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2005 Submarine Ring of Fire Expedition

The Big Balancing Act

Focus
Hydrothermal vent chemistry at subduction volcanoes

Grade Level
9-12 (Chemistry/Earth Science)

Focus Question
What chemical changes occur in hydrothermal circulation systems?

Learning Objectives
Students will be able to define and describe hydrothermal circulation systems.

Students will be able to explain the overall sequence of chemical reactions that occur in hydrothermal circulation systems.

Students will be able to compare and contrast "black smokers" and "white smokers."

Given data on chemical enrichment that occurs in hydrothermal circulation systems, students will be able to make inferences about the relative significance of these systems to ocean chemical balance compared to terrestrial runoff.

Materials
- ❒ Copies of "Hydrothermal Circulation Worksheet," one copy for each student or student group
- ❒ (Optional) copies of "The Cauldron Beneath the Seafloor" one copy for each student or student group (see "Resources;" alternatively, students can be directed to obtain this article)

Audio/Visual Materials
None

Teaching Time
One or two 45-minute class periods

Seating Arrangement
Classroom style if students are working individually, or groups of two to four students

Maximum Number of Students
30

Key Words
Hydrothermal circulation
Hydrothermal fluid
Black smoker
White smoker
Temperature
Pressure
Ring of Fire
Asthenosphere
Lithosphere
Magma
Fault
Transform boundary
Convergent boundary
Divergent boundary
Subduction
Tectonic plate

Background Information
The Ring of Fire is an arc of active volcanoes and earthquake sites that partially encircles the Pacific Ocean Basin. The location of the Ring of Fire coin-

cides with the location of oceanic trenches and volcanic island arcs that result from the motion of large pieces of the Earth's crust (tectonic plates). Tectonic plates consist of portions of the Earth's outer crust (the lithosphere) about 5 km thick, as well as the upper 60 - 75 km of the underlying mantle. The plates move on a hot flowing mantle layer called the asthenosphere, which is several hundred kilometers thick. Heat within the asthenosphere creates convection currents (similar to the currents that can be seen if food coloring is added to a heated container of water). These convection currents cause the tectonic plates to move several centimeters per year relative to each other.

The junction of two tectonic plates is known as a plate boundary. Where two plates slide horizontally past each other, the junction is known as a transform plate boundary. Movement of the plates causes huge stresses that break portions of the rock and produce earthquakes. Places where these breaks occur are called faults. A well-known example of a transform plate boundary is the San Andreas fault in California.

Where tectonic plates are moving apart, they form a divergent plate boundary. At these boundaries, magma (molten rock) rises from deep within the Earth and erupts to form new crust on the lithosphere. Most divergent plate boundaries are underwater (Iceland is an exception), and form submarine mountain ranges called oceanic spreading ridges.

If two tectonic plates collide more or less head-on, they produce a convergent plate boundary. Usually, one of the converging plates moves beneath the other in a process called subduction. Subduction produces deep trenches, and earthquakes are common. As the sinking plate moves deeper into the mantle, increasing pressure and heat release fluids from the rock causing the overlying mantle to partially melt. The new magma rises and may erupt violently to form volcanoes that often form arcs of islands along the convergent boundary. These island arcs are always landward of the neighboring trenches. This process can be visualized as a huge conveyor belt on which new crust is formed at the oceanic spreading ridges and older crust is recycled to the lower mantle at the convergent plate boundaries. The Ring of Fire marks the location of a series of convergent plate boundaries in the western Pacific Ocean.

The Mariana Arc is part of the Ring of Fire that lies to the north of Guam in the western Pacific. Here, the fast-moving Pacific Plate is subducted beneath the slower-moving Philippine Plate, creating the Marianas Trench (which includes the Challenger Deep, the deepest known area of the Earth's oceans). The Marianas Islands are the result of volcanoes caused by this subduction, which frequently causes earthquakes as well. In 2003, the Ocean Exploration Ring of Fire expedition surveyed more than 50 volcanoes along the Mariana Arc, and discovered that ten of these had active hydrothermal systems (visit http://oceanexplorer.noaa.gov/explorations/03fire/welcome.html for more information on these discoveries). The 2004 Submarine Ring of Fire Expedition focussed specifically on hydrothermal systems of the Mariana Arc volcanoes, and found that these systems are very different from those found along mid-ocean ridges (visit http://oceanexplorer.noaa.gov/explorations/04fire/welcome.html for more information). The 2005 Submarine Ring of Fire Expedition will explore hydrothermally active volcanoes in the Kermadec Arc, an area where tectonic plates are converging more rapidly than any other subduction zone in the world.

