

# Fluid-rock interaction modeling of epidotization in the plagiogranites of the Troodos ophiolite, Cyprus

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## INTRODUCTION

Theoretical models of cooling lithosphere predict that at least one-third of the heat at mid-ocean ridges must be removed by non-conductive means, presumably through hydrothermal circulation and subsequent venting on the seafloor (Haymon and Macdonald, 1985). In recent years, numerous high-temperature hydrothermal vents have been located (Haymon and Macdonald, 1985). The heat source thought to be driving hydrothermal activity is the upwelling of magma beneath the spreading axis. Seismic studies confirm the existence of such crustal magma chambers beneath fast spreading centers (Hale et al, 1982).

Temperature, flow rates, and chemistry of vent fluid compositions have been documented for modern vents, however, the chemical evolution of seawater to vent fluids is more difficult to define. The generally accepted model of hydrothermal systems is that cold seawater enters the newly solidified crust in the area surrounding the spreading axis, descending as deep as the roof of the underlying magma chamber (Sleep, 1984). On the way, this seawater reacts with the oceanic crust, losing some constituents and gaining others. When the seawater is heated to near its critical temperature, it becomes extremely buoyant and escapes to the seafloor any way possible. In the process, it may migrate along faults and fissures either parallel or perpendicular to the axis before discharging.

There are several types of vents, each defined by their fluid and chimney chemistries and fluid temperatures. High-temperature black smoker venting is the type of modern venting thought to be represented in the geologic record as massive sulfide mines (Haymon and Macdonald, 1985). These vents are characterized by jets of fluid at temperatures ranging from 300 to near 400° C discharging rapidly from copper sulfide-rich chimneys. The clear fluid is almost instantaneously blackened by the precipitation of fine grained sulfide mineral particles upon mixing with cold seawater.

The geologic record exposed in ophiolites like Troodos in Cyprus provide some clues regarding the chemical processes at work in hydrothermal systems. For example, epidiosites are quartz- and epidote-rich rocks which are thought to represent the reaction zones in which ocean crust reacted with circulating, seawater-derived hydrothermal fluid to form the metal-rich fluids responsible for the massive sulfide deposits found in Troodos (Schiffman et al, 1987, Richardson et al, 1987). The high variance mineral assemblages, pervasive alteration, and recrystallized textures suggest epidiosites represent highly permeable zones of focused and continuous upflow (Schiffman et al, 1987). Epidotization in the sheeted dikes of the Troodos ophiolite in Cyprus reveal the plumbing system for black smokers venting on the Tethyan seafloor during the Cretaceous.

Although epidiosites are prominent in the sheeted dikes, epidotization is also evident in plagiogranites (leucocratic intrusive bodies of unknown origin) found between the dikes and gabbros. Plagiogranites are intrusive bodies of questionable origin found at the base of the sheeted dike complex in Troodos. Estimates of primary plagiogranite composition consist of primarily quartz and sodic-plagioclase with varying amounts of hornblende. Nearly all plagiogranites in the Solea graben are moderately to heavily altered. Alteration products included chlorite, epidote, secondary quartz and sphene (Twining, this volume). Although epidotization in the sheeted dikes has been well-defined (Richardson et al, 1987; Bettison-Varga et al, 1995), the origin of hydrothermal fluids in the plagiogranites has not been considered. Epidiosite-forming fluids may have been either deuteritic fluids exsolving off the underlying magma chamber or modified seawater in a continuation of the system active in the sheeted dikes. The results of some laboratory-based fluid-rock experiments suggest the fluid responsible for epidiosite alteration was a seawater or slightly modified seawater composition (Bischoff and Rosenbauer, 1987; Seyfried and Bischoff, 1981). Previous geochemical modeling of epidiosites in dikes suggests that epidiosite alteration may result from reaction of modified seawater and a greenschist facies dike composition. This study investigates the fluid-rock interactions in plagiogranites in a similar manner.

Modeling the chemical mass balance of hydrothermal systems allows insight into understanding water-rock interaction in submarine hydrothermal environments. It is not possible with current technologies to observe directly the processes of fluid-rock interaction within hydrothermal systems. Laboratory experiments can determine with significant accuracy the mineralogical and chemical results of

reacting specific rock and fluid compositions. Modeling allows for theoretical experiments which may not be practical in a laboratory setting, but which help identify such subsurface processes. In this study I used the computer modeling programs The Geochemist's Workbench (GWB) (Craig Bethke, University of Illinois) and EQ3/6 (Thomas Wolery, LLNL) to identify possible initial fluid and rock compositions present in the formation of epidote in the plagiogranites of the Solea graben of Troodos.

