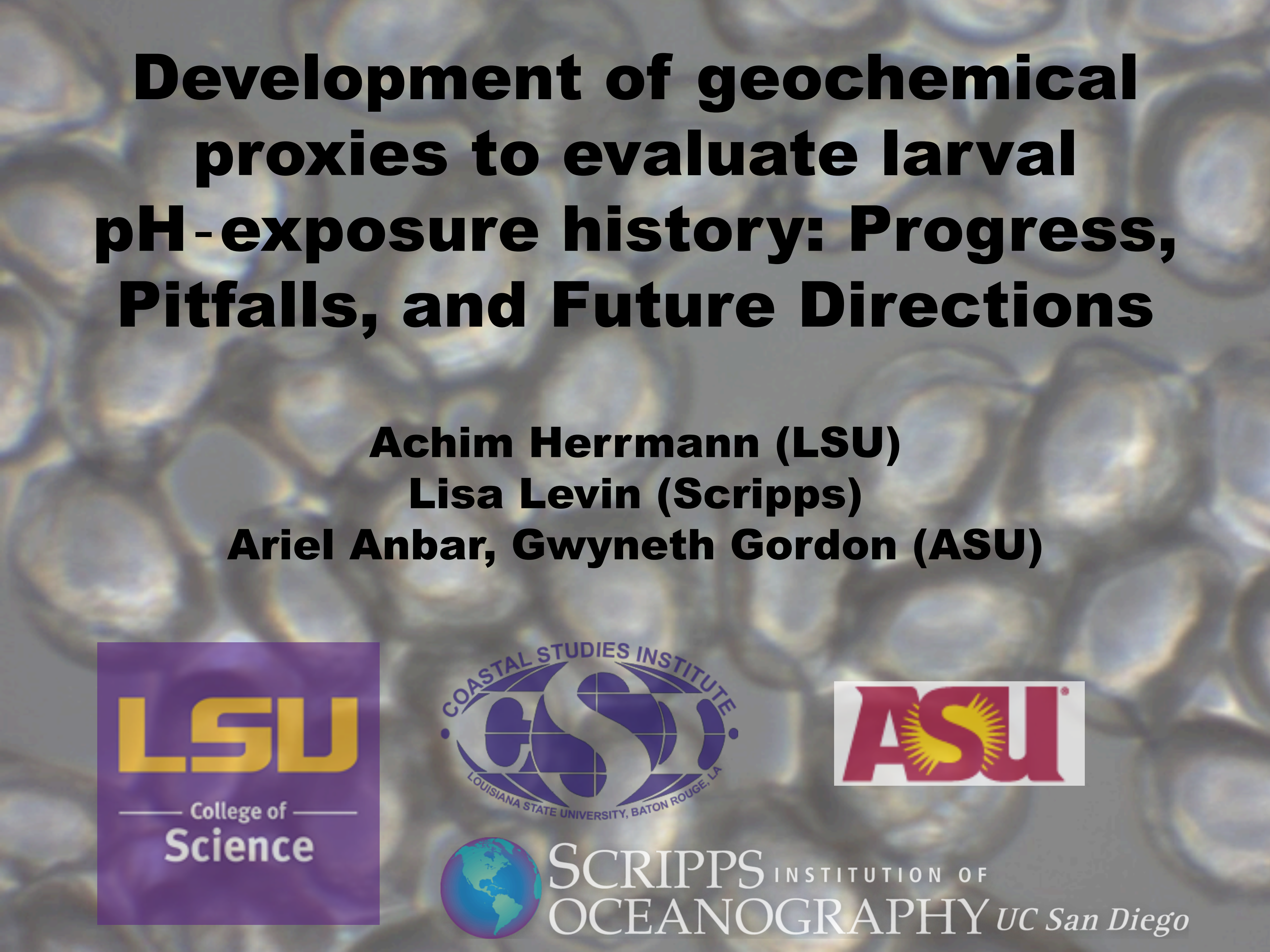
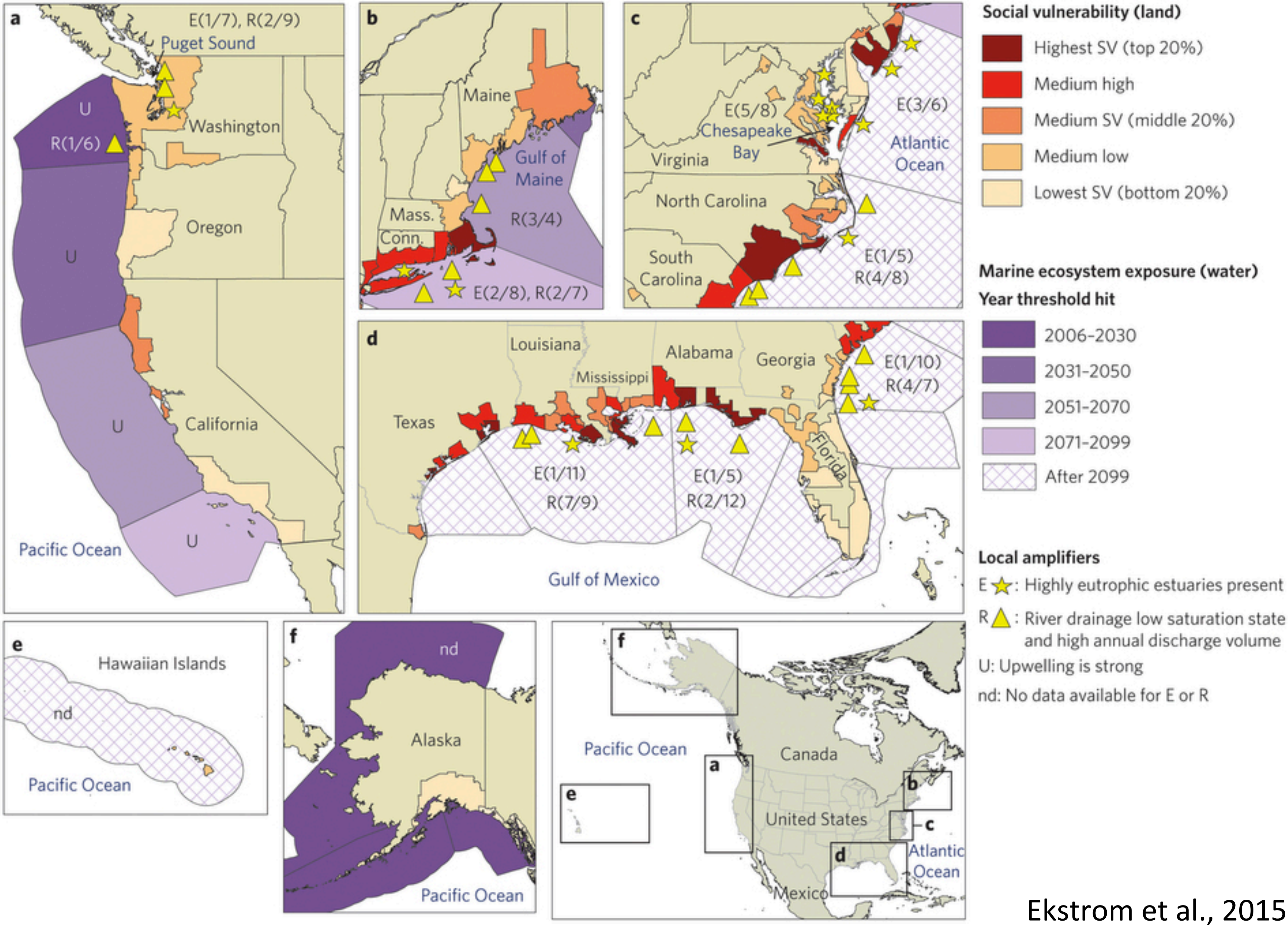


