

## Grant Submission Document

### Project Title:

H<sub>2</sub>S sequestration into geothermal systems

### The number and name of the WP the proposal refers to

**WP6 – Sustainability – Environment**  
**Task 6.3: Mitigation of environmental impact**

### Project Coordinator/ Managing Entity

**Organization:** University of Iceland

**Name of Coordinator:** Andri Stefánsson  
**Phone / email:** +354-525 4252 /as@hi.is

**Name of Finance Manager:** Sigurður Guðnason  
**Phone / email:** +354-525 4800 /sgud@raunvis.hi.is

### Other Participants

**Organization:** Reykjavík Energy  
**Name of contact person:** Ingvi Gunnarsson  
**Phone / email:** +354-516 6000/ingvi.gunnarsson@or.is

**Organization:** Landsvirkjun  
**Name of contact person:** Sigurður H. Markússon  
**Phone / email:** +354-515 4000/sigurdurm@lv.is

**Organization:** MIT, USA  
**Name of contact person:** Shuhei Ono  
**Phone / email:** +617-253 0474/sono@mit.edu

### Project Key Words

H<sub>2</sub>S, sequestration, feasibility, geochemistry

### Project Abstract

H<sub>2</sub>S is commonly emitted into the atmosphere from geothermal power plants, causing potential environmental problems. One possibility disposal method for H<sub>2</sub>S is injection back into the geothermal systems whereas H<sub>2</sub>S may mineralise forming sulphides. The project “H<sub>2</sub>S sequestration into geothermal systems” aims at defining the geochemistry of geothermal H<sub>2</sub>S sequestration and its geochemical feasibility. Emphasis will be made on studying the rate of H<sub>2</sub>S mineralization, possible oxidation to sulphuric acid and together with geochemical modelling assess the optimal conditions of H<sub>2</sub>S disposal. The project is a joint effort between scientists that have contributed to this subject in years passed.

## Eligibility Rules

For application to be eligible the following points shall be kept in mind.

- *The proposal needs to be submitted no later than 23:00 GMT on November 20<sup>th</sup> 2011*
- *The Coordinator of the proposal needs to be GEORG participant.*
- *The Grant submission document shall neither exceed 10 pages (including front page, this page, figures, tables and references, but excluding cv's) nor shall it exceed the maximum number of words for each section of the document.*
- *The budget plan shall be prepared and demonstrated according to Section I- Chapter 6 of the "Proposal & Award Policies & Procedures Guide" for the 4<sup>th</sup> Call.*
- *The proposal shall address clearly problems and questions of importance for development of the geothermal sector. For information on GEORGs objectives please find GEORG - WP description at [www.georg.hi.is](http://www.georg.hi.is)*

### Eligibility check list:

	Yes	No
<i>Is the coordinator of the proposal a GEORG participant?</i>		
<i>Does the proposal follow all applied rules regarding format of the proposal?</i>		
<i>Does the proposal follow all applied rules regarding the budget</i>		
<i>Does the proposal address clearly problems and questions of importance for development of the geothermal sector?</i>		
<i>Is the proposal, incl. all required appendixes, submitted in due time?</i>		

**Proposal that do not fulfill the eligibility rules listed above will not be evaluated by the Review Committee.**

## **Project description**

### ***General descriptions***

Hydrogen sulphide (H<sub>2</sub>S) is among the major components in geothermal fluids, with concentrations ranging from a few ppb to levels of hundreds of ppm (Arnórsson 1995a, 1995b). Hydrogen sulphide is volatile and is commonly emitted into the atmosphere from geothermal power plants, causing potential environmental problems.

Several methods are employed in cleaning H<sub>2</sub>S emissions including oxidation to form elemental sulphur or sulphuric acid (Sanopoulos and Karabelas, 1997). One method includes injection of H<sub>2</sub>S into geothermal systems where it may be mineralized into sulphides including pyrite. Reykjavík Energy and Landsvirkjun, Iceland, are currently considering such an injection into the geothermal system at Hellisheidi, Námafjall and Krafla, where geothermal gas (CO<sub>2</sub>, H<sub>2</sub>S, N<sub>2</sub> and H<sub>2</sub>) will be separated in a gas abatement station and the H<sub>2</sub>S (+CO<sub>2</sub>) stream mixed at the surface with water prior to injection into the geothermal aquifer.

