Sulfur geochemistry of the Santa Elena (Costa Rica) ultramafics; R/V JOIDES Resolution JRES-149, JRES-173, JRES-209 cruises in the Iberia Abyssal Plain, Iberian Margin, and Mid-Atlantic Ridge from 1993-2003

Website: https://www.bco-dmo.org/dataset/663969

Data Type: Cruise Results **Version**: 03 November 2016 **Version Date**: 2016-11-03

Proiect

» Identifying the controls on biological activity in serpentinites (Controls on biological activity)

Program

» Center for Dark Energy Biosphere Investigations (C-DEBI)

| Contributors | Affiliation | Role |
|-----------------------|---|------------------------|
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Dataset Description

Sulfur geochemistry of the Santa Elena (Costa Rica) ultramafics.

Related publications:

Schwarzenbach EM, Gill BC, Gazel E, Madrigal P (2016) Sulfur and carbon geochemistry of the Santa Elena peridotites: Comparing oceanic and continental processes during peridotite alteration. Lithos 252–253:92-108. doi:10.1016/j.lithos.2016.02.017

Methods & Sampling

Santa Elena samples:

Sample preparation and mineralogy: Ultramafic basement rocks were sampled throughout the Santa Elena Ophiolite. Carbonate deposits associated with Mg-HCO₃ and Ca-OH springs in the eastern part of the ophiolite were sampled at various locations within riverbeds. All analytical measurements and sample preparation of the Santa Elena peridotites and carbonates were performed at the Department of Geosciences at Virginia Tech. The carbonate samples were prepared by drilling out individual depositional layers of carbonates to reveal heterogeneities within different layers or crushed with an agate mortar for bulk rock analysis. Carbonate precipitates from the rivers were first dried at 40 degrees C in the oven. Before sample analyses all samples were homogenized by hand with the agate mortar. The mineralogy of the carbonates was then determined by X-ray diffraction on a Rigaku MiniFlex XRD using the powder diffraction analysis package PDXL.

Bulk rock powders were prepared for all the ultramafic rocks. To remove contamination from weathering, the outermost 1-2 cm of the rock samples were cut away. The samples were then cleaned in an ultrasonic bath prior to powdering them with a shatter box using an alumina dish. These bulk rock powders were subsequently analyzed for their carbon and sulfur geochemistry.

Sulfur geochemistry:

We determined the isotopic composition and contents of the acid volatile sulfide (AVS or also referred to elsewhere as the monosulfide fraction), chromium reducible sulfide (CRS or also called disulfide fraction) and the sulfate. Sulfur extractions were performed following a modified version of the methods of Canfield et al. (1986). Acid volatile sulfide was first extracted by reacting 20-25g of bulk rock powder with 6N HCl in an inert N₂-atmosphere. The residual sample was then reacted with an acidified $CrCl_2$ solution to extract the chromium-reducible sulfide. In both cases the liberated H₂S was precipitated as ZnS in a zinc acetate solution and subsequently converted to Ag_2S through reaction with a 0.1M $AgNO_3$ solution. The sulfate fraction was recovered by reacting the solution from the AVS extraction with $BaCl_2$ to form $BaSO_4$. The amounts of AVS, CRS and sulfate were determined gravimetrically and were subsequently corrected based on the sulfur content of the precipitate as determined on the EA, since co-precipitation of other phases during the wet chemical extraction could not be completely prevented.

The isotopic composition of the AVS, CRS and sulfate were determined on a Vario ISOTOPE EA attached to an Isoprime 100 IRMS. To ensure complete combustion during EA-analyzes, vanadium pentoxide (V_2O_5) was added to the samples. Sulfur isotope values are reported in standard delta-notation relative to the Vienna-Canyon Diablo Troilite (V-CDT) standard. During measurements the international sulfide (A_2S) standards IAEA-S-1 (A_3S) and IAEA-S-2 (A_3S) and IAEA-S-3 (A_3S) and the sulfate (A_3S) standards IAEA-S-3 (A_3S) and IAEA-S-3 (A_3S) and IAEA-S-3 (A_3S) were used to place our samples on the V-CDT scale. Reproducibility is better than 0.2% for all sulfur analyses (samples and standards), and the relative precision of sulfur contents is within 3%.

Data Processing Description

Total sulfide = S content AVS + S content CRS

Total sulfur content = S content AVS + S content CRS + Sulfate

Detection limits:

Sulfide and sulfate contents: Determined by the sulfur extraction procedure and the total amount available to perform bulk rock sulfur extractions. Approximately 4ppm

BCO-DMO Processing:

- moved group/sample type into its own column;
- replaced "n.d." with nd and "<1.o.d." with BDL;
- replaced spaces with underscores;
- replaced commas with semi-colons;
- removed % signs from data column "degre of serpentinization";
- modified parameter names to conform with BCO-DMO naming conventions.