Development of geochemical proxies to evaluate larval pH-exposure history: Progress, Pitfalls, and Future Directions

Achim Herrmann (LSU)
Lisa Levin (Scripps)
Ariel Anbar, Gwyneth Gordon (ASU)

LSU College of Science
Coastal Studies Institute CSI Louisiana State University, Baton Rouge, LA
ASU
Scripps Institution of Oceanography UC San Diego



Ekstrom et al., 2015

Ocean acidification and the Permo-Triassic mass extinction

M. O. Clarkson,[1*†] S. A. Kasemann,[2] R. A. Wood,[1] T. M. Lenton,[3] S. J. Daines,[3] S. Richoz,[4] F. Ohnemueller,[2] A. Meixner,[2] S. W. Poulton,[5] E. T. Tipper[6]

Ocean acidification triggered by Siberian Trap volcanism was a possible kill mechanism for the Permo-Triassic Boundary mass extinction, but direct evidence for an acidification event is lacking. We present a high-resolution seawater pH record across this interval, using boron isotope data combined with a quantitative modeling approach. In the latest Permian, increased ocean alkalinity primed the Earth system with a low level of atmospheric CO_2 and a high ocean buffering capacity. The first phase of extinction was coincident with a slow injection of carbon into the atmosphere, and ocean pH remained stable. During the second extinction pulse, however, a rapid and large injection of carbon caused an abrupt acidification event that drove the preferential loss of heavily calcified marine biota.

The Permo-Triassic Boundary (PTB) mass extinction, at ~252 million years ago (Ma), represents the most catastrophic loss of biodiversity in geological history and played a major role in dictating the subsequent evolution of modern ecosystems (1). The PTB extinction event spanned ~60,000 years (2) and can be resolved into two distinct marine extinction pulses (3). The first occurred in the latest Permian [Extinction Pulse 1 (EP1)] and was followed by an interval of temporary recovery before the second pulse (EP2), which occurred in the earliest Triassic. The direct cause of the mass extinction is widely debated, with a diverse range of overlapping mechanisms proposed, including widespread water column anoxia (4), euxinia (5), global warming (6), and ocean acidification (7).

Models of PTB ocean acidification suggest that a massive and rapid release of CO_2 from Siberian Trap volcanism acidified the ocean (7). Indirect evidence for acidification comes from the interpretation of faunal turnover records (3, 8), potential dissolution surfaces (9), and Ca isotope data (7). A rapid input of carbon is also potentially recorded in the negative carbon isotope excur-
sion (CIE) that characteriz
(10, 11). The interpretation
however, debated (12–16) ar
tance to understanding th
anthropogenically driven oc

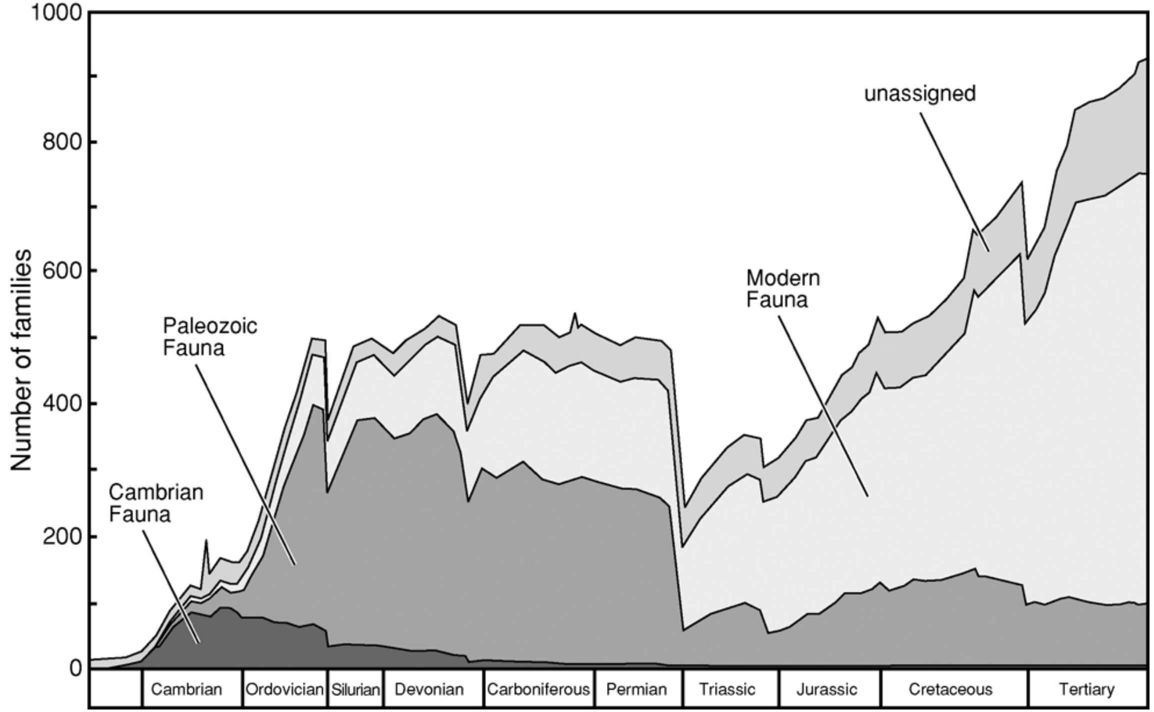
To test the ocean acidific
have constructed a proxy r
across the PTB using the bo
sition of marine carbonates
used a carbon cycle model (
to explore ocean carbonate
scenarios that are consisten
and published records of o
bance and environmental c
this combined geochemical, g
ing approach, we are able to
that encompasses the most r
which then allows us to re
chronological phases of car
tion, each with very different
sequences for the Late Perr
Earth system.

We analyzed boron and o
from two complementary tr
marine, open-water carbonat
United Arab Emirates (U.A
tional facies and stable ca
($\delta^{13}C$) are well constraine
PTB interval, the U.A.E. fo
carbonate platform that re
to the central Neo-Tethyan
Conodont stratigraphy and th
are used to constrain the age model (17).

The PTB in the Tethys is characterized by two negative $\delta^{13}C$ excursions interrupted by a short-term positive event (10). There is no consensus as to the cause of this "rebound" event and so we instead focus on the broader $\delta^{13}C$ trend. Our $\delta^{13}C$ transect (Fig. 1B) starts in the Changhsingian (Late Permian) with a gradual decreasing trend, interrupted by the first negative shift in $\delta^{13}C$ at EP1 (at 53 m, ~251.96 Ma) (Figs. 1B and 2). This is followed by the minor positive rebound event (at 54 m, ~251.95 Ma) (Figs. 1B and 2) before the minima of the second phase of the negative CIE (58 to 60 m, ~251.92 Ma) (Figs. 1B and 2) that marks the PTB itself. After the CIE minimum, $\delta^{13}C$ gradually increases to ~1.8 per mil (‰) and remains relatively stable during the earliest Triassic and across EP2.