It is generally accepted that the major elemental composition including H<sub>2</sub>S concentration of geothermal fluids is controlled by local equilibrium with common secondary minerals (e.g. Giggenbach, 1980, 1981; Arnórsson et al., 1983; Stefánsson and Arnórsson, 2000; Gudmundsson and Arnórsson, 2005) including pyrite, pyrrhotite, prehnite and epidote as well as possibly magnetite (Stefánsson and Arnórsson, 2002). Therefore, elevated H<sub>2</sub>S concentrations may lead to sulphide mineralization as well as some iron oxide and aluminium silicate formation. However, the exact response of the system, including the rate and quantity of H<sub>2</sub>S mineralization, redox reactions and the associated fluid chemistry, is somewhat unclear.

Previous work on volatile gas disposal has mainly focused on reaction modelling and experiments regarding CO<sub>2</sub> (e.g. Gunter et al., 2000; Johnson et al., 2001; McPherson and Lichtner, 2001; Xu et al., 2004, 2005, 2006, 2007; Knauss et al., 2005; White et al., 2005; Zerai et al., 2006; Jacquemet et al., 2008; Palandri and Kharaka, 2008; Gessner et al., 2009; Crandell et al., 2010; Gysi and Stefánsson, 2011). Less is known about H<sub>2</sub>S disposal under geothermal conditions. Based on geochemical modelling, Stefánsson et al. (2011) concluded that the optimal conditions for H<sub>2</sub>S sequestration into geothermal systems are temperatures between 200-250°C whereas mineralization rates may be assumed fast and most of the Fe<sup>2+</sup> goes into pyrite formation. Some key questions still need to be answered including the effect of H<sub>2</sub>S supply (*p*H<sub>2</sub>S) on the fluid–rock interaction, rate and mechanism of H<sub>2</sub>S mineralization, and possible oxidation of H<sub>2</sub>S to sulphuric acid under geothermal conditions.

The focus of the proposed project will be twofold. Firstly, laboratory experiments will be conducted to study the interaction of H<sub>2</sub>S-rich water with basalt and rhyolite. Based on this, the reaction path, H<sub>2</sub>S mineralization rate and possible H<sub>2</sub>S oxidation rate will be studied. Secondly, using data obtained in the first part, data on fluid composition and secondary mineralogy from selected geothermal systems and geochemical modelling, the optimal conditions for H<sub>2</sub>S sequestration into geothermal systems will be studied.

Here the group seeks funding from GEORG to co-finance the project including experimental running cost and salaries for a Ph.D. student and a young scientist.

## ***Scientific – and/or Technical Merit***

Environmental effects of power production constitute some of the most serious environmental problems of today. Geothermal energy production is generally regarded relatively environmentally friendly, yet the anthropogenic emissions from geothermal power plants cannot be regarded negligible. This includes emission of gases like H<sub>2</sub>S (Axtmann, 1975a,b; Bargagli et al., 1997; Kristmannsdóttir and Ármannsson, 2003; Rybach, 2003; Arnórsson, 2004; Ármannsson et al., 2005, 2008; Daysh and Chrisp, 2009).

In recent years considerable focus has been on making geothermal utilization more environmental friendly. Among the main tasks posed on the industry in Iceland are regulations regarding H<sub>2</sub>S emission and atmospheric concentrations ([www.idnadarraduneyti.is/](http://www.idnadarraduneyti.is/) og [www.umhverfisraduneyti.is/](http://www.umhverfisraduneyti.is/)). Four main approaches have been suggested in order to clean H<sub>2</sub>S emissions from geothermal power plants: (1) the Claus process, (2) liquid redox sulfur recovery (LRSR) processes, (3) the burn/scrub process and (4) water absorption and injection (Trimeric Corp., 2011). The first three processes are well established but expensive to set up and run resulting in increased energy prices. The last method involves mixing the H<sub>2</sub>S with water at surface and injecting it into the geothermal system. This approach has never been tried before but preliminary studies indicate the cost to be considerably less compared to the other methods. However, the geochemical aspects of H<sub>2</sub>S sequestration into geothermal systems are somewhat unclear.

Based on geochemical modelling, Stefánsson et al. (2011) concluded that the optimal geochemical conditions for H<sub>2</sub>S sequestration into the Hellisheidi geothermal system, Iceland, are <250°C whereas injection into higher temperatures may result in insufficient mass of mineralization of sulfides. However, some basic questions are still unanswered including the rate (efficiency) of mineralization and possible oxidation of H<sub>2</sub>S to sulphuric acid. The latter may result in the formation of acid reservoir fluids (pH<3) with serious consequences for production. To address these problems more knowledge is needed on the basic geochemistry of H<sub>2</sub>S-water-rock interaction, such information obtained by performing controlled laboratory experiments.

