Investigations of Deep-Sea Hydrothermal Samples for Isotopic Composition and Interfering Compounds Using CRDS.

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Abstract

Hydrothermal fluids from two vent sites along the East Scotia Ridge, E2 and E9, were analyzed for their hydrogen and oxygen isotopic values using a Picarro L1115-*i* CRDS. The fluids display varying salinity, sulfate and hydrogen sulfide content. None of the samples analyzed in this work showed any signs of spectroscopic interference. Isotopic values of the fluids were combined with salinity, magnesium and silica measurements to determine the possible role of magmatic inputs and phase separation. Oxygen isotope values (reported relative to VSMOW) range from -0.2 to +1.4 ‰ and hydrogen values range from -1.8 to +2.1 ‰. Oxygen isotope values of black smokers at each site differ on average by ~0.4 ‰. Relatively higher $\delta^{18}O$ values at E2 indicate water-rock reactions may be more prevalent here than at E9. Low salinity and δD enrichment at E9 could indicate phase separation. Overall the data suggest that final fluid compositions reflect several complex processes during hydrothermal alteration.

Introduction

Hydrothermal vent fluid emitted at the ocean floor strongly impacts ocean chemistry, global heat transfer, and alters the ocean crust. Vent fluids can be used to determine water-rock reactions and fluid inputs below the seafloor [1]. Stable oxygen and hydrogen isotopes are especially informative in determining the source and evolution of the fluid. Cavity Ring-Down Spectroscopy (CRDS) is used to determine the delta values of the fluid as it rapidly and simultaneously provides precise stable isotope data for both oxygen and hydrogen.

Hydrothermal vents are found at spreading centres where new ocean crust is generated. Seawater circles through the fresh crust cooling it convec- tively and altering it's composition through fluid-rock reactions (Fig. 1). Hydrothermal vents are typically found along the circum-global Mid-Ocean Ridge (MOR) mountain chain.

In the Scotia Sea, subduction of the South American (SAM) Plate beneath the Sandwich Plate has created a back-arc spreading centre (Fig. 2), resulting in the 9 ridge segments which form the East Scotia Ridge (ESR) (Fig. 3) [2]. It is possible that dehydrated fluid from the subducting slab contributes to hydrothermal circulation at the ESR and can be detected isotopically.

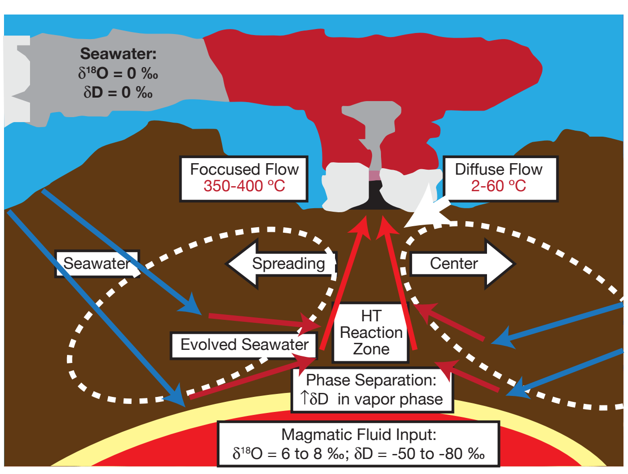


Figure 1: The hydrothermal water cycle. Fluid-rock reactions occur throughout all stages of the cycle. Phase separation and magmatic fluid input occur in the reaction zone. When fluid rises slowly from the reaction zone, sub-surface mixing with seawater can occur, as is often the case with diffusive vents. Focused upward flow results in black smokers; after Deep Sea Vent Communities; http://www.indiana.edu/~g105lab/images/gaia_chapter_13/vent_communities.htm.

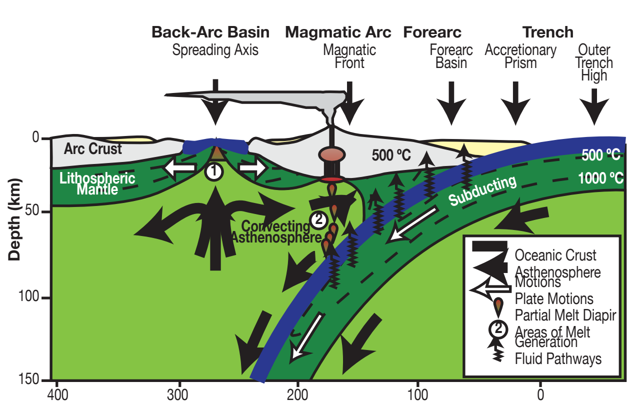


Figure 2: Dehydration of the subducting slab results in mantle melt which erupts forming island arc chains. Back-arc spreading causes a ridge to form in the back-arc basin, similar to a MOR.