### GEOCHEMICAL MODELING

Both GWB and EQ3/6 employ various thermodynamic databases created from published experimental data to simulate the solution equilibrium steps of water-rock interaction. The capabilities and assumptions of each program are similar although the formatting of experiments is different, as each was written for a different operating system. Considering the fewer limitations and greater options of EQ3/6 over GWB, only the methods and results of EQ3/6 will be presented here. The program EQ3 determines the aqueous species distribution of the given input fluid, which then becomes the initial system (fluid composition) in the program EQ6. EQ6 then simulates reactions by titrating the specified reactant minerals by volume percent into the fluid. What intuitively describes the interactions in a hydrothermal system, in which fluid is circulating and reacting the rock, is the reverse of the approach of the program, in which rock is added to the fluid incrementally. The program begins adding reactant to the system and the reaction progresses until the entire new system has reached equilibrium. Therefore, it is possible to specify the reaction step size, and the output provides documentation of the behavior of both fluid and rock at each reaction step.

In addition to specifying the concentrations of fluid and rock components, most other parameters for this hypothetical system can be directly or indirectly controlled. For example, temperature, pH, gas fugacities, solid solution, and grain size are direct input parameters. There are options for swapping other gaseous phases for aqueous phases in the basis ( a list of available minerals, aqueous and gaseous species), for varying temperature along the reaction path, and for creating a closed or a flow-through system.

The necessary simplifications of modeling introduce limitations and assumptions. One of the limitations in this study is the pressure of the reactions, which can not be independently defined in the program. Each of the thermodynamic databases was formulated based on laboratory experiments of each species identified in the basis at various pressures and a range of temperatures, and according to a different thermodynamic model (i.e. Debye-Huckel, Harvey-Moller-Weare, Pitzer). Therefore, the pressure is predetermined by the database used. There are limited options for pressure-correcting the databases (due to incomplete data on the behavior of phases at higher pressures), but those were beyond the scope of this project. Such corrections should be pursued in further work on this type of deep-seated hydrothermal system.

### RESULTS AND DISCUSSION

All three fluid compositions used in this study are taken from published laboratory experimental data, specifically 1) unmodified seawater (Von Damm et al, 1985; Bischoff and Rosenbauer, 1987), 2) seawater modified by Juan de Fuca basalt (Seyfried and Bischoff, 1981), and 3) vent fluid compositions from the East Pacific Rise (Von Damm et al, 1985) (Figure 1). Plagiogranite compositions come from the geochemical results of Kim Twining and Shannon Hayes, who both participated in the Keck program. As all plagiogranite samples from Troodos (even those from the CY-4 drill core) were moderately to heavily altered, the primary plagiogranite composition was estimated as accurately as possible. Plagiogranite compositions fall into two categories, quartz-rich granitoids and tonalites (Figure 1). Temperature for reactions with plagiogranite were set at 300°C, based on the temperatures from fluid inclusions within the epidote of plagiogranites which range between 284 and 312° C (Hayes, this volume). The pressure set by the chosen database was at most 85.8 bars, much lower than the theoretical pressure of 500 bars expected at the base of the sheeted dikes.

Runs were formatted with the suppression of certain unrealistic minerals. The program uses the database to determine which phases would be the most stable, without consideration of the environment of formation as determined from field observation. It is left to the user to limit the product assemblage through suppression of improbable phases in the given context.

Reported here are results from three data runs, each using the same average quartz-rich granitoid plagiogranite composition for comparison, and sequentially seawater, modified seawater, and East Pacific Rise vent fluid. Product minerals for reaction with seawater include both andradite and grossular, chalcocite, copper, cuprite, prehnite, sphalerite, and tremolite (Figure 2A). This reaction does not create an epidote + quartz + chlorite assemblage. This verifies the obvious, that seawater penetrating oceanic crust must

undergo chemical evolution before it will create an epidosite alteration assemblage in plagiogranites at 300°C.

Product minerals for the reaction with modified seawater include low albite, epidote, hematite, magnetite, pyrophyllite, quartz, talc, and wairakite (Figure 2B). Notice that quartz, albite, and magnetite do not fluctuate, indicating they are in equilibrium with the fluid. This reaction creates an epidosite-like assemblage. Epidote and quartz are present, along with excess reactant minerals (albite, magnetite, and paragonite). This is similar to the results found by the fluid-rock interaction modeling experiments in the sheeted dikes (Bettison-Varga et al, 1995).