One of the main focuses of the proposed project is to apply recently developed experimental methods that have been successfully applied for studying CO<sub>2</sub>-water-rock interaction and CO<sub>2</sub> sequestration using batch and plug flow reactors. Using similar setup for studying H<sub>2</sub>S-water-rock interaction information on reaction path, possible H<sub>2</sub>S oxidation and H<sub>2</sub>S mineralization rates may be obtained. The results obtained provide the fundamental input for geochemical modelling used to optimize H<sub>2</sub>S sequestration conditions, i.e. *p*H<sub>2</sub>S, temperature, injection water type (cold water, condensed steam or waste water) etc. The project is further intended to bring together experienced scientists working within the field of geothermal chemistry and the geothermal industry, a fruitful training environment for young scientists and students within the institutes of the applicants as well as providing a possible platform for future work and discussion on the chemical impact of geothermal power production in Iceland and elsewhere.

## ***Innovation / Entrepreneurship***

The innovative character of the proposed project is to define the geochemical aspects and geochemical feasibility of H<sub>2</sub>S sequestration into high-temperature geothermal systems. This in turn can be combined with chemical engineering and knowledge of the structure, temperature and hydrology of a given

geothermal system to facilitate H<sub>2</sub>S disposal. The detailed knowledge and methods on H<sub>2</sub>S sequestration into geothermal systems will hopefully become acknowledged and if proven to be successful may provide the bases of possibly the easiest and cheapest way in the future for H<sub>2</sub>S disposal from geothermal.

The main entrepreneurship involves the geochemical assessment and feasibility of H<sub>2</sub>S sequestration into geothermal systems. Such a disposal method for H<sub>2</sub>S, if successful, is likely to be relatively simple and inexpensive than more common methods applied in geothermal with possible important influences on energy prices.

It is our hope that the results of the project will promote the position of geothermal power production worldwide as a green energy alternative as well as placing Icelandic companies and scientists in forefront in environmental issues related to geothermal power production.

### ***Education / Dissemination***

Currently one graduate student at the M.Sc. level and one postdoctoral researcher are working on the geochemistry of H<sub>2</sub>S in geothermal systems. This includes Jóhann Gunnarsson Robin (M.Sc student, H<sub>2</sub>S chemistry in geothermal fluids at Krafla, University of Iceland) and Nicole S. Keller (Postdoctoral Source and fate of sulfur in geothermal systems traced by sulphur isotopes, University of Iceland).

Here the group seeks funding from GEORG to co-finance the project including salaries for a new Ph.D. student, postdoctoral researcher and running cost for direct study of the geochemistry of H<sub>2</sub>S and geochemical feasibility of H<sub>2</sub>S sequestration in geothermal systems.

### ***Managerial***

The participating group of institutions comprises University of Iceland (UI), MIT, USA (MIT), Reykjavik Energy (OR), and Landsvirkjun (LV). Access to sampling and instrumental facilities (UI, MIT), data on fluid composition (UI, OR, LV) and access to geothermal power plants and sites (OR, LV) is guaranteed. The research group consists of highly experienced scientists within the field of geothermal fluid geochemistry that is currently working on H<sub>2</sub>S sequestration into geothermal systems at Hellisheidi and Námafjall. The Science Institute, University of Iceland (UI) head office will be responsible for the financial management of the project.

The main leaders of the research project are: from UI: Andri Stefansson, associated professor in geothermal geochemistry; from MIT: Shuhei Ono, professor of isotope and sulphur geochemistry; from OR: Ingvi Gunnarsson, scientist; from LV: Sigurdur H. Markússon, project manager. The group will have access to other scientists and technical help within their institutions. The students and postdoctoral scientists involved in the project include Jóhann Gunnarsson Robin (UI) and Nicole Keller (UI). In addition a young scientist will be incorporated into the project.

It is our believe that there is good opportunity at the moment to continue working on H<sub>2</sub>S sequestration into geothermal systems as a possible method for H<sub>2</sub>S disposal. Reykjavik Energy has worked on this problem for several years and Landsvirkjun has made the first steps as well. However, there are still unanswered questions particularly related to the geochemistry of H<sub>2</sub>S sequestration. In addition, the proposed project will involve a joint effort of researchers and students and hopefully result in well trained geothermal geochemists for the future.