Underwater volcanism produces hot springs in the middle of cold, deep ocean waters. These springs (known as hydrothermal vents) were first discovered in 1977 when scientists in the submersible Alvin visited an oceanic spreading ridge near the Galapagos Islands, and made one of the most exciting discoveries in 20th century biology. Here they found rocky chimneys venting hot fluid and surrounded by large numbers of animals that had never been seen before. Since they were first discovered, hydrothermal systems around spreading ridges have been intensively studied. In contrast, the hydrothermal systems around convergent plate boundaries are relatively unexplored.

"Hydrothermal circulation" refers to a cycle in which seawater penetrates the ocean crust, is heated by volcanic activity, then re-emerges as "hydrothermal fluid." This fluid is quite different from the surrounding seawater. In addition to being much hotter (temperatures often exceed 350°C), hydrothermal fluids are acidic, enriched with metals, and have high concentrations of dissolved gases including hydrogen sulfide. These changes result from a variety of chemical reactions between the heated seawater and rocks of the ocean crust. Some reactions cause chemicals to dissolve out of the rocks, while other reactions remove different chemicals from the seawater. As the fluids emerge into the colder seawater, many dissolved metals precipitate out of solution, forming chimney-like structures, and producing dense clouds that resemble smoke.

Prior to the discovery of hydrothermal systems, it was assumed that terrestrial runoff provided the primary input of minerals and other chemicals into the Earth's oceans. But as more has been learned about hydrothermal systems, scientists have begun to ask whether these systems might have a significant influence as well. In this lesson, students will investigate some of the characteristics of hydrothermal fluids, and make inferences about their relative importance to the chemical balance of the Earth's oceans.

Learning Procedure

1. To prepare for this lesson, read the Submarine Ring of Fire 2004 background essay on hydrothermal vent chemistry (http://oceanexplorer.noaa.gov/explorations/04fire/background/chemistry/media/chemistry_600.html and "The Cauldron Beneath the Seafloor" (see "Resources"). You will need to make copies of the latter article for students or student groups, unless you plan to have the students obtain the article on their own.
2. Lead a brief review of the concepts of plate tectonics and continental drift and how they are related to underwater volcanic activity and hydrothermal vent systems (you may want to use resources from NOAA's hydrothermal vent Web site (http://www.pmel.noaa.gov/vents/home.html) to supplement this discussion). Introduce the Ring of Fire, and describe the processes that produce the island arcs.
3. Tell students that their assignment is to investigate hydrothermal systems and to make calculations that will allow them to draw inferences about the relative importance of these systems to the chemistry of Earth's oceans. Provide each student or student group with copies of the "Hydrothermal Circulation Worksheet" and "The Cauldron Beneath the Seafloor" (or direct them to the Web site where this article may be found).
4. Lead a discussion of students' worksheets. The following points should emerge during this discussion:

   Low temperature chemical reactions in the Recharge Zone take place at temperatures up to about 60 °C. Low temperature reactions that result in the formation of iron oxides and hydroxides also remove dissolved oxygen from seawater. At temperatures above 150°C, precipitation of clay minerals and chlorite removes all of the magnesium that was originally present in seawater. Chlorite is actually a group of minerals (Iron Aluminum Magnesium Silicate Hydroxides) whose general formula is
   $(Fe, Mg, Al)_6(Si, Al)_4O_{10}(OH)_8$
   This formula also suggests that the reactions would consume hydroxyl ions, thus reducing the pH and making the solution more acidic.

   The low temperature reactions in the Recharge Zone also include reactions that break down the original rock minerals, and this process causes potassium and other alkali metals to be transferred from seawater into the rocks. But as clay minerals and chlorite form at higher temperatures, the increased acidity of the fluid causes some of these minerals to be leached back out of the rocks.

Anhydrite is calcium sulfate ($CaSO_4$), which exhibits "retrograde solubility," meaning that the chemical becomes less soluble with increasing temperatures. When temperatures rise above 150°C, anhydrite precipitates out of solution.

In the Reaction Zone, reactions take place at temperatures as high as 350 - 400°C. Students should realize that the "normal" boiling point of water is 100°C at sea level, but the boiling point increases with increasing pressure (the converse is also true; students may be more familiar with the fact that boiling point decreases at lower atmospheric pressures caused by high altitudes). At a depth of 2000 meters, at which the pressure is about 201 atmospheres, the boiling point of water is above 400°C. Students may also be aware that increased concentration of dissolved substances can also elevate the boiling point, but pressure is the dominant factor in the case of hydrothermal fluids.

The hot, acidic fluid in the Reaction Zone leaches a variety of metals from the surrounding rocks, and rises back to the seafloor. When the hot fluid encounters the much colder deep ocean water, the reduction in temperature causes many of the dissolved metals to precipitate. The cloud of metal particles thus created resembles smoke, hence the term, "black smoker." Some of the precipitated particles form metal sulfide chimneys. If the hydrothermal fluid mixes with colder seawater while it is still inside the ocean's crust, the precipitation and metal sulfide deposition will occur beneath the seafloor. When the hydrothermal fluid vents from the seafloor, the result is a "white smoker" since the dark metal particles have already precipitated out of the fluid.