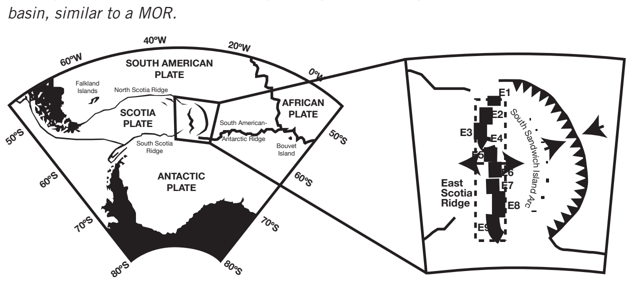


Figure 3: Tectonic setting of the East Scotia Ridge and location of segments E2 and E9; after Fretzdorff et al., [2]

Fluid alteration occurs during three stages of the hydrothermal circulation cell: recharge, reaction and discharge [1]. Fluid-rock reactions occur throughout the cycle. Magnesium is removed during recharge and is therefore an important indicator of hydrothermal alteration. Phase separation and possible magmatic input occur in the reaction zone, where temperatures can exceed 400 °C. At this point the fluid reverts its course and rises rapidly to the surface in the discharge phase. On contact with cold seawater, some dissolved species immediately precipitate, forming black smoke that gives these vents their names. When a direct conduit to the surface is absent, the fluid gets 'stuck' beneath the surface and migrates more slowly upwards. It can be mixed with recharging seawater, causing minerals to precipitate below the seafloor as temperature decreases. These vents are called diffusive vents [1].

Fluid alteration occurs throughout the hydrothermal water cycle due to chemical reactions mostly with the surrounding rocks, but due to other processes as well (Fig. 1). Stable oxygen and hydrogen isotope values change as a result of:

1. Water-rock interactions: increase $\delta^{18}O$
2. Phase separation: phase dependent – increase δD
3. Magmatic Dehydration: increase $\delta 1^8O$
4. Mixing with Seawater: shift $\delta^{18}O$ and δD towards 0 ‰

Isotopic Analysis Technique

Samples were injected directly into a Picarro A0211 high precision vaporizer. The combination of vacuum (< 2 militorr) and elevated temperature (110 °C) resulted in the immediate and complete vaporization of the sea water. The vapor concentration within the chamber was allowed to equilibrate before introduction into a Picarro L1115-*i* water isotope analyzer. This mechanism of allowing complete vaporization prior to analysis is critical for high precision measurements of $\delta^{18}O$ which are required for sea water analysis. After introduction into the analyzer the vapor was measured using CRDS (cavity ringdown spectroscopy). CRDS is a well established optical spectroscopy technique in which the analyte gas is passed through a ultra-high path length optical cavity. Spectral measurements are performed at cavity resonance for a selected near-infrared region where all the principle isotopologues of water exhibit absorption features. The resulting spectra are converted into individual isotopologue concentrations using customized spectral pattern recognition algorithms. The concentrations of the different isotopologues are ratioed and calibrated relative to VSMOW by analyzer software and reported in real time. Additionally the spectra were measured for presence of organic contamination using ChemCorrect™ software – none was detected in this sample set.

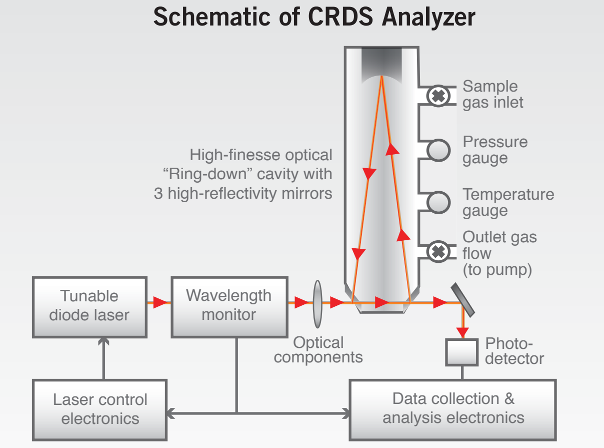
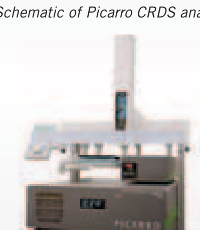


Fig. 4: Schematic of Picarro CRDS analyzer showing optical cavity and sample gas flow.