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Data Files

File

table3.csv(Comma Separated Values (.csv), 3.62 KB)
MD5:5c451860d6a81d5f5d6caf70b8a0ce89

Primary data file for dataset ID 663969

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Parameters

| Parameter | Description | Units |
|----------------------------|--|----------------------------------|
| sample_group | Sample group/type | unitless |
| sample_name | Sample name | unitless |
| lat | Latitude; positive values = North | decimal degrees |
| lon | Longitude; positive values = East | decimal degrees |
| description | Sample description | unitless |
| degree_of_serpentinization | Degree of serpentinization (percent) | unitless |
| S_content_AVS | Sulfur concentration of the Acid volaltile sulfur (AVS) fraction of the bulk rock | parts per million (ppm) |
| S_content_CRS | Sulfur concentration of the chromium reduceable sulfur (CRS) fraction of the bulk rock | parts per million (ppm) |
| total_sulfide | Total sulfide | parts per million (ppm) |
| S_content_sulfate | Sulfur content of sulfate | parts per million (ppm) |
| total_S_content | Total sulfur content | parts per million (ppm) |
| SO4_to_total_sulfur | Ratio of SO4 to total sulfur | unitless |
| delta34S_AVS | Delta 34S of AVS relative to the V-CDT (Vienna Canon Diablo Troilite) standard | per mille |
| delta34S_CRS | Delta 34S CRS relative to the V-CDT (Vienna Canon Diablo Troilite) standard | per mille |
| delta34S_sulfate | Delta 34S of sulfate relative to the V-CDT (Vienna Canon Diablo Troilite) standard | per mille |

| mineralogy | Sulfide/metal mineralogy: dissem. sulfides = disseminated sulfides; ptl = pentlandite; po = pyrrhotite; hz = heazlewoodite; mgt = magnetite; aw = awaruite; cc = chalcocite; cp = chalcopyrite; bn = bornite; cub = cubanite; sm = smythite; vl = violarite; sug = suggakiite; sam = samaniite; Cu = native Cu or Cu-Fe-Ni alloys; (Santa Elena data from Schwarzenbach et al., 2014; Voltri Massif data from Schwarzenbach, 2011) | unitless |
|------------|--|----------|
| | 2011) | |

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Instruments

| Dataset- specific Instrument Name | Vario ISOTOPE elemental analyzer |
|--|---|
| Generic Instrument Name | Elemental Analyzer |
| Dataset- specific Description | TC contents, d13CTC and d13CTOC were determined on a Vario ISOTOPE elemental analyzer (EA) coupled to an Isoprime 100 isotope ratio mass spectrometer (IRMS). |
| Generic Instrument Description | Instruments that quantify carbon, nitrogen and sometimes other elements by combusting the sample at very high temperature and assaying the resulting gaseous oxides. Usually used for samples including organic material. |

| Dataset- specific Instrument Name | Isoprime 100 |
|--|--|
| Generic Instrument Name | Isotope-ratio Mass Spectrometer |
| Dataset- specific Description | TC contents, d13CTC and d13CTOC were determined on a Vario ISOTOPE elemental analyzer (EA) coupled to an Isoprime 100 isotope ratio mass spectrometer (IRMS). The d13CTIC and d18OTIC and TIC contents were analyzed on a MultiFlowGeo headspace sampler attached to an Isoprime 100 IRMS. |
| | The Isotope-ratio Mass Spectrometer is a particular type of mass spectrometer used to measure the relative abundance of isotopes in a given sample (e.g. VG Prism II Isotope Ratio Mass-Spectrometer). |

| Dataset-specific Instrument Name | Rigaku MiniFlex XRD | |
|--------------------------------------|--|--|
| Generic Instrument Name | X-ray diffractometer | |
| Dataset-specific Description | The mineralogy of the carbonates was then determined by X-ray diffraction on a Rigaku MiniFlex XRD using the powder diffraction analysis package PDXL. | |
| Generic Instrument Description | Instruments that identify crystalline solids by measuring the characteristic spaces between layers of atoms or molecules in a crystal. | |

Deployments

JRES-149

| Website | https://www.bco-dmo.org/deployment/663681 | |
|------------|--|--|
| Platform | R/V JOIDES Resolution | |
| Report | http://dmoserv3.whoi.edu/data_docs/C-DEBI/cruise_reports/149PREL.PDF | |
| Start Date | 1993-03-10 | |
| End Date | 1993-05-25 | |

IRES-173

| Website | https://www.bco-dmo.org/deployment/663682 | |
|-----------------|--|--|
| Platform | R/V JOIDES Resolution | |
| Report | http://dmoserv3.whoi.edu/data_docs/C-DEBI/cruise_reports/173prel.PDF | |
| Start Date | 1997-04-15 | |
| End Date | 1997-06-15 | |