## Financing:

Cost item		Requested funding		Other financing		Total
2012/2013	Salaries					14'250
	Operational expenses					1'500
	Travel expenses					0
	<b>Total 2012/2013:</b>	7'150	45%	8'600	55%	15'750
2013/2014	Salaries					14'250
	Operational expenses					1'500
	Travel expenses					350
	<b>Total 2013/2014:</b>	7'500	47%	8'600	53%	16'100
2014/2015	Salaries					14'250
	Operational expenses					1'500
	Travel expenses					350
	<b>Total 2014/2015:</b>	7'500	47%	8'600	53%	16'100
<b>Grand Total</b>		<b>22'150</b>	<b>46%</b>	<b>25'800</b>	<b>54%</b>	<b>47'950</b>

Consortium: UI, RE, LV, MIT  
 Name of Project: H<sub>2</sub>S sequestration into geothermal systems

ISK '000	Year	Unit cost	Year 1 2012/2013		Year 2 2013/2014		Year 3 2014/2015		Grand Total
			Man-months	Total	Man-months	Total	Man-months	Total	
<b>Salaries including overhead</b>									
UI	PhD student	450	12	5'400	12	5'400	12	5'400	16'200
UI	Postdoc	550	12	6'600	12	6'600	12	6'600	19'800
UI	AS	900	1	900	1	900	1	900	2'700
RE	IG	900	1	450	1	450	1	450	1'350
LV	SHM	900	1	450	1	450	1	450	1'350
MIT	SO	900	1	450	1	450	1	450	1'350
<b>Total</b>			27	14'250	27	14'250	27	14'250	42'750
<b>Operational exp.</b>									
a Experimental apparatus maintainance				500		500		500	1'500
b Chemical analysis				1'000		1'000		1'000	3'000
c									0
<b>Total</b>				1'500		1'500		1'500	4'500
<b>Travel expenses</b>									
a Conferences						350		350	700
b									0
c									0
<b>Total</b>			0			350		350	700
<b>Total cost</b>				15'750		16'100		16'100	47'950
<b>Financing</b>									
a Rannis, LV-grant and UI-grant				6'350		6'350		6'350	19'050
b UI, RE, LV, MIT				2'250		2'250		2'250	6'750
<b>Total other financing</b>				8'600	55%	8'600	53%	8'600	25'800
<b>Requested funding from GEORG</b>				7'150	45%	7'500	47%	7'500	22'150
<b>Total financing</b>				15'750		16'100		16'100	47'950
									100%

## **Explanation of cost:**

*Salaries:* The salaries of participants' contribution more than half a month per year are incorporated into the proposed project. Here we apply for covering salaries, including overhead cost, of a PhD student and a young scientist for 3 years.

*Operational expenses:* The experimental apparatus maintenance and chemical analysis include all running cost for experiments and shipment for analysis to MIT, USA. It should be pointed out that the value of the equipment itself is estimated >25 m.kr, not included here.

*Travel expenses:* The travel expenses include two conferences in 2013 and 2014.

## **Work plan and time schedule:**

The project involves three major tasks. These are

### *WP 6.3 – H<sub>2</sub>S oxidation under geothermal conditions*

This subtask will involve experimental work on the oxidation rate of H<sub>2</sub>S during water-rock interaction under geothermal conditions (150-300°C) as a function of  $p_{\text{H}_2\text{S}}$  and  $p_{\text{H}_2}$ . It is intended to perform experiments using a mixed-flow reactor on the interaction of H<sub>2</sub>S-rich fluids with basalts and rhyolites. From the results, the stability and possible oxidation rates of H<sub>2</sub>S may be assessed

### *WP 6.3 H<sub>2</sub>S-water-rock interaction and H<sub>2</sub>S mineralization rate*

This subtask will involve experimental work on the interaction of H<sub>2</sub>S-rich fluids with basalts and rhyolites as a function of  $p_{\text{H}_2\text{S}}$  and  $p_{\text{H}_2}$  and under geothermal conditions (150-300°C). The experiments will be carried out in batch type reactors and the secondary mineralogy and fluid chemistry studied as a function of time. From the results, the reaction path of H<sub>2</sub>S-water-rock interaction and H<sub>2</sub>S mineralization rates may be assessed. The experimental work will be complemented with geochemical simulations.

