Fe ₈₈

*Total Fe reported as FeO.

Table 3. Feldspar Analyses from Altered Basalt.

Sample	JT-30-1	JT-50-2	JT-50-2	JT-60-3	JT-70-1	JT-70-1
oxide	weight%	weight%	weight%	weight%	weight%	weight%
SiO ₂	67.39	67.12	65.36	67.27	67.64	67.05
TiO ₂	-	-	-	-	0.07	0.02
Al ₂ O ₃	20.45	20.69	20.93	20.46	20.65	20.63
Cr ₂ O ₃	-	-	0.05	0.01	-	-
FeO*	0.07	0.18	0.35	0.10	0.12	0.27
MnO	0.04	-	-	-	-	0.01
MgO	0.03	0.01	0.44	-	0.03	0.38
CaO	0.94	1.01	1.04	0.71	0.58	1.04
Na ₁ O	10.75	10.80	11.03	10.87	11.18	10.54
K ₂ O	0.06	0.08	0.07	0.10	0.05	0.09
Total	99.73	99.89	99.27	99.52	100.32	100.03
Composition						
	Ab ₉₅	Ab ₉₅	Ab ₉₅	Ab ₉₆	Ab ₉₇	Ab ₉₄

*Total Fe reported as FeO.

Table 4. Layered Silicate Analyses from Altered Basalts. A defocused electron beam was used in these analyses. H_2O and Fe_2O_3 content are discussed in the text.

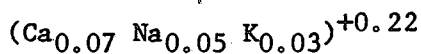
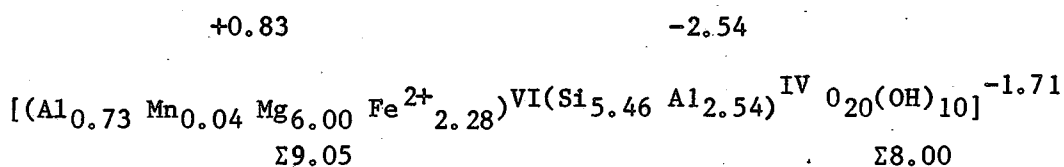
Sample oxide	JT-30-1 weight%	JT-50-2 weight%	JT-50-2 weight%	JT-60-3 weight%	JT-70-1 weight%	JT-70-1 weight%
SiO_2	32.43	31.47	30.75	31.93	31.75	31.43
TiO_2	0.03	-	0.06	-	-	-
Al_2O_3	15.90	16.00	15.94	15.99	15.87	15.66
Cr_2O_3	0.04	0.06	0.01	-	0.06	0.03
FeO^*	15.43	15.69	15.61	17.02	17.55	17.31
MnO	0.24	0.26	0.25	0.27	0.27	0.29
MgO	24.03	23.32	23.34	22.90	22.90	22.84
CaO	0.27	0.36	0.36	0.21	0.36	0.48
Na_2O	0.19	0.14	0.11	0.10	0.04	0.09
K_2O	0.21	0.15	0.12	0.12	0.09	0.11
Total	88.77	87.45	86.55	88.54	88.89	88.24

*Total Fe reported as FeO .

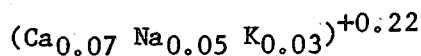
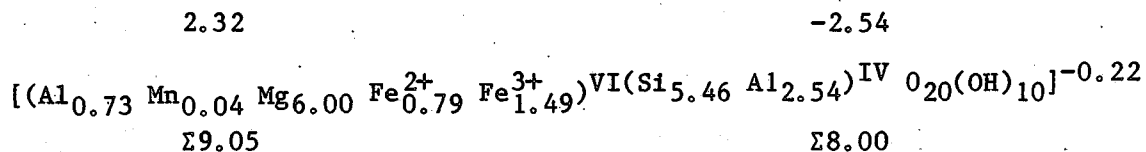
APPENDIX B: Calculation of the structural formula for a mixed-layer chlorite/smectite (regularly interstratified) from sample JT-50-2.

oxide	weight% (normaliz- ed to 100)	equiva- lent weight	gram-equiva- lents of cations	cation valence per unit cell	cations per unit cell
SiO ₂	35.97	15.01	2.40	21.82	5.46
Al ₂ O ₃	18.30	16.99	1.08	9.82	3.27
FeO	17.94	35.93	0.50	4.55	2.28
MnO	0.30	35.47	0.0085	0.08	0.04
MgO	26.67	20.16	1.32	12.00	6.00
CaO	0.41	28.04	0.015	0.14	0.07
Na ₂ O	0.16	30.99	0.0052	0.05	0.05
K ₂ O	0.17	47.10	0.0036	0.03	0.03

A. Uncorrected for Fe³⁺



B. Corrected for 5% Fe as Fe³⁺.



See text for discussion of equations A and B.

APPENDIX C: Fluid Inclusion Study Results

Sample #	Homogenization Temperature (°C)	Freezing Point (°C)	Sample Description
JT-50-2a	215	-	15mm triangular inclusion- probably primary
JT-70-1a	225	> -5	25mm polygonal inclusion - probably primary
JT-70-1b	146	-	15mm rectangular inclusion - secondary (?)
JT-70-1c	173	-	37mm elongate-possibly between two crystals-primary

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