JRES-209

| Website | https://www.bco-dmo.org/deployment/663685 | |
|-----------------|--|--|
| Platform | R/V JOIDES Resolution | |
| Report | http://dmoserv3.whoi.edu/data_docs/C-DEBI/cruise_reports/209PREL.PDF | |
| Start Date | 2003-05-06 | |
| End Date | 2003-07-03 | |

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Project Information

Identifying the controls on biological activity in serpentinites (Controls on biological activity)

Coverage: Costa Rica; Mid-Atlantic Ridge; Iberian Margin

Project description from C-DEBI:

Serpentinization – the hydrothermal alteration of ultramafic rocks – is a unique mineralogical process that results in H2 and CH4 – rich fluids that can support microbial communities. Using a combination of petrographic observations, bulk rock and *in-situ* sulfur isotope signatures of variably serpentinized peridotites from four different geotectonic environments we provide new constraints on the factors that support microbial activity. The studied samples overall suggest that redox conditions reflected by the presence of pyrite and pyrrhotite represent the fluid chemistry that favors microbial activity. This fluid chemistry, i.e., the prevailing hydrogen and sulfur fugacities of the fluid, are thereby correlated to high water-rock ratios and increased incorporation of seawater-derived species such as sulfate and carbonate. These species serve as major energy sources of microbial activity. In contrast, highly reducing conditions and limited fluid input limits or even prevents microbial activity within serpentinites due to insufficient availability of these species. Interaction with carbonate and sulfate-bearing meteoric waters is likely an essential process that supports microbial activity in continental serpentinization environments. Overall, this study shows that apart from fluid temperatures being within the limits of life, the fluid chemistry (redox conditions and availability of e.g. carbonate and sulfate) are the primary factors that control the presence or absence of microbial communities within serpentinizing peridotites. This study highlights the importance of combining bulk rock and *in-situ* stable

isotope data with petrographic and mineralogical observations in order to better constraint the presence of microbial communities within the subsurface of peridotite-hosted hydrothermal systems.

Note: This project was funded by a C-DEBI Research Grant.

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Program Information

Center for Dark Energy Biosphere Investigations (C-DEBI)

Website: http://www.darkenergybiosphere.org

Coverage: Global

The mission of the Center for Dark Energy Biosphere Investigations (C-DEBI) is to explore life beneath the seafloor and make transformative discoveries that advance science, benefit society, and inspire people of all ages and origins.

C-DEBI provides a framework for a large, multi-disciplinary group of scientists to pursue fundamental questions about life deep in the sub-surface environment of Earth. The fundamental science questions of C-DEBI involve exploration and discovery, uncovering the processes that constrain the sub-surface biosphere below the oceans, and implications to the Earth system. What type of life exists in this deep biosphere, how much, and how is it distributed and dispersed? What are the physical-chemical conditions that promote or limit life? What are the important oxidation-reduction processes and are they unique or important to humankind? How does this biosphere influence global energy and material cycles, particularly the carbon cycle? Finally, can we discern how such life evolved in geological settings beneath the ocean floor, and how this might relate to ideas about the origin of life on our planet?

C-DEBI's scientific goals are pursued with a combination of approaches:

- (1) coordinate, integrate, support, and extend the research associated with four major programs—Juan de Fuca Ridge flank (JdF), South Pacific Gyre (SPG), North Pond (NP), and Dorado Outcrop (DO)—and other field sites;
- (2) make substantial investments of resources to support field, laboratory, analytical, and modeling studies of the deep subseafloor ecosystems;
- (3) facilitate and encourage synthesis and thematic understanding of submarine microbiological processes, through funding of scientific and technical activities, coordination and hosting of meetings and workshops, and support of (mostly junior) researchers and graduate students; and
- (4) entrain, educate, inspire, and mentor an interdisciplinary community of researchers and educators, with an emphasis on undergraduate and graduate students and early-career scientists.

Note: Katrina Edwards was a former PI of C-DEBI; James Cowen is a former co-PI.

Data Management:

C-DEBI is committed to ensuring all the data generated are publically available and deposited in a data repository for long-term storage as stated in their <u>Data Management Plan (PDF)</u> and in compliance with the <u>NSF Ocean Sciences Sample and Data Policy</u>. The data types and products resulting from C-DEBI-supported research include a wide variety of geophysical, geological, geochemical, and biological information, in addition to education and outreach materials, technical documents, and samples. All data and information generated by C-DEBI-supported research projects are required to be made publically available either following publication of research results or within two (2) years of data generation.

To ensure preservation and dissemination of the diverse data-types generated, C-DEBI researchers are working with BCO-DMO Data Managers make data publicly available online. The partnership with BCO-DMO helps ensure that the C-DEBI data are discoverable and available for reuse. Some C-DEBI data is better served by specialized repositories (NCBI's GenBank for sequence data, for example) and, in those cases, BCO-DMO provides dataset documentation (metadata) that includes links to those external repositories.

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Funding

| Funding Source | Award |
|--|-------------|
| NSF Division of Ocean Sciences (NSF OCE) | OCE-0939564 |

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