Our boron isotope record shows a different pattern to the carbon isotope excursion. The boron isotope ratio ($\delta^{11}B$) is persistently low (Fig. 1C) at the start of our record during the late-Changhsingian, with an average of 10.9 ± 0.9‰ (1σ). This is in agreement with $\delta^{11}B$ values (average of 10.6 ± 0.6‰, 1σ) reported for early-

large drop in P_{CO_2}, and independent proxy data



After Sepkoski 1981 from Etter 2007

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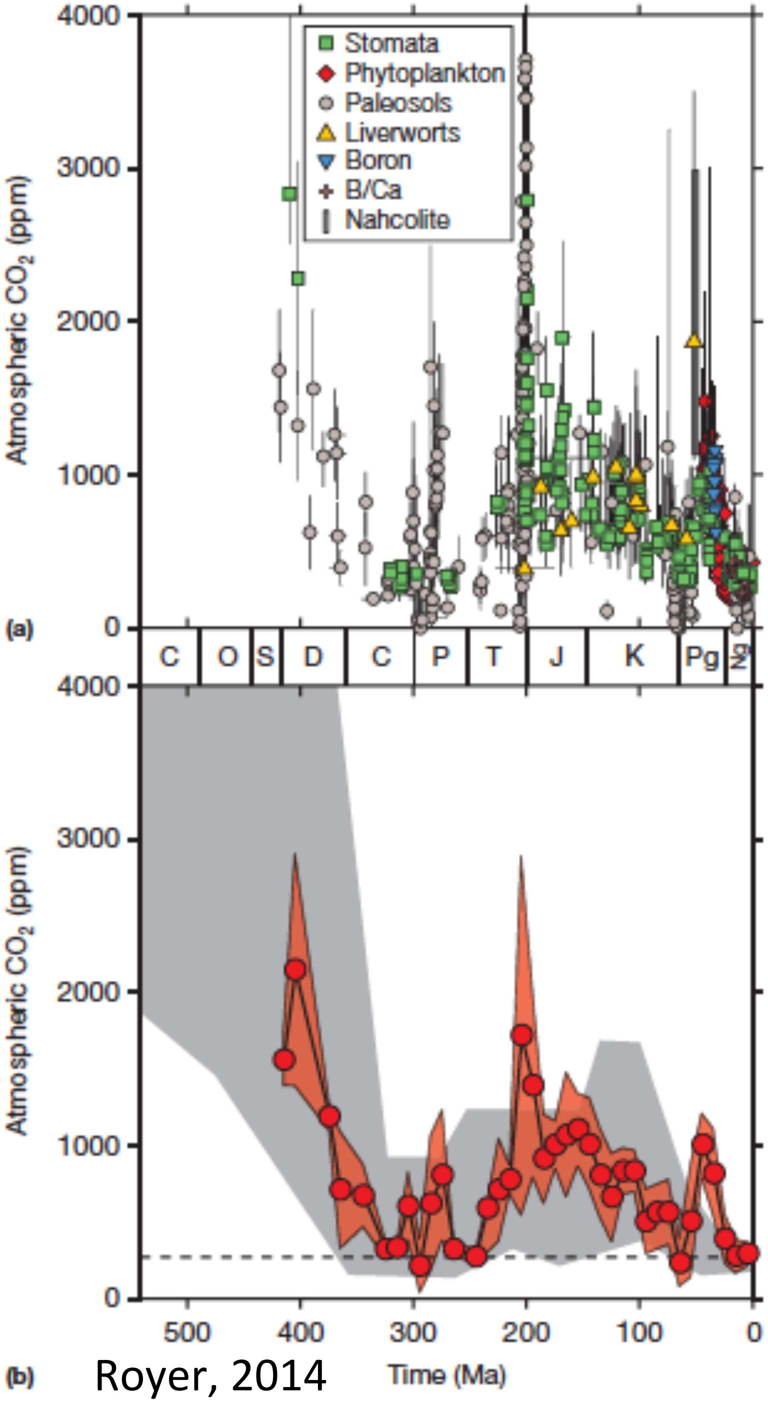
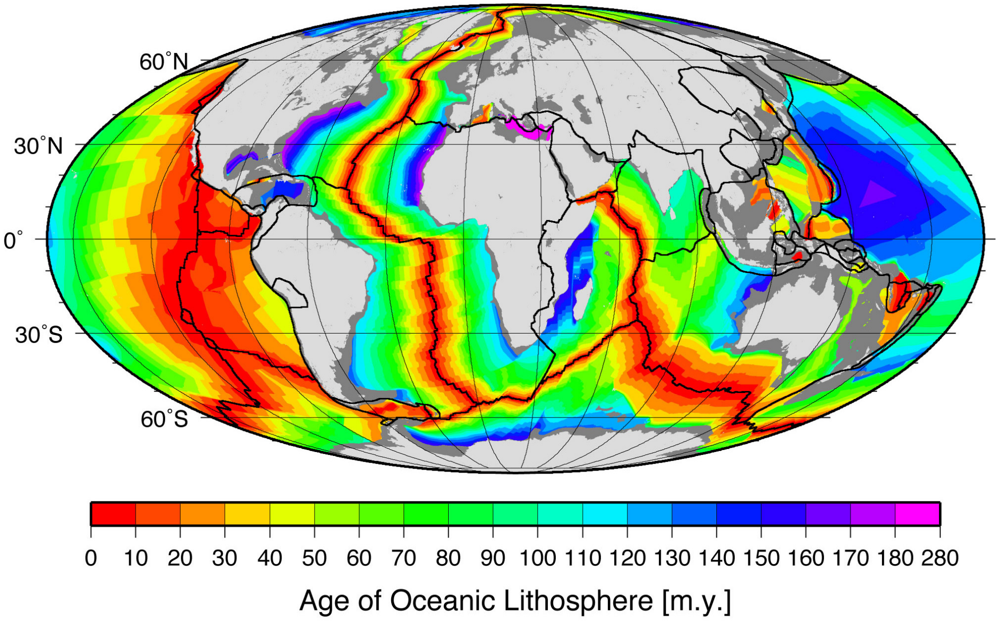
*Corresponding author. E-mail: matthew.clarkson@otago.ac.nz
†Present address: Department of Chemistry, University of Otago, Union Street, Dunedin, 9016, Post Office Box 56, New Zealand.



