

Project Report  
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### **Introduction:**

The purpose of this project is to simulate conditions in hydrothermal systems on Europa using geochemical models. The ultimate goal of the research is to investigate the possibility of life developing in Europa's subsurface ocean. We want to address these questions:

- How does a hydrothermal vent evolve with temperature?
- What organic compounds may form at europian hydrothermal vents?
- Under what conditions will organic compounds form?
- Is the chemical energy in Europa's ocean sufficient to sustain microbial life?

### **Background Information:**

To better understand geochemical processes occurring on Europa's seafloor, we investigated the effects of varying Fe-content in the seafloor rock and varying temperature. Iron is important in such geochemical processes as the production of methane through serpentinization (e.g. *Allen and Seyfried, 2003*) and can be a nutrient for microbes (*Russell and Hall, 2006; Park and Kim, 2001*). It can also offer clues as to the state of differentiation of Europa's core/mantle. If Europa is fully differentiated and contains an iron core, we would expect there to be little iron in the mantle and ocean floor whereas a homogeneous Europa would have iron evenly dispersed throughout the ocean floor. Furthermore, the composition of the ocean is a result of water-rock interactions at the seafloor. This project investigated the effects of temperature on geochemical processes, comparing high temperature (> 250°C) hydrothermal vents (*Kelley et al., 2001*) to lower temperature (~20°C) cold seeps (e.g. *Orphan et al., 2002*).

### **Objectives:**

The purpose of this project was to build geochemical models to simulate conditions in potential hydrothermal vents on Europa's ocean floor. These models will help in understanding the formation and evolution of hydrothermal vents and Europa's ocean and explore the possibility of the development and sustenance of life.

### **Approach:**

The Geochemist's Workbench (GWB) modeling software (*Bethke, 2008*) uses aqueous and mineral chemistry to simulate user-specified geochemical conditions in the range from 0°C < T < 300°C. GWB tracks the chemical reactions between the basis species (what the user defines) and the secondary species (the products of the chemical reactions) in terms of the reaction coefficients. For example, the reaction



can be written in terms of each components' chemical potentials,  $\mu$

$$d\mu_D + e\mu_E - b\mu_B - c\mu_C = 0.$$

Using the definition of chemical potential

$$\mu_X = \mu_X^0 + RT \ln a_X$$

where  $\mu_X$  is the chemical potential of species X,  $\mu_X^0$  is the standard state chemical potential, and  $a_X$  is the activity of species X, and the equation for Gibb's free energy

$$\Delta G^0 = -RT \ln K$$

where R is the gas constant, T is the absolute temperature and K is the equilibrium constant, we can solve for the equilibrium constant K

$$K = \frac{a_D^d a_E^e}{a_B^b a_C^c}$$

in terms of the activities of each species in the reaction. In general terms, the equilibrium constant is equal to the activity product Q that is used for reactions that are not in equilibrium. This term takes into account the activity coefficients which describe the non-ideal behavior of species in solution. Finally, comparing the equilibrium constant with the activity product, we calculate the saturation index (SI) which describes how saturated a species is in solution.

$$SI = \log\left(\frac{Q}{K}\right)$$

When  $Q = K$ ,  $SI = 0$  which means the solution is saturated with respect to that particular species.

Two compositions of ocean floor were considered in this study: terrestrial basalt and CI chondrite. Basaltic rock is composed of various concentrations of Fe- and Mg-rich olivine and pyroxene endmembers. Typical terrestrial ocean basalt is Mg-rich, containing more forsterite, enstatite and diopside than their Fe-rich counterparts fayalite, ferrosilite and hedenbergite. CI chondrites, a primitive meteorite thought to represent the oldest solid material in the solar system, were also used in this study because they are believed to have formed in the outer asteroid belt in the same region of the solar system as Europa formed. They have also been used in previous models investigating the formation of Europa and its ocean (Kargel *et al.*, 2000). The origin of sulfates observed in CI chondrites is still debatable. Some suggest they are a result of aqueous alteration early in the rock's history (e.g. Lee, 1993) whereas others argue that they are of terrestrial origin resulting from weathering after the meteorite reached Earth's

surface (McKinnon and Zolensky, 2003). For reasons of simplicity, sulfates were excluded from CI chondrite compositions in this project but warrant further investigation in future studies.