Instrument foot print: 54 cm x 60 cm
Instrument weight: ~ 40 Kg
Power consumption: 500 Watts @ 110V

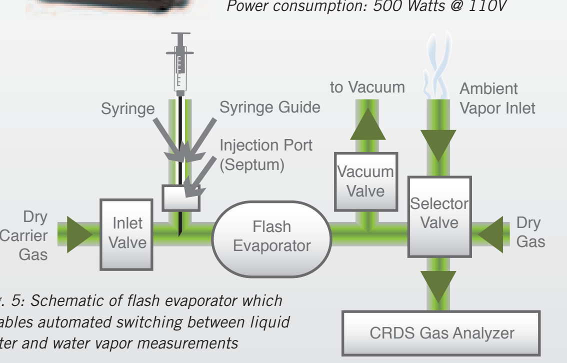


Fig. 5: Schematic of flash evaporator which enables automated switching between liquid water and water vapor measurements

Methods

37 hydrothermal fluid samples were obtained by the captain and crew of the RSS James Cook Cruise 042 using the remotely operated vehicle Isis (Fig. 6 A and B). Both black smoker and diffusive vent samples were obtained from segments E2 and E9 of the ESR (Fig. 7 A and B). Sub-samples were taken for the measurement of alkalinity, pH, gases, anions, silica and oxygen and hydrogen stable isotopes. Isotope analysis was carried out in collaboration with Picarro, Inc.

Samples were centrifuged to remove suspended solids prior to analysis using CRDS. A freshwater sample was run as a 'wash' after every 10 samples to prevent clogging of the syringe. Each sample was analyzed by 10 sequential injections. Results were based on the last 8 injections.

Figure 6A: RSS James Cook (Images copyright of Leighton Rolley)

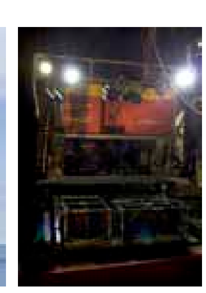


Figure 6B: Isis remote operated vehicle

Results

All measured $\delta^{18}O$ and δD values were within ±2 ‰ of Standard Mean Ocean Water (SMOW) (Table 1). Precision of samples did not exceed the performance specifications of 0.10 ‰ and 0.50 ‰ for $\delta^{18}O$ and δD, respectively.

- E2 vents were more enriched in both $\delta^{18}O$ and δD (Fig. 7A).
- Diffusive vents were less enriched than black smokers (Fig. 7A) and had a much higher mg content than black smokers (Fig. 7C).
- Salinity at all E2 vents was similar to seawater; black smokers at E9 had lower salinity compared with diffusive vents at this site. (Fig. 7B)
- Silica content was highest at E2 black smokers (Fig. 7D).

Figure 7A: Vent sampling at E2 black smokers. Titantium samplers were fired simultaneously into vent orifices to ensure identical collection of samples.

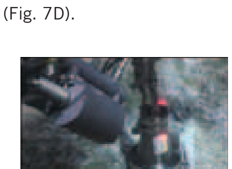


Figure 7B: Diffuse flow sampling at E2. A heavy 'skirt' was used to create a seal and prevent seawater entrainment during sampling.

$\delta^{18}O$ Site:	E2 Black Smoker	E2 Diffusive	E9 Black Smoker	E9 Diffusive
n	11	6	12	4
Min (‰)	0.8	-0.2	0.3	-0.1
Max (‰)	1.4	0.0	1.1	0.3
Mean (‰)	**1.0**	**-0.1**	**0.6**	**0.1**
Median (‰)	0.9	0.0	0.6	0.0
Standard Deviation	0.2	0.1	0.2	0.2

δD Site:	E2 Black Smoker	E2 Diffusive	E9 Black Smoker	E9 Diffusive
n	11	6	12	4
Min (‰)	-0.8	-0.5	-0.2	-0.6
Max (‰)	1.8	0.7	2.1	-0.1
Mean (‰)	**0.7**	**0.2**	**0.6**	**-0.4**
Median (‰)	1.3	0.2	0.4	-0.4
Standard Deviation	1.0	0.4	0.6	0.2

Table 1: δ^{180} and δD minimum and maximum, mean, median and standard deviation at E2 and E9 black smoker and diffusive vents; n is the number of fluids analyzed.

Discussion

The evolution of $\delta^{18}O$ and δD from typical seawater (VSMOW $\delta^{18}O$ and δD = 0 ‰) was a clear indication that hydrothermal alteration occurred in all sampled waters. Positive $\delta^{18}O$ values for black smokers were as expected from water-rock reactions, since basalts of the ocean crust have higher $\delta^{18}O$ values than seawater (MOR basalt $\delta^{18}O$ = 5.8 ‰ [4]).