Royer, 2014



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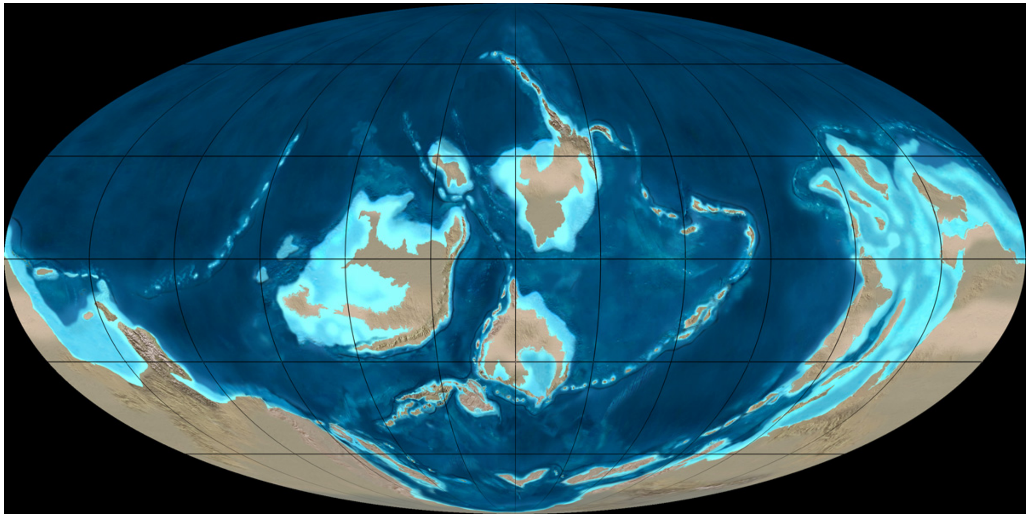
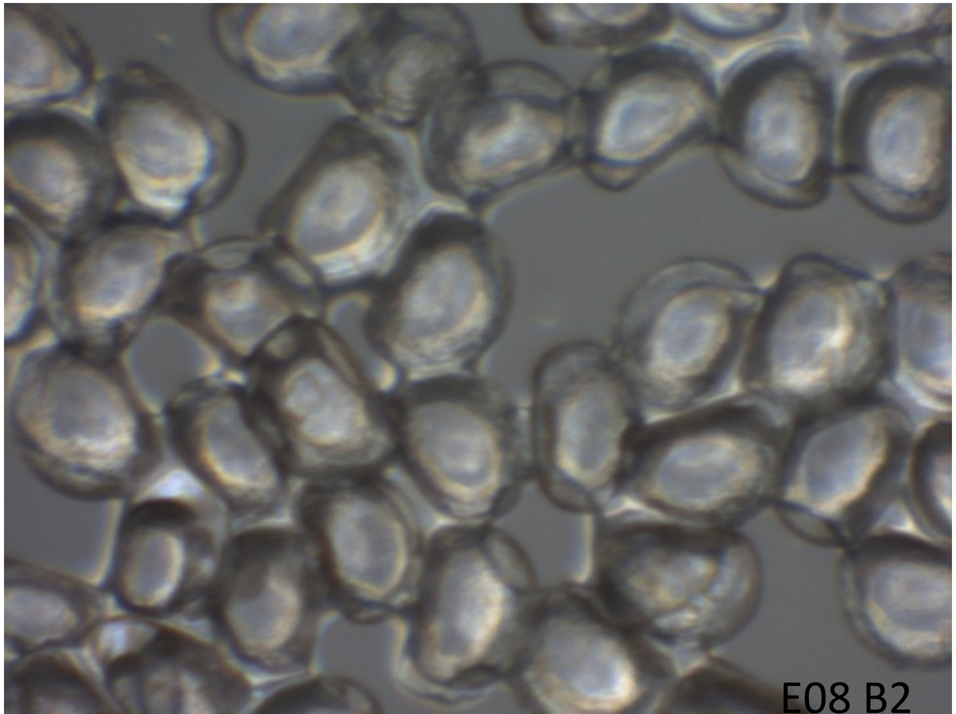
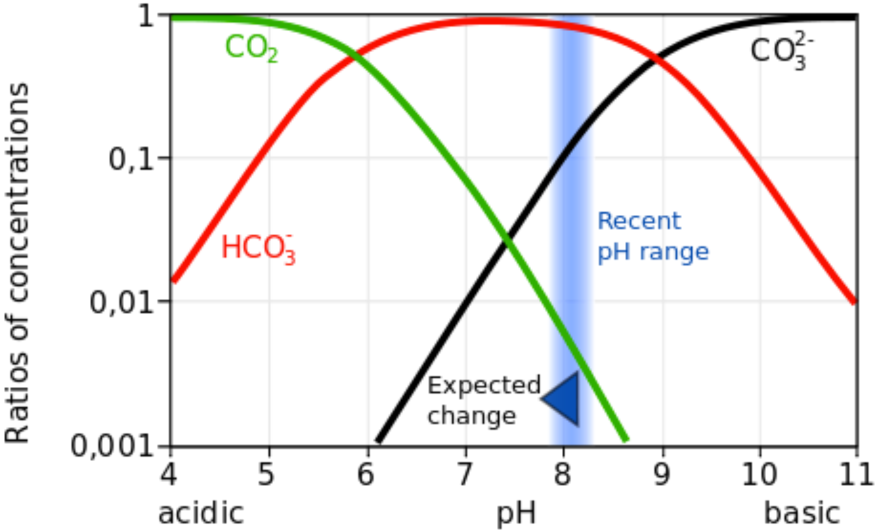


https://www2.nau.edu/rcb7/450moll.jpg

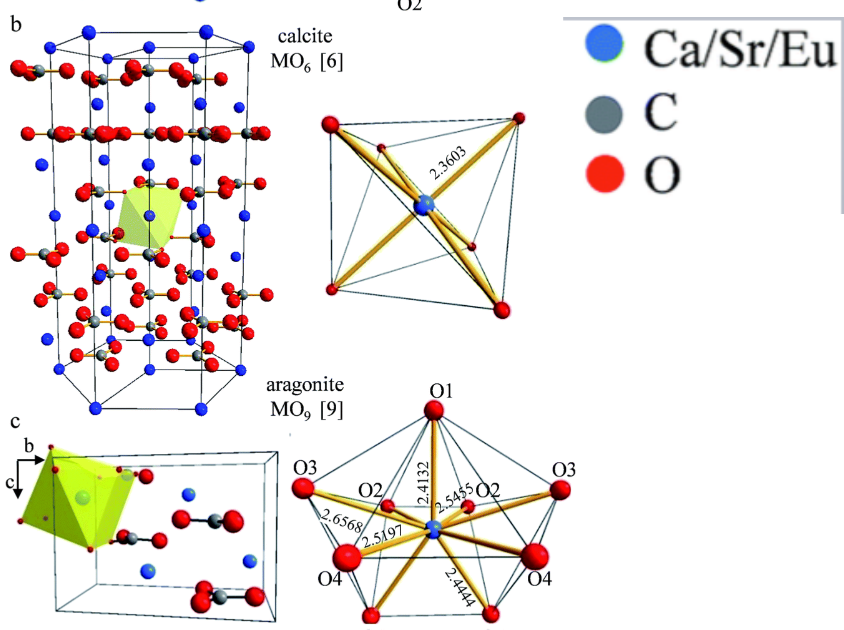
The Collaborative Project
Scripps-ASU-LSU

- Mussel larvae growth experiments
- Elemental changes (LA-ICPMS)
- Uranium isotopes (MC-ICPMS)
- Calcium isotopes (MC-ICPMS)
- B isotopes (SIMS)

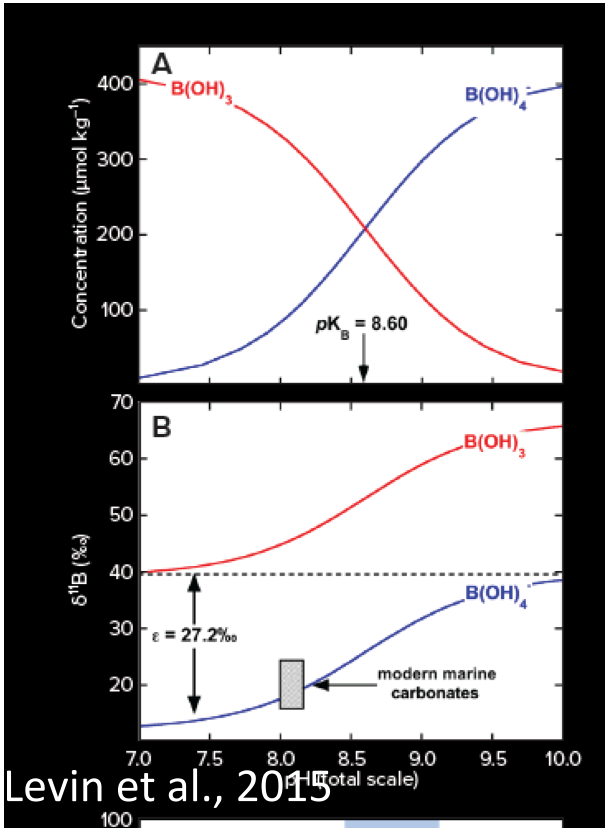




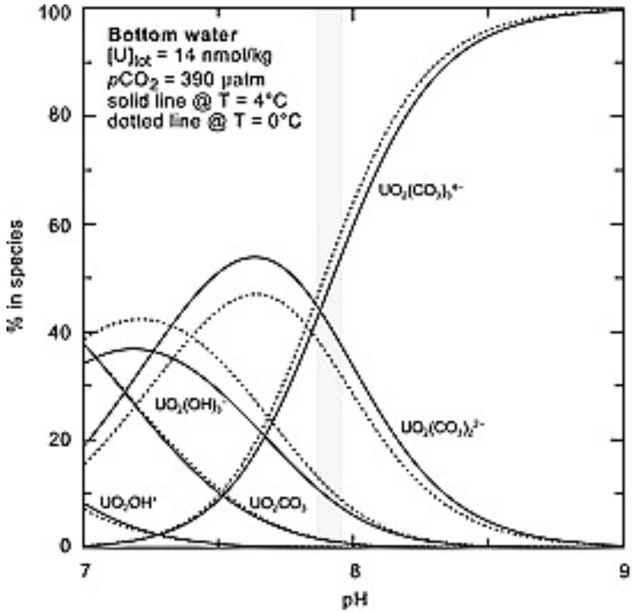
http://chemistry.stackexchange.com



Blanco-Gutierrez et al., 2014



Levin et al., 2015



Reitzsch et al., 2011

The Collaborative Project

- Rearing Mussel Larvae (Scripps)