Four models are discussed in detail here; more are outlined here and discussed in more detail later. The first model constructed was a “Control” model that used terrestrial compositions for the initial rock and seawater (Table 1). Two models, “50/50” and “CI chondrite” investigated the effects of varying the initial rock composition, specifically varying the Fe/Mg content. “50/50” used equal mass concentrations of each basaltic endmember and “CI chondrite” used the composition of a typical CI chondrite, employing concentrations that result in typical Mg/Si ratios in CI chondrites (von Michaelis et al., 1968). Table 2 lists in detail each mineral used in the initial rock composition input parameters. The three above mentioned models were run at 275°C. To study the effects of temperature on the evolution of a hydrothermal vent and to simulate the conditions at methane cold seeps on terrestrial seafloors (Orphan et al., 2002), the “Control” model was also run at 20°C (Table 1). The “50/50” and “CI chondrite” models have also been run at low temperatures but not analyzed in detail and will not be discussed here.

|             | Model                 | Description                                     |
|-------------|-----------------------|---|
|             | Control               | Terrestrial basalt and seawater                 |
| Rock        | 50/50                 | Equal mass concentrations of basalt endmembers  |
|             | CI chondrite          | CI chondrite composition w/o $\text{SO}_4^{2-}$ |
| Temperature | Control Low T         | Control, T = 20°C                               |
|             | 50/50 Low T(*)        | 50/50, T = 100°C                                |
|             | CI chondrite Low T(*) | CI chondrite, T = 25°C                          |

**Table 1:** Models discussed in this study. (\*) “50/50 Low T” and “CI chondrite Low T” models have been run but not analyzed in detail and are excluded from this report.

| Model                | Mineral      | Formula   | Amount (mass %) |
|----------------------|--------------|---|-----------------|
| <b>Control</b>       | Forsterite   | $\text{Mg}_2\text{SiO}_4$                       | 67.5            |
| <b>Fe/Mg = 0.064</b> | Fayalite     | $\text{Fe}_2\text{SiO}_4$                       | 7.5             |
|                      | Enstatite    | $\text{MgSiO}_3$                                | 15              |
|                      | Diopside     | $\text{CaMg}(\text{SiO}_3)_2$                   | 10              |
| <b>50/50</b>         | Forsterite   | $\text{Mg}_2\text{SiO}_4$                       | 16.67           |
| <b>Fe/Mg = 0.744</b> | Fayalite     | $\text{Fe}_2\text{SiO}_4$                       | 16.67           |
|                      | Enstatite    | $\text{MgSiO}_3$                                | 16.67           |
|                      | Ferrosilite  | $\text{Fe}_2\text{SiO}_4$                       | 16.67           |
|                      | Diopside     | $\text{CaMg}(\text{SiO}_3)_2$                   | 16.67           |
|                      | Hedenbergite | $\text{CaFe}(\text{SiO}_3)_2$                   | 16.67           |
| <b>CI chondrite</b>  | Dolomite     | $\text{CaMg}(\text{CO}_3)_2$                    | 8.33            |
|                      | Chrysotile   | $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$ | 25              |
|                      | Forsterite   | $\text{Mg}_2\text{SiO}_4$                       | 8.33            |
|                      | Enstatite    | $\text{MgSiO}_3$                                | 8.33            |
|                      | Diopside     | $\text{CaMg}(\text{SiO}_3)_2$                   | 25              |
|                      | Pyrrhotite   | $\text{Fe}_{0.875}\text{S}$                     | 8.33            |
|                      | Troilite     | $\text{FeS}$                                    | 8.33            |
|                      | Magnetite    | $\text{Fe}_3\text{O}_4$                         | 8.33            |

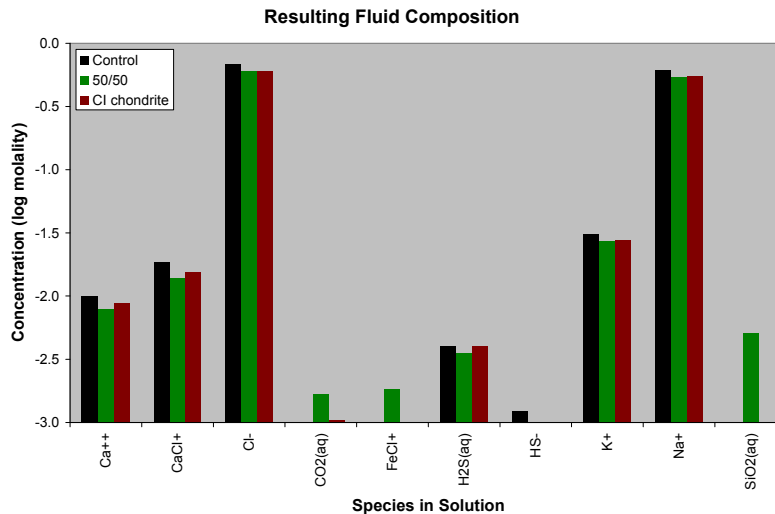
**Table 2:** Input parameters for models “Control”, “50/50” and “Cl chondrite” with respective Fe/Mg ratios.