### *WP6.3 – H<sub>2</sub>S geochemistry and sequestration into geothermal systems*

This subtask aims at gathering data on fluid composition and secondary mineralogy in selected geothermal systems in Iceland, Krafla, Námafjall and Hellisheidi. Combined with the results on H<sub>2</sub>S-water-rock interaction and H<sub>2</sub>S oxidation rates obtained in the first two tasks of this study the geochemical behaviour and feasibility of H<sub>2</sub>S sequestration into geothermal systems will be evaluated.

***Time schedule:***

<b>Subtask</b>	<b>Start</b>	<b>Finish</b>	<b>Deliverable/Milestone</b>
H <sub>2</sub> S oxidation under geothermal conditions	01/01/12	01/01/14	Rate of H <sub>2</sub> S oxidation
H <sub>2</sub> S-water-rock interaction and H <sub>2</sub> S mineralization rate	01/01/12	01/01/14	Rate of H <sub>2</sub> S mineralization
H <sub>2</sub> S geochemistry and sequestration into geothermal systems	01/01/12	01/01/15	Geochemical feasibility of H <sub>2</sub> S sequestration into geothermal systems
Writing and introduction of the results	01/01/13	01/01/15	Introduction and publication of the results

## Appendix I Applicant CV

**Name:** Andri Stefánsson  
**Date of birth:** 22.12.1972  
**Nationality:** Icelandic  
**Work address:** Institute of Earth Sciences, University of Iceland  
 Sturlugata 7, 101 Reykjavík, Iceland  
**Work Tel:** +354-525 4252  
**E-mail:** as@hi.is



### Higher education

1992-1994 University of Glasgow. Major in Geography and Chemistry  
 1994-1996 University of Iceland. B.Sc. with major in Geology.  
 1996-1998 University of Iceland. M.Sc. in Geochemistry.  
 1998-2002 ETH Zurich, Switzerland. Ph.D. in Geochemistry.

### Professional and research experience

2010- Visiting Research Professor, LMTG, CNRS/Univ. Toulouse/Obs. Midi-Pyr., France.  
 2009- Associated Professor, Institute of Earth Sciences, University of Iceland  
 2002- Research scientist, Institute of Earth Sciences, University of Iceland.  
 2002- Geothermal Geochemistry Consulting  
 2006- Teacher of geothermal geochemistry at University of Akureyri, RES Iceland, UNU.

### Selected recent publications

- Stefánsson, A.,** Arnórsson, S., Gunnarsson, I., Kaasalainen, H., Gunnlaugsson, E. (2011) The geochemistry and sequestration of H<sub>2</sub>S into the geothermal system at Hellisheidi, Iceland. *J. Volc. Geotherm. Res.* 202, 179-188.
- Gysi, A.P., **Stefánsson, A.** (2011) CO<sub>2</sub>-water-basalt interaction. Numerical simulation of low temperature CO(2) sequestration into basalts. *Geochim. Cosmochim. Acta* 75, 4728-4751.
- Kaasalainen H., **Stefánsson A.** (2011) Sulfur speciation in natural hydrothermal waters, Iceland, *Geochim. Cosmochim. Acta* 75, 2777-2791.
- Stefánsson, A.** and Seward T.M. (2008) The hydrolysis of iron(III) in hydrothermal solutions. *Chemical Geology* 249, 227-245.
- Arnórsson, S., **Stefánsson, A.**, and Bjarnason, J.Ö. (2007) Fluid-fluid equilibria in geothermal systems. *Rev. Min. Geochem.* 65, 259-312.
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- Stefánsson, A.,** and Seward, T.M. (2004) Gold(I) complexing in aqueous sulphide solutions to 500°C at 500 bar. *Geochimica et Cosmochimica Acta* 68, 4121-4143.
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- Stefánsson, A.,** Gíslason, S.R., and Arnórsson, S. (2001) Dissolution of primary minerals of basalt in natural waters II. Mineral saturation state. *Chemical Geology* 172, 251-276.

## Curriculum Vitae

### Personal information

Name: Ingvi Gunnarsson  
Date of birth: 12.08.1971  
Home address: Prastarhöfði 59  
270 Mosfellsbær  
Iceland  
  
Work address: Reykjavík Energy  
Bæjarhálsi 1  
110 Reykjavík  
Iceland  
  
Work Tel: +354-5166000  
Fax: +354-5166008  
E-mail: ingvi.gunnarsson@or.is

### Higher education

1993-1997 University of Iceland. B.Sc. in Geology  
1997-1999 University of Iceland. M.Sc in Geochemistry

### Professional and research experience

2008-present Geochemist at Reykjavík Energy  
1999-2008 Research scientists and teacher at Science Institute University of Iceland.  
1996-1999 Research assistant, Science institute, University of Iceland, for Prof. Stefán Arnórsson and Dr. Sigurður R. Gíslason.