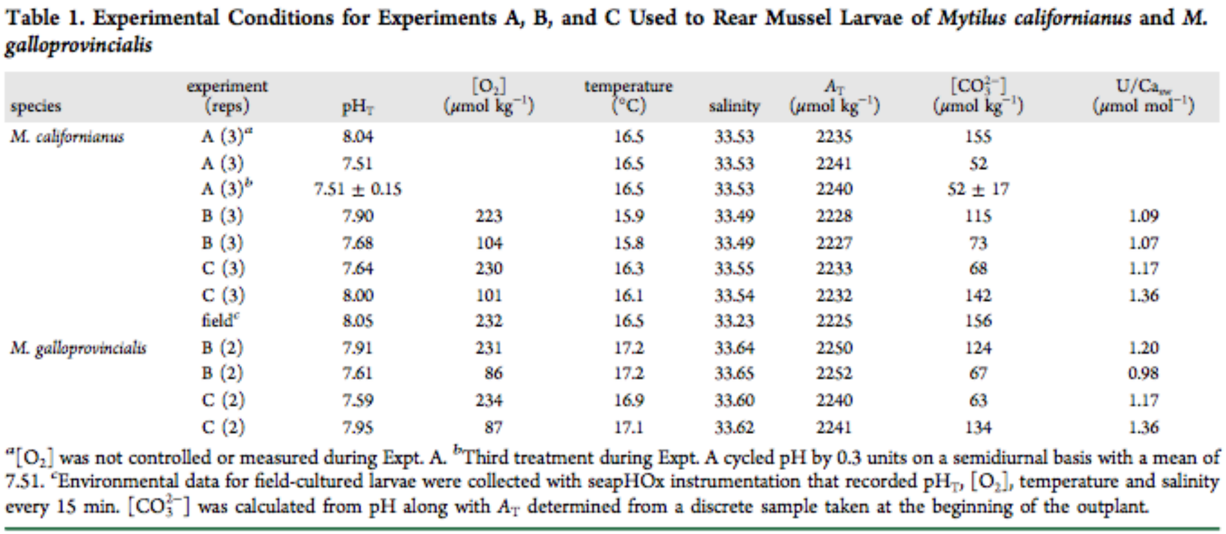
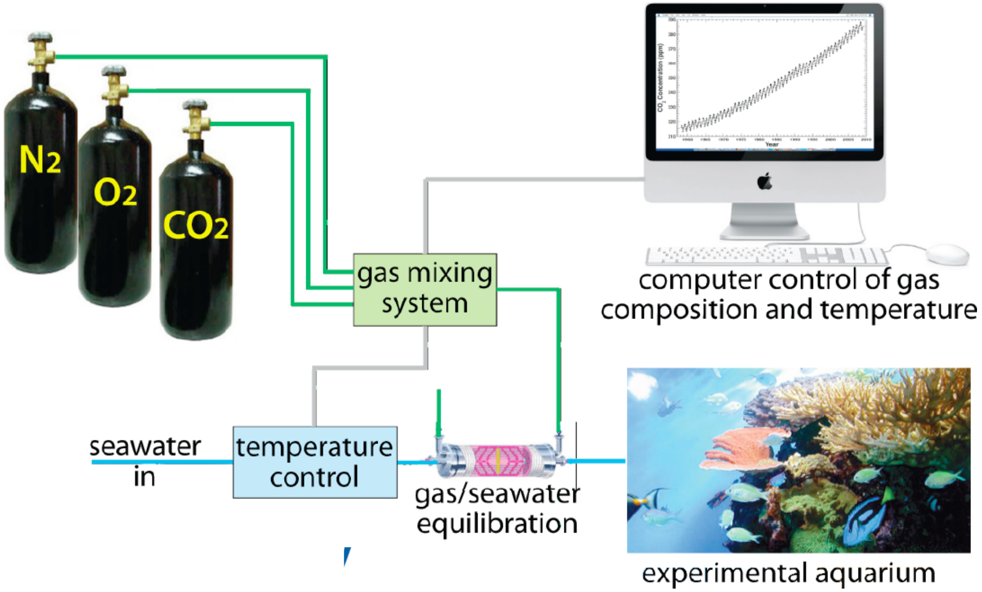


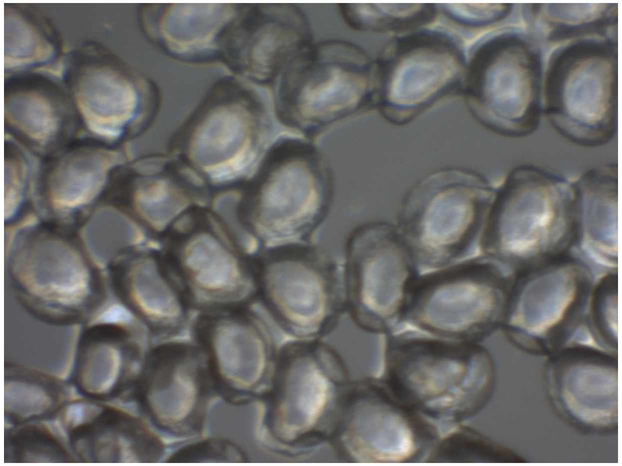
Table 1. Experimental Conditions for Experiments A, B, and C Used to Rear Mussel Larvae of *Mytilus californianus* and *M. galloprovincialis*

species	experiment (reps)	$\mathrm{pH_T}$	$[\mathrm{O_2}]$ (μmol kg^{-1})	temperature (°C)	salinity	A_T (μmol kg^{-1})	$[\mathrm{CO_3^{2-}}]$ (μmol kg^{-1})	$\mathrm{U/Ca_{sw}}$ (μmol mol^{-1})
M. californianus	A (3)[a]	8.04		16.5	33.53	2235	155	
	A (3)	7.51		16.5	33.53	2241	52	
	A (3)[b]	7.51 ± 0.15		16.5	33.53	2240	52 ± 17	
	B (3)	7.90	223	15.9	33.49	2228	115	1.09
	B (3)	7.68	104	15.8	33.49	2227	73	1.07
	C (3)	7.64	230	16.3	33.55	2233	68	1.17
	C (3)	8.00	101	16.1	33.54	2232	142	1.36
	field[c]	8.05	232	16.5	33.23	2225	156	
M. galloprovincialis	B (2)	7.91	231	17.2	33.64	2250	124	1.20
	B (2)	7.61	86	17.2	33.65	2252	67	0.98
	C (2)	7.59	234	16.9	33.60	2240	63	1.17
	C (2)	7.95	87	17.1	33.62	2241	134	1.36

[a] $[\mathrm{O_2}]$ was not controlled or measured during Expt. A. [b] Third treatment during Expt. A cycled pH by 0.3 units on a semidiurnal basis with a mean of 7.51. [c] Environmental data for field-cultured larvae were collected with seapHOx instrumentation that recorded $\mathrm{pH_T}$, $[\mathrm{O_2}]$, temperature and salinity every 15 min. $[\mathrm{CO_3^{2-}}]$ was calculated from pH along with A_T determined from a discrete sample taken at the beginning of the outplant.