## Results:

### *Varying Initial Rock Composition:*

Varying the initial rock composition in the models yielded little change in the resulting fluid composition. Figure 1 shows the concentrations of the major components in the resulting fluid of the three models. Several other species were present but only species with concentrations above 0.001 molal are shown here. All three fluids were Na-Cl solutions with similar concentrations of  $\text{Ca}^{++}$ ,  $\text{CaCl}^+$ ,  $\text{Cl}^-$ ,  $\text{H}_2\text{S}(\text{aq})$ ,  $\text{K}^+$  and  $\text{Na}^+$ . The “50/50” model showed higher concentrations of  $\text{CO}_2(\text{aq})$ ,  $\text{FeCl}^+$  and  $\text{SiO}_2(\text{aq})$  while only the “Control” model was enriched in  $\text{HS}^-$  (Fig. 1).

Varying the initial rock composition had a greater effect on the resulting mineral precipitation. Figure 2 shows the mass of each mineral that precipitated in each simulation. The low Fe-content simulation “Control” resulted in the precipitation of Mg-rich minerals such as monticellite and brucite (Table 3). The high Fe-content model “50/50” precipitated minnesotaite (Fe-rich mica) and different Mg-rich minerals such as talc and tremolite. The “Cl chondrite” model precipitated minerals different from the “Control” and “50/50” models such as troilite, calcite, pyrite and diopside. Other minerals were present but only minerals that precipitated more than 0.1 grams are shown here.



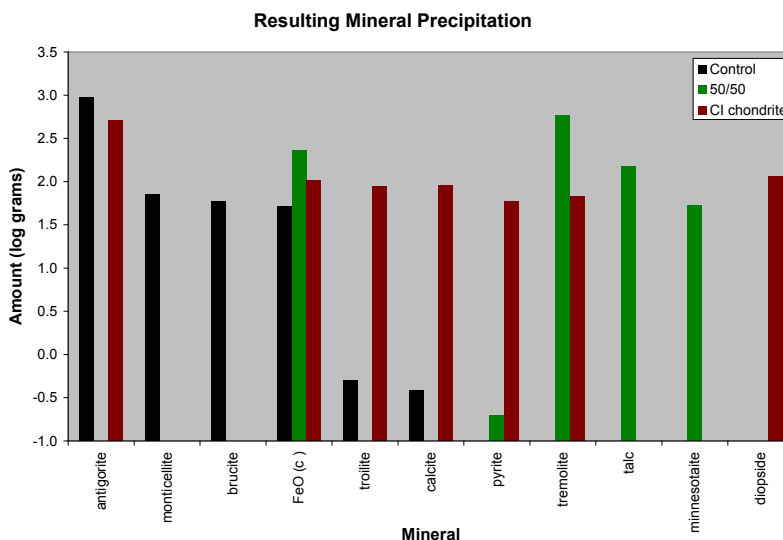
**Figure 1:** Resulting fluid compositions of the three models showing differences resulting in varying the initial rock composition.

### *Varying Temperature:*

Each of the above mentioned models were run at 275°C. To study the effect of temperature on the resulting fluid composition and mineral precipitation, the “Control” model was also run at  $T = 20^\circ\text{C}$ . Figure 3 shows the resulting fluid composition of the “Control Low T” models compared to the “Control” model. Again, other species were present but of concentrations lower than 0.001 molal and were excluded here. “Control Low T” also resulted in a Na-Cl solution enriched in  $\text{K}^+$  but the concentrations of minor constituents varied greatly.

While “Control” was enriched in H<sub>2</sub>S(aq), “Control Low T” was enriched in H<sub>2</sub>(aq) and slightly more HS<sup>-</sup>. Other species enriched in the low-temperature model relative the high-temperature model were NaCl, NaOH, OH<sup>-</sup>, and of particular interest, CH<sub>4</sub>(aq) (Fig. 3).