### Selected Publications

- Gunnarsson I, Sigfússon B, Stefánsson A, Arnórsson S, Scott SW and Gunnlaugsson, E (2011) Injection of H<sub>2</sub>S from Hellisheiði power plant, Iceland. Proceedings Thirty-Sixth Workshop on Geothermal Reservoir Engineering, Stanford.
- Arnórsson, S., Bjarnason, JO., Giroud N., **Gunnarsson, I.** and Stefánsson A. (2006) Sampling and analysis of geothermal fluids. *Geofluids*. 6 (3), 203-216.
- Gunnarsson, I.**, Arnórsson, S. and Jakobsson, S. (2005) Precipitation of poorly crystalline antigorite under hydrothermal conditions. *Geochimica et Cosmochimica Acta* 69, 2813-2828.
- Gunnarsson, I.** and Arnórsson, S. (2005) Impact of silica scaling on the efficiency of heat extraction from high-temperature geothermal fluids. *Geothermics* 34. 320-329.
- Arnórsson, S., **Gunnarsson, I.**, Stefánsson, A., Andréadóttir, A., and Sveinbjörnsdóttir, Á.E. (2002) Major element chemistry of surface- and ground waters in basaltic terrain, N-Iceland. I. Primary mineral saturation. *Geochimica et Cosmochimica Acta* 66, 4015-4046.
- Gunnarsson I.** and Arnórsson S. (2000) Amorphous silica solubility and the thermodynamic properties of H<sub>4</sub>SiO<sub>4</sub> in the range of 0° to 350°C at P<sub>sat</sub>. *Geochim. Cosmochim. Acta* 64, 2295-2307.

CV

**Sigurður H. Markússon**

Landsvirkjun, Project manager - Geothermal

**Date of birth** 7. May 1980

**Address:** Þórðarsveigur 32, 113 Reykjavík

**e-mail:** sigurdurm@lv.is

Higher Education

2009 - 2010 Geochemistry – PhD program, Toulouse France

2007- 2009 Geochemistry – M.Sc. University of Iceland

2002-2006 Geology – B.Sc. University of Iceland

Professional Experience

2011 Landsvirkjun, Project manager - Geothermal

2010-2011 Efla, Geothermal

2006-2008 Efla, structural geology

**Selected publications**

Markússon, S. H. and Stefánsson, A. (2011) Geothermal surface alteration of basalts, Krysuvik Iceland-Alteration mineralogy, water chemistry and the effects of acid supply on the alteration process. *Journal of Volcanology and Geothermal Research*, v 206, p. 46–59.

Markússon, S. H., Stefánsson, A., Fridriksson, T., Acid sulfate alteration of basalts in active geothermal systems Krýsuvík, Iceland. *Geochimica et Cosmochimica Acta. Supplement, Volume 73*, p.A835. Goldschmidt jarðefnafræðiráðstefnan í Davos, Sviss. Júní 2009.

## **Shuhei Ono**

Assistant Professor of Geochemistry  
Earth, atmospheric and planetary sciences  
Massachusetts Institute of Technology  
E-34-254, 42-44 Carleton Street  
Cambridge MA 02139-4307, USA  
+617-253 0474  
e-mail: sono@mit.edu

## **Professional Preparation**

Waseda University (Tokyo) Geology B.S., 1994  
Waseda University (Tokyo) Economic Geology M.E., 1996  
Pennsylvania State University Geochemistry Ph.D., 2001  
Carnegie Institution of Washington Geochemistry Postdoc, 2002 -07

## **Appointments**

2007 - Assistant Professor, Earth, Atmospheric and Planetary Sciences-MIT  
2005 - 07 Agouron Geobiology Fellow  
2002 - 05 Carnegie Postdoctoral Fellow, Carnegie Institution of Washington

## **Selected recent publications**

- Bosak, T., Bush, J., Flynn, M., Liang, B., Ono, S., Petroff, A. P., and M.S. Sim (2010), Formation and stability of oxygen-rich bubbles that shape photosynthetic mats, *Geobiology* 8, 1-11
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