Frieder et al., 2014





Boron Work - SIMS

- Instrumentation Cameca IMS 6f at ASU

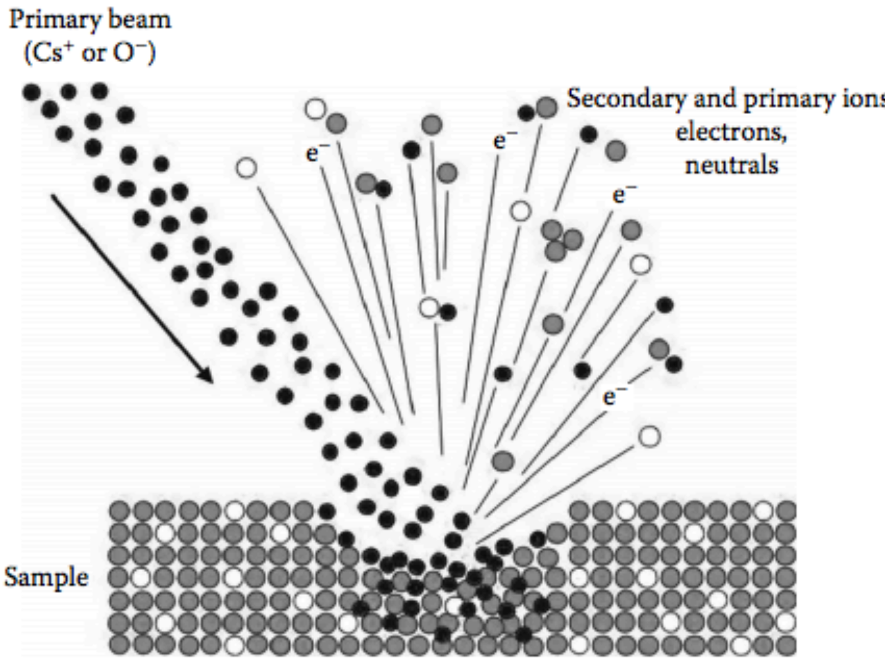
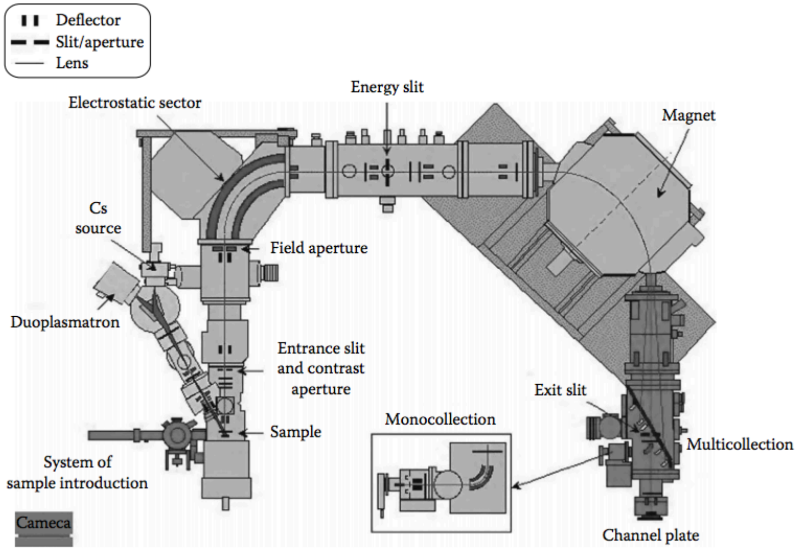
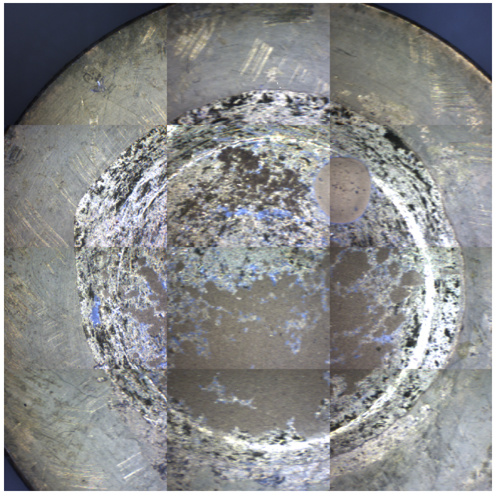


Figure 16.3 Sputtering of the surface of a sample by a primary beam of oxygen (O⁻) or cesium (Cs⁺) ions. By the impact of this high-energy beam (typically 10–13 keV), elements constitutive of the sample are ejected as mono- or pluriatomic secondary ions, electrons, and neutrals. The secondary ions are then accelerated toward the mass spectrometer of the ion probe. (Modified after Ireland, T.R., *Adv. Anal. Geochem.*, 2, 1–118, 1995.)