Completed Table 1 should resemble the following:

Chemical	Concentration in Hydrothermal Fluid (mM)	Concentration in Seawater (mM)	Net Enrichment (mM)
Sodium	537	464	73
Potassium	17.1	9.8	7.3
Calcium	30.8	10.2	20.6
Magnesium	0	52.7	-52.7
Manganese	680	0	680
Iron	5590	0.0015	5590
Sulfate	0	27.9	-27.9
Copper	98 - 120	.007	98 - 120
Zinc	47 - 53	0.01	47 - 53

Calculations to complete Table 2 are straightforward, provided students keep track of the decimal point. For example, Table 1 indicates that the net enrichment of calcium in hydrothermal fluid is 20.6 mM, which is equivalent to 0.0206 mole/liter. So the annual calcium flux in a hydrothermal circulation of 1.7×10^{14} liters would be

(0.0206 mole/liter) • (1.7×10^{14} liters) = 0.035 x 10^{14} mole = 3.5 x x 10^{12} mole

Similarly, since the net enrichment of magnesium in hydrothermal fluid is -52.7 mM, the annual magnesium flux in a hydrothermal circulation of 1.7×10^{14} liters would be

(0.0527 mole/liter) • (1.7×10^{14} liters) = -0.089 x 10^{14} mole = -8.9 x x 10^{12} mole

These calculations show that hydrothermal fluid is a source of calcium (and any other chemical with a positive flux) for Earth's ocean, and is a sink for magnesium (and any other chemical with a negative flux). These data suggest that for some chemicals, hydrothermal circulation may be equally significant to ocean chemical balance as terrestrial runoff. Be sure students understand that since only a small fraction of the Earth's hydrothermal systems have been located, let alone studied, these estimates are very approximate and preliminary.

The Bridge Connection

www.vims.edu/bridge/ – In the "Site Navigation" menu on the left, click on "Ocean Science Topics," then "Habitats," then "Deep Sea" for resources and links related to hydrothermal vents.

The "Me" Connection

Studies of hydrothermal systems have already provided insight into how ore deposits that are mined on land for various metals may have been formed. Have students write a brief essay in which they explain how knowledge of hydrothermal systems might connect with other natural features or processes of personal importance.

Connections to Other Subjects

English/Language Arts, Geography

Assessment

Work sheets and class discussions provide opportunities for assessment.

Extensions

1. Have students visit http://oceanexplorer.noaa.gov to keep up to date with the latest Ring of Fire Expedition discoveries.

2. Visit the MARVE (Marine Virtual Explorer) Web site of the Stanford University School of Earth Sciences (http://pangea.stanford.edu/projects/marve/) for a simulated research dive in the Alvin submersible to a hydrothermal vent field on the East Pacific Rise.

Resources

http://oceanexplorer.noaa.gov – Follow the Ring of Fire Expedition daily as documentaries and discoveries are posted each day for your classroom use.

http://oceanexplorer.noaa.gov/explorations/04fire/background/chemistry/media/chemistry_600.html – Background essay on hydrothermal vent chemistry from the 2004 Submarine Ring of Fire expedition

Humphris, S. E. and T. McCollom. The cauldron beneath the seafloor. *Oceanus* 41(2):18-21. Available online at http://oceanusmag.whoi.edu/v41n2/humphris.html.

http://pubs.usgs.gov/publications/text/dynamic.html#anchor19309449 – Online version of "This Dynamic Earth," a thorough publication of the U.S. Geological Survey on plate tectonics written for a non-technical audience

http://pubs.usgs.gov/pdf/planet.html – "This Dynamic Planet," map and explanatory text showing Earth's physiographic features, plate movements, and locations of volcanoes, earthquakes, and impact craters

http://ridge2000.bio.psu.edu/ – Web site of RIDGE 2000, a long-term program of scientific research on mid-ocean ridges and other tectonic spreading centers, including classroom materials, and technical resources

http://oceanexplorer.noaa.gov/explorations/03fire/logs/subduction_vr.html – 3-dimensional "subduction zone" plate boundary video

http://oceanexplorer.noaa.gov/explorations/03fire/logs/ridge.html – 3-dimensional structure of a "mid-ocean ridge," where two of the Earth's tectonic plates are spreading apart

National Science Education Standards

Content Standard A: Science as Inquiry

- Abilities necessary to do scientific inquiry
- Understandings about scientific inquiry

Content Standard B: Physical Science

- Structure and properties of matter
- Chemical reactions
- Motions and forces
- Interactions of energy and matter