The resulting minerals that precipitated also depended on temperature. Figure 4 shows the resulting mineral precipitation of the “Control Low T” model compared to that of the “Control” model. Again, minerals of less than 0.1 grams were excluded from this study. Both models had similar amounts of antigorite, brucite, FeO(c), and troilite but the low-temperature model precipitated much more andradite (Ca,Fe silicate; Table 3) as opposed to monticellite (Ca,Mg silicate) in the high-temperature model (Fig. 4).



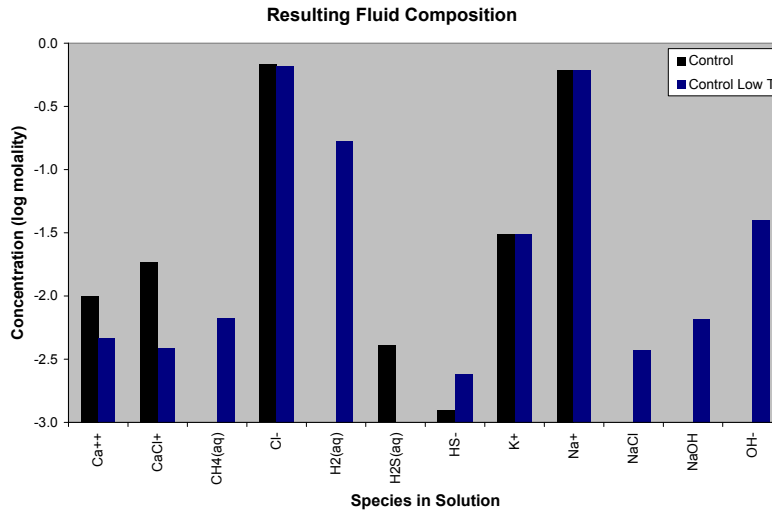
**Figure 2:** Mass of each mineral that precipitated in each simulation.

| Mineral      | Chemical Formula  | Type          |
|--------------|---|---------------|
| Andradite    | Ca <sub>3</sub> Fe <sub>2</sub> (SiO <sub>4</sub> ) <sub>3</sub>                  | Garnet        |
| Antigorite   | Mg <sub>24</sub> Si <sub>17</sub> O <sub>42.5</sub> (OH) <sub>2</sub>             | Serpentine    |
| Brucite      | Mg(OH) <sub>2</sub>   | Hydroxide     |
| Calcite      | CaCO <sub>3</sub>   | Carbonate     |
| Diopside     | CaMg(SiO <sub>3</sub> ) <sub>2</sub>  | Clinopyroxene |
| FeO(c)       | FeO   | Oxide         |
| Minnesotaite | Fe <sub>3</sub> Si <sub>4</sub> O <sub>10</sub> (OH) <sub>2</sub>                 | Mica          |
| Monticellite | CaMgSiO <sub>4</sub>  | Olivine       |
| Pyrite       | FeS <sub>2</sub>  | Sulfide       |
| Talc         | Mg <sub>3</sub> Si <sub>4</sub> O <sub>10</sub> (OH) <sub>2</sub>                 | Mica          |
| Tremolite    | Ca <sub>2</sub> Mg <sub>5</sub> Si <sub>8</sub> O <sub>22</sub> (OH) <sub>2</sub> | Amphibole     |
| Troilite     | FeS   | Sulfide       |

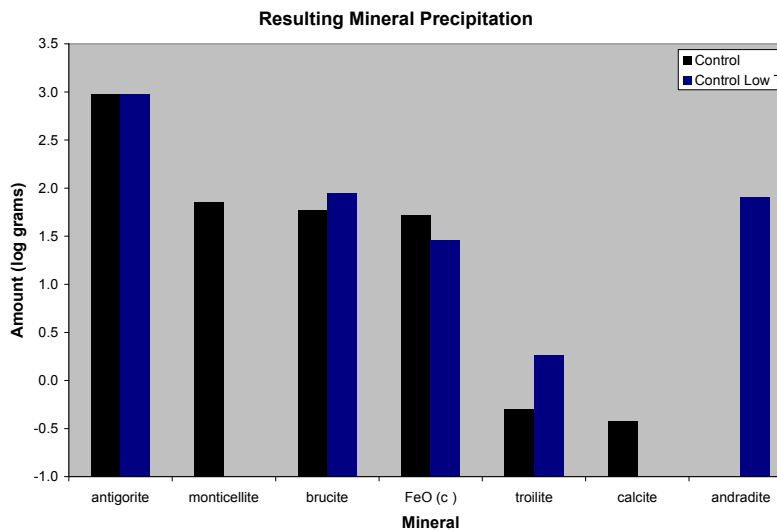
**Table 3:** Chemical formulae for each mineral precipitated in the models.