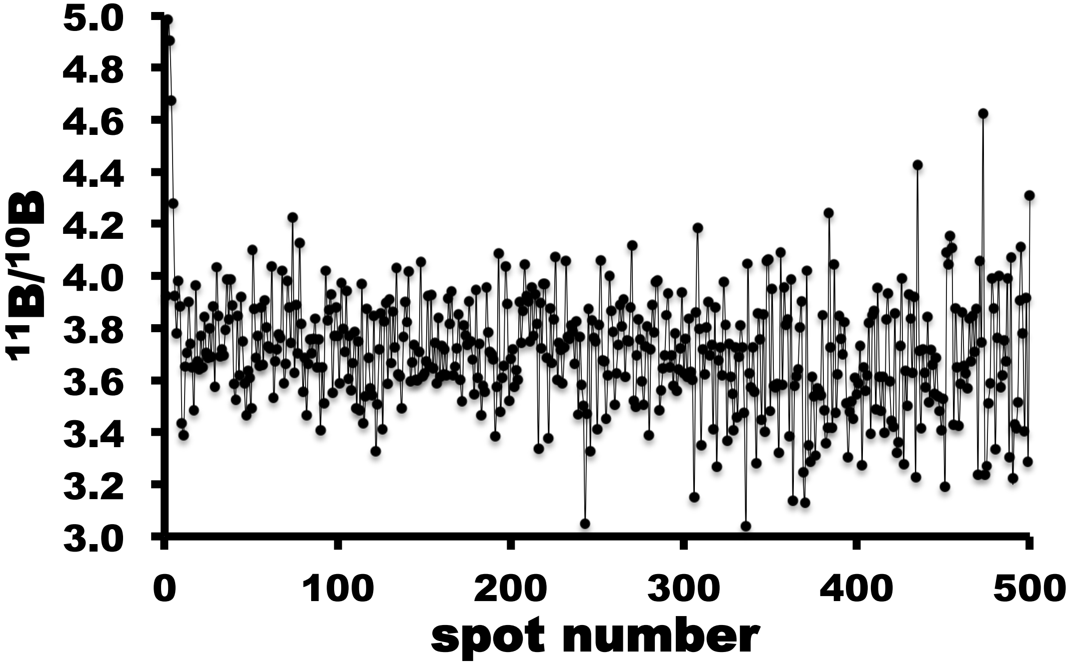


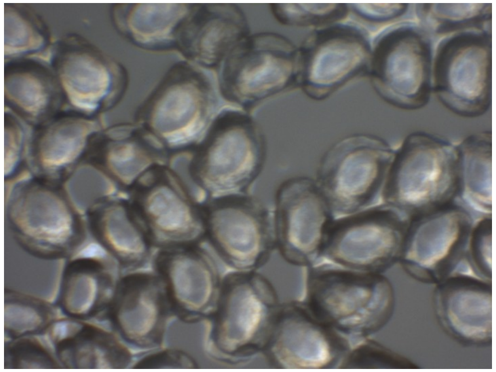


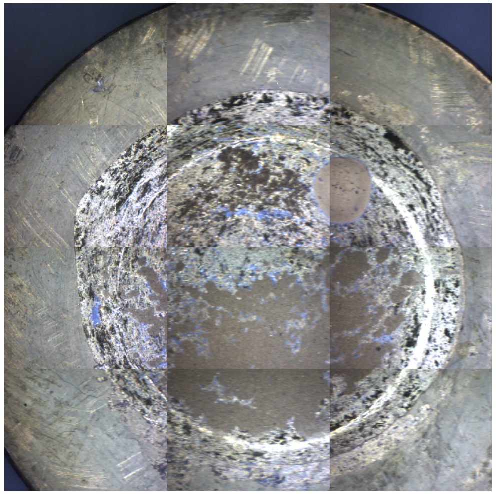
Rollion-Bard and Blamart, 2014

Boron Work - SIMS

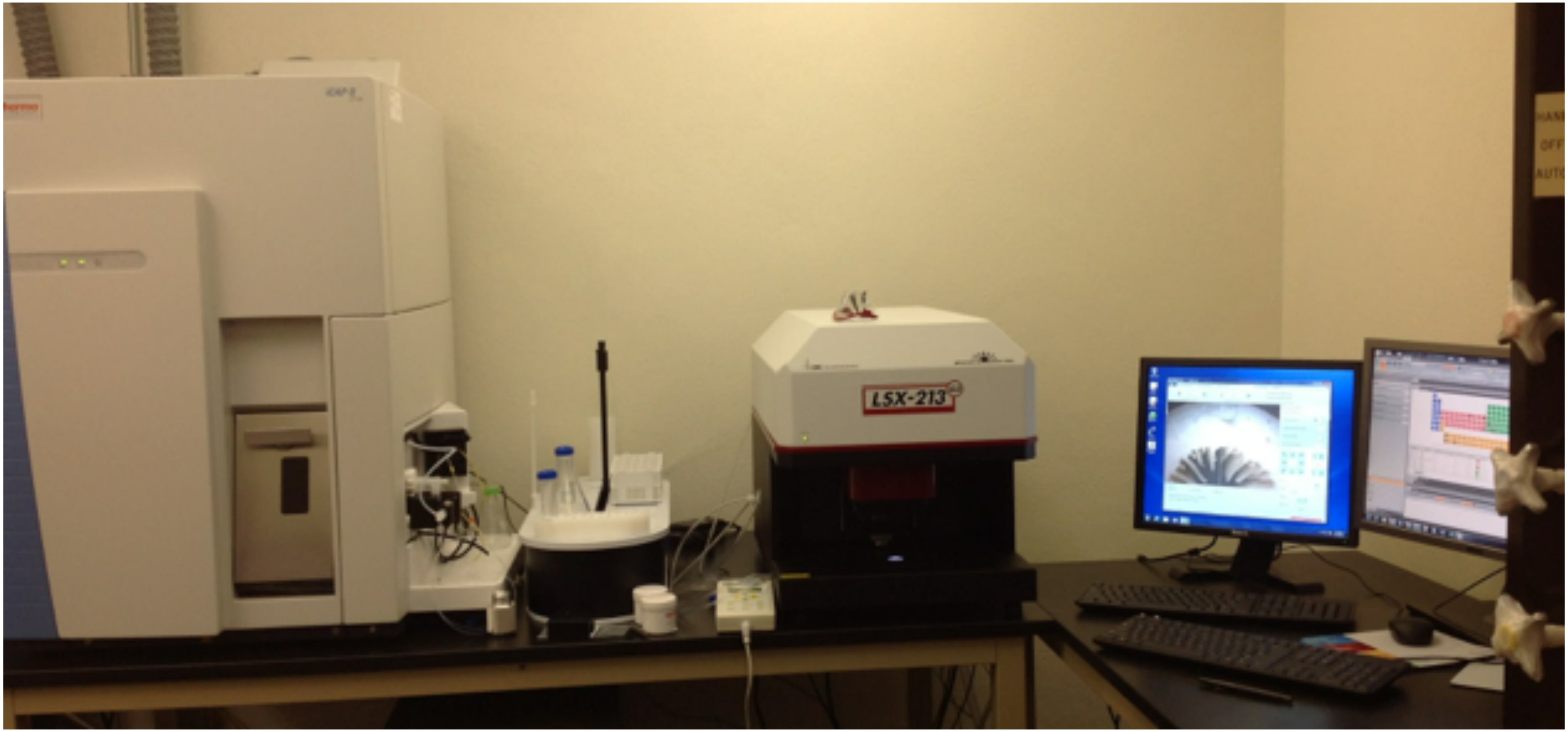
- Instrumentation Cameca 6f at ASU
- Problems: IMF and low precision