Content Standard D: Earth and Space Science

- Geochemical cycles
- Origin and evolution of the Earth system

Content Standard E: Science and Technology

- Understandings about science and technology

Content Standard F: Science in Personal and Social Perspectives

- Natural resources

For More Information

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Hydrothermal Circulation Worksheet

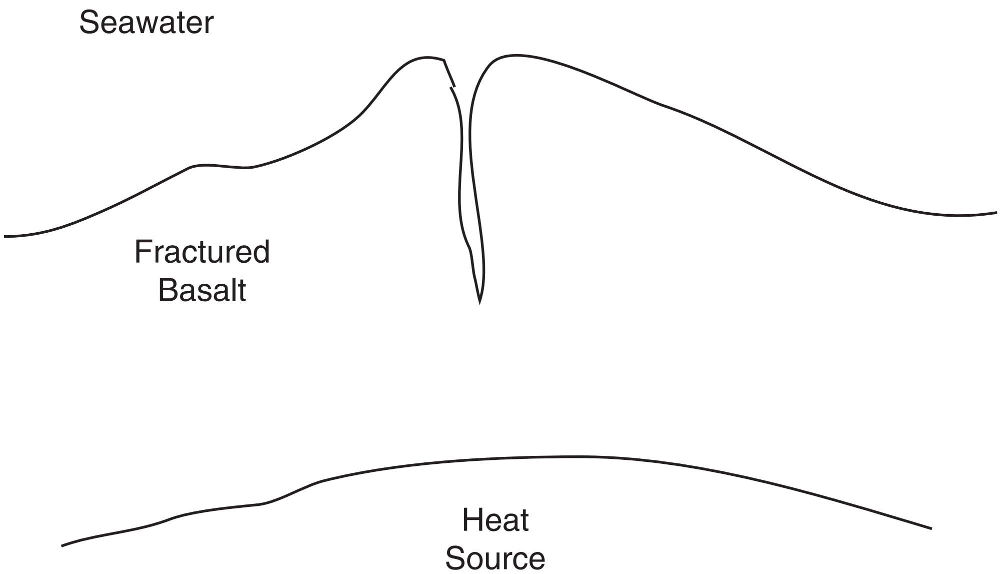

Figure 1

1. On FIgure 1, Label Recharge Zone, Reaction Zone, Upflow Zone, and draw arrows to show the path of water as it moves through the hydrothermal circulation system.

2. In the Recharge Zone, chemical reactions between seawater and minerals of the oceanic crust take place at relatively low temperatures, up to about __________ °C.

3. In some of these low temperature reactions, iron in the rocks is replaced by iron oxides and hydroxides. These reactions also remove __________ from the seawater.

4. At temperatures above 150°C, clay minerals and chlorite precipitate out of seawater in the Recharge Zone. This removes all of the _______________ that was originally present in seawater, and also consumes hydroxyl ions, which makes the fluid more __________.

5. What is the chemical formula for anhydrite? _______________

6. What happens to anhydrite when temperatures rise above 150°C?

____

7. What is "retrograde solubility?"

____

8. What happens to potassium and other alkali metals in the Recharge Zone?

____

9. In the Reaction Zone, reactions take place at temperatures as high as _________°C.

10. If the boiling point of water is 100°C, how can hydrothermal fluids formed from seawater have temperatures exceeding 300°C?

____

11. What causes "black smokers?"

____

12. How are "black smokers" and "white smokers" chemically different?

____

13. Fill in the blanks in Table 1, and calculate the net enrichment in hydrothermal fluid (for example, if the concentration of a chemical is 5 mM in seawater and 15 mM in hydrothermal fluid, the net enrichment is 10 mM; if the concentration is 15 mM in seawater and 5 mM in hydrothermal fluid, the net enrichment is -10 mM).

14. Table 2 provides estimates of annual input of selected chemicals to Earth's oceans from terrestrial runoff. Use your data in Table 1 to estimate the annual flux of these chemicals from hydrothermal circulation, assuming that the annual global production of hydrothermal fluid is 1.7×10^{14} liters.

Table 1

Chemical	Concentration in Hydrothermal Fluid (mM)	Concentration in Seawater (mM)	Net Enrichment (mM)
Sodium			
Potassium			
Calcium			
Magnesium			
Manganese			
Iron			
Sulfate			
Copper			
Zinc			

Table 2

	Annual Input from Terrestrial Runoff (moles)	Annual Flux from Hydrothermal Circulation (moles)
Magnesium	5×10^{12}	
Sulfate	4×10^{12}	
Calcium	12×10^{12}	
Potassium	1.9×10^{12}	

15. From the data in Table 2, what do you infer about the potential significance of hydrothermal circulation to the chemical balance of the oceans?