### Discussion and Conclusions:

In all high-temperature models, the resulting fluid composition was a Na-Cl-rich solution. This is most likely an artifact of the input parameters for the initial fluid in the models. To test this, we will run a model that uses a MgSO<sub>4</sub>-rich solution as the initial fluid rather than a Na-Cl-rich fluid (see “Future Work” section).



**Figure 3:** Resulting fluid compositions of high- (275°C) and low- (20°C) temperature models.



**Figure 4:** Resulting mineral compositions of high- (275°C) and low- (20°C) temperature models.

The composition of the initial rock had a greater effect on the resulting mineral precipitation than it did on the resulting fluid. The low Fe-content model “Control” resulted in more Mg-rich minerals precipitating (such as monticellite and brucite) whereas the higher Fe-content models “50/50” and “Cl chondrite” resulted in more of the Fe-mica minnesotaite. This shows the importance of the initial rock composition on the resulting mineral composition. Higher initial Fe-content will result in more Fe-rich minerals. Fe-content can also provide evidence for the state of the interior of the planetary body. If Fe-rich minerals are determined to result from hydrothermal vents on the ocean floor, we can conclude that the ocean floor itself is probably also Fe-rich. This would suggest that Europa’s rocky interior is not fully differentiated since a differentiated body, like Earth, would be depleted of iron in the uppermost parts of its rocky layers.

Temperature was also an important factor in the resulting fluid and mineral compositions. The fluid resulting from “Control” (275°C) was enriched in Ca<sup>++</sup>, CaCl, and H<sub>2</sub>(aq),

while the low temperature model (at 20°C) resulted in a fluid rich in CH<sub>4</sub>(aq), NaCl, NaOH, and OH<sup>-</sup>. Of particular interest in the low-temperature models is the production of methane (CH<sub>4</sub>) since this is similar to terrestrial methane cold seeps (*Orphan et al., 2002*). More detailed analysis on this result is needed to determine what exact chemical reaction is occurring to produce methane at low temperatures rather than at high temperatures (see “Future Work” section). Mineral composition also varied with temperature. Both models resulted in the precipitation of antigorite and brucite which have been shown to result from serpentinization at hydrothermal vents on Earth (e.g. *Vance et al., 2007*). However, more of the Fe-silicate andradite precipitated in the low-temperature model whereas more of the Mg-rich silicate monticellite precipitated in the high-temperature model, even though both models began with the same concentrations of Fe and Mg in the initial rock and fluid.

#### *Implications for Europa:*

This project used geochemical modeling to investigate the evolution of a potential hydrothermal vent at the bottom of Europa’s subsurface ocean. Hydrothermal vents affect the composition of the ocean and the minerals that precipitate from the vent are highly dependent on the composition of the initial rock. In addition, mineral precipitation and resulting fluid composition were strongly affected by the temperature of the system. Thus, varying ocean floor rock composition or temperature will yield very different mineral precipitates and fluid composition. Some of these mineral phases and fluids can be transported to the surface via convective circulation through the ocean and surface eruption where they can be detected from orbit. Mineral phases observed on the surface therefore may be suggestive of the subsurface environment.

#### **Future Work:**

Further analysis on the current models is needed. Namely, we will determine the stoichiometry of the chemical reactions that result in the observed mineral precipitation. We will also further analyze the methane production in the low-temperature models, pH and redox reactions to determine the energy available for microbial metabolism.

Furthermore, we will vary the composition of the initial fluid in the hydrothermal vent to determine its effects on final fluid and mineral precipitation. Specifically, we will run a model using pure water to simulate the conditions under which Europa’s ocean formed, then we will use a sulfate-rich (rather than chloride-rich) initial fluid to study the evolution of the hydrothermal vent.

The sulfate content in Europa’s ocean is still a topic of debate. Some argue that Europa’s ocean is sulfate-rich (*Kargel et al., 2000*) while others suggest the ocean is sulfide-rich (*McKinnon and Zolensky, 2003*). The state of the sulfur is a vital component in understanding the possibility of life in Europa’s ocean because there are well-known terrestrial species of microbes that employ sulfate-reduction/methane-oxidation reactions for metabolic energy (*McCollom, 1999; Zolotov and Shock, 2003*). To investigate these biologic possibilities, we will study the effects of varying the initial fluid composition in the hydrothermal vent, looking specifically at sulfate and sulfide content.

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