All diffusive vent samples were closer in composition to seawater than black smokers, suggesting subsurface mixing with seawater. High magnesium content corroborates seawater mixing [1]. The minimal presence of Mg observed in black smokers implies possible seawater entrainment during sampling.

A strong positive relationship exists between $\delta^{18}O$ and silica content at both locations. E2 vents had the highest $\delta^{18}O$ and silica values, which may indicate lower fluid-rock ratios in the reaction zone beneath E2 or higher magmatic water input into the hydrothermal system at this site.

Higher water content in magmas producing E2 basalts could be a result of increased slab dehydration occurring at the northern end of the subducting SAM Plate compared to the southern end.

Phase separation may be occurring at the E9 vent fields where δD enrichment and low salinity in black smokers could suggest that the vapour phase was sampled.

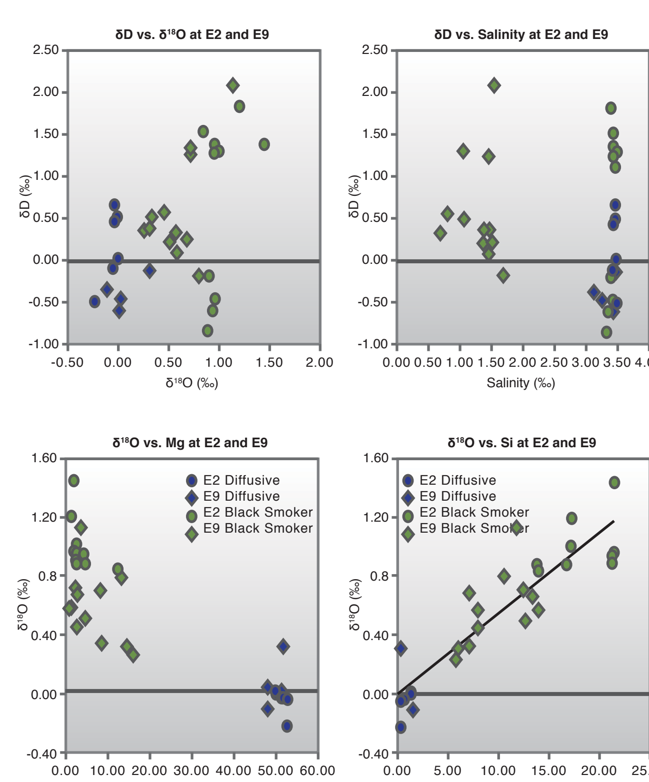


Figure 8: Plots of δ-values versus selected measured components of hydrothermal fluids from E2 and E9 black smoker and diffusive vents. A) δD vs. $\delta^{18}O$ B) δD vs. Salinity C) $\delta^{18}O$ vs. Magnesium and D) $\delta^{18}O$ vs. Silica content.

Conclusions

These results show that CRDS is an extremely useful tool for determining $\delta^{18}O$ and δD values of salty waters. This method will be useful in future studies investigating the isotopic composition of contaminated fluids. The isotopic data presented here, combined with salinity, magnesium and silica content were used to determine the processes involved in hydrothermal alteration of seawater. Results reveal different processes occurring at the E2 and E9 vent fields. The $\delta^{18}O$ value and silica content of E2 black smokers indicate increased amounts of water-rock reactions at this site compared with E9. Increased $\delta^{18}O$ could also be the result of magmatic fluid input, with a composition unique to back-arc spreading centres where a subducting slab underlies the heat source. Low salinity and δD enrichment at E9 black smokers may result from sampling the vapour from phase-separated fluid. The chemical compositions reflect several complex processes during hydrothermal alteration, which can be identified using O and H stable isotopes.

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References

[1] Humphris, S.E., et al. (Ed.), Seafloor Hydrothermal Systems: Physical, Chemical, Biological and Geological Interactions. American Geophysical Union. (1995). [2] Fretzdorff, S., et al., "Petrogenesis of the back-arc East Scotia Ridge, South Atlantic Ocean" J. Petrol. 43 (2002) 1435-1467. [3] Winter, J.D. "Subduction-related igneous activity part I: island arcs", Igneous and Metamorphic Petrology. USA (2001) 293-315. [4] Muehlenbacks, K., Clayton, R.N. "Oxygen isotope composition of the oceanic crust and its bearing on seawater", J. Geophys. Res. 81 (1976) 4365-4369.