Product minerals for reaction with East Pacific Rise vent fluid include low albite, chalcocite, copper, epidote, hematite, magnetite, pyrophyllite, quartz, sphalerite, talc, and wairakite (Figure 2C). Again quartz and magnetite are in equilibrium since they are excess reactants. These results are interesting in light of some conclusions drawn by other studies, which claim that the hydrothermal fluids responsible for black smoker vents (and supposedly also epidosite-forming) are formed at depth in the system and are relatively unchanged during their ascent and discharge on the seafloor (Seyfried and Bischoff, 1981). If this were the case, it would be expected that the fluid compositions venting in black smokers today would also be producing epidosite alteration at depth. The findings in this study appear to contradict that, and thus do not support the claims of these other studies.

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	modified seawater	seawater (ppm)	EPR vent fluid
Na+	450	432	463
K+	11.43	23.2	9.8
Ca++	29.14	15.6	10.2
Mg++	.493	.004	52.6
Cl-	525	489	540
SiO2(aq)	9.92	17.6	.18
Fe++	.041	1.66	<.001
Al+++	.01	.015	<.001
Zn++	.001	.106	.01
Mn++	.095	.96	<.001
SO4-	.739	8.63	27.9
Cu+	0	.035	.007
pH	4.8	4.47	7.8
log f O2(g)	-32.41	-29.8	-1.24

	quartz-rich granitoid	tonalite (%)
quartz	61	50
albite low	23	30
pargasite	4	8
magnetite	3	2

Figure 1: Fluid compositions and plagiogranite compositions used as input; modified seawater composition from Seyfried and Bischoff, 1981; seawater composition from Von Damm et al, 1985; Ocean Bottom Seismograph vent, East Pacific Rise (Von Damm et al, 1985); plagiogranite compositions from Kim Twining (this volume).

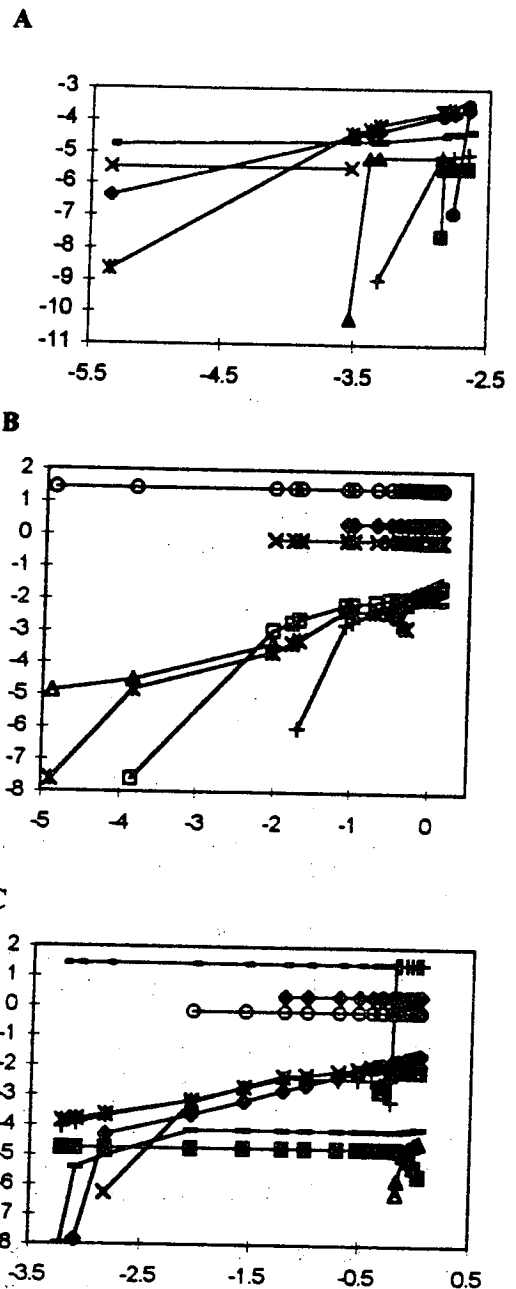
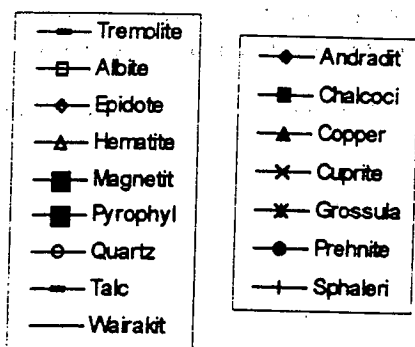


Figure 2: a) seawater and plagiogranite reaction; b) modified seawater and basalt reaction; c) East Pacific Rise vent fluid and plagiogranite, all using EQ3/6, 300°C, 85 bars pressure. Axes of each plot are log reaction progress versus log moles of product mineral.