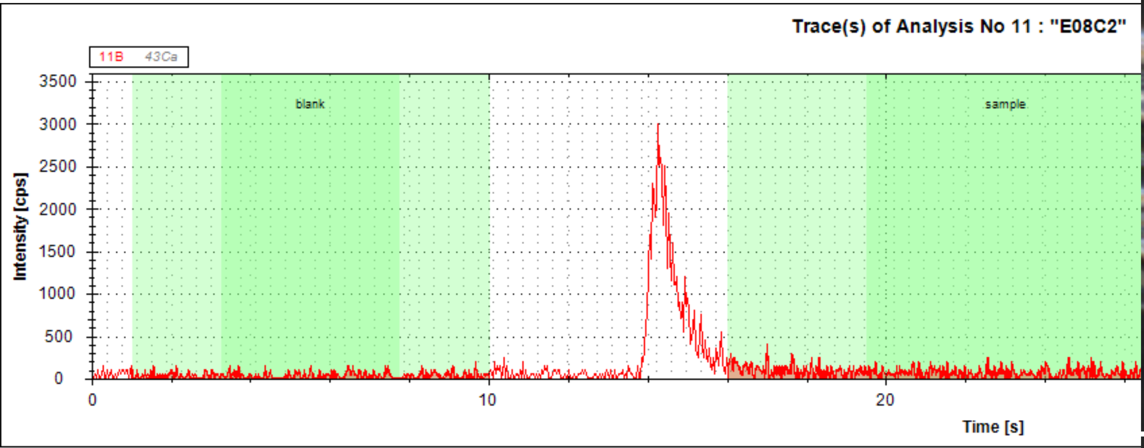


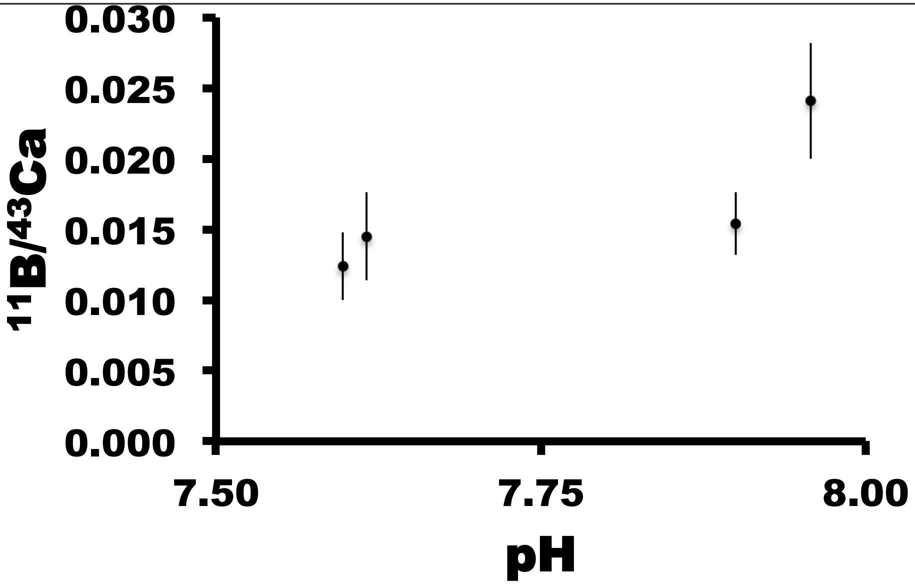
LA-ICPMS: Elemental proxies

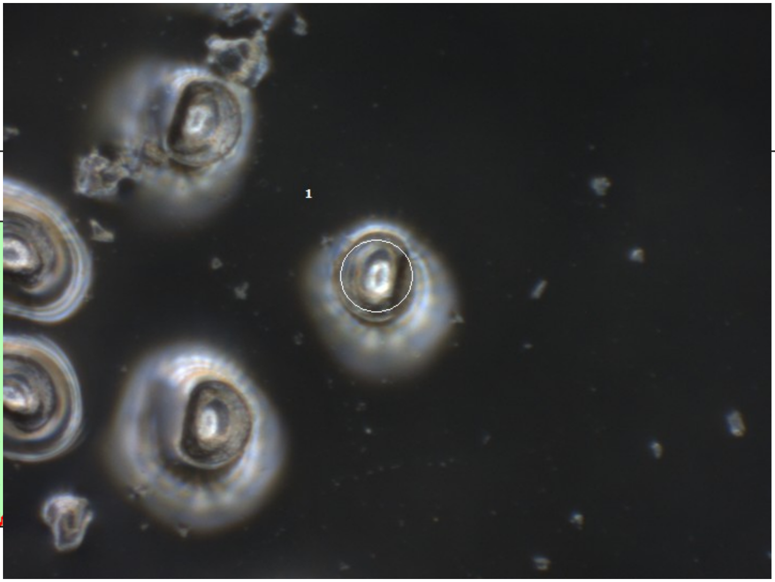


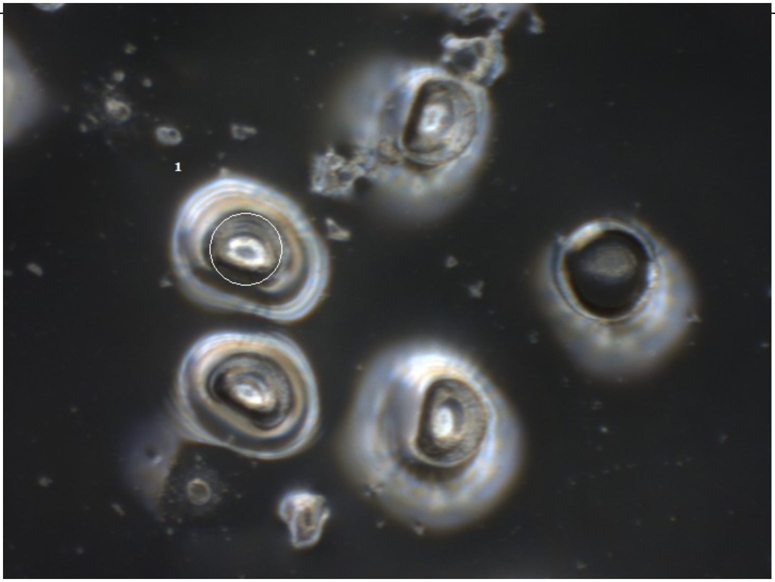
Mussel Larvae

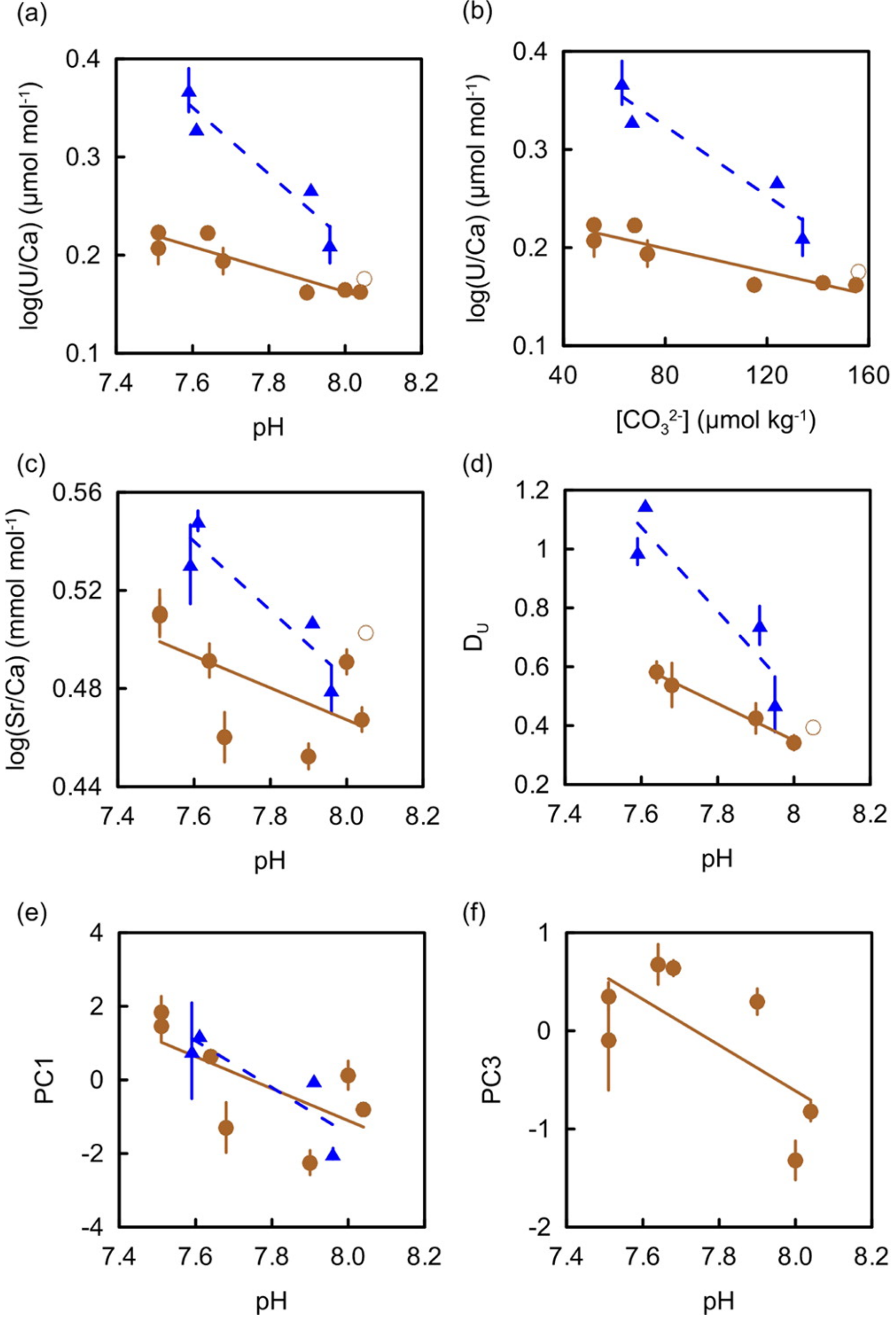
- 100 µm, 2%, 10 HZ, 30 shots
- DW: 0.01 ^{11}B, 0.01 ^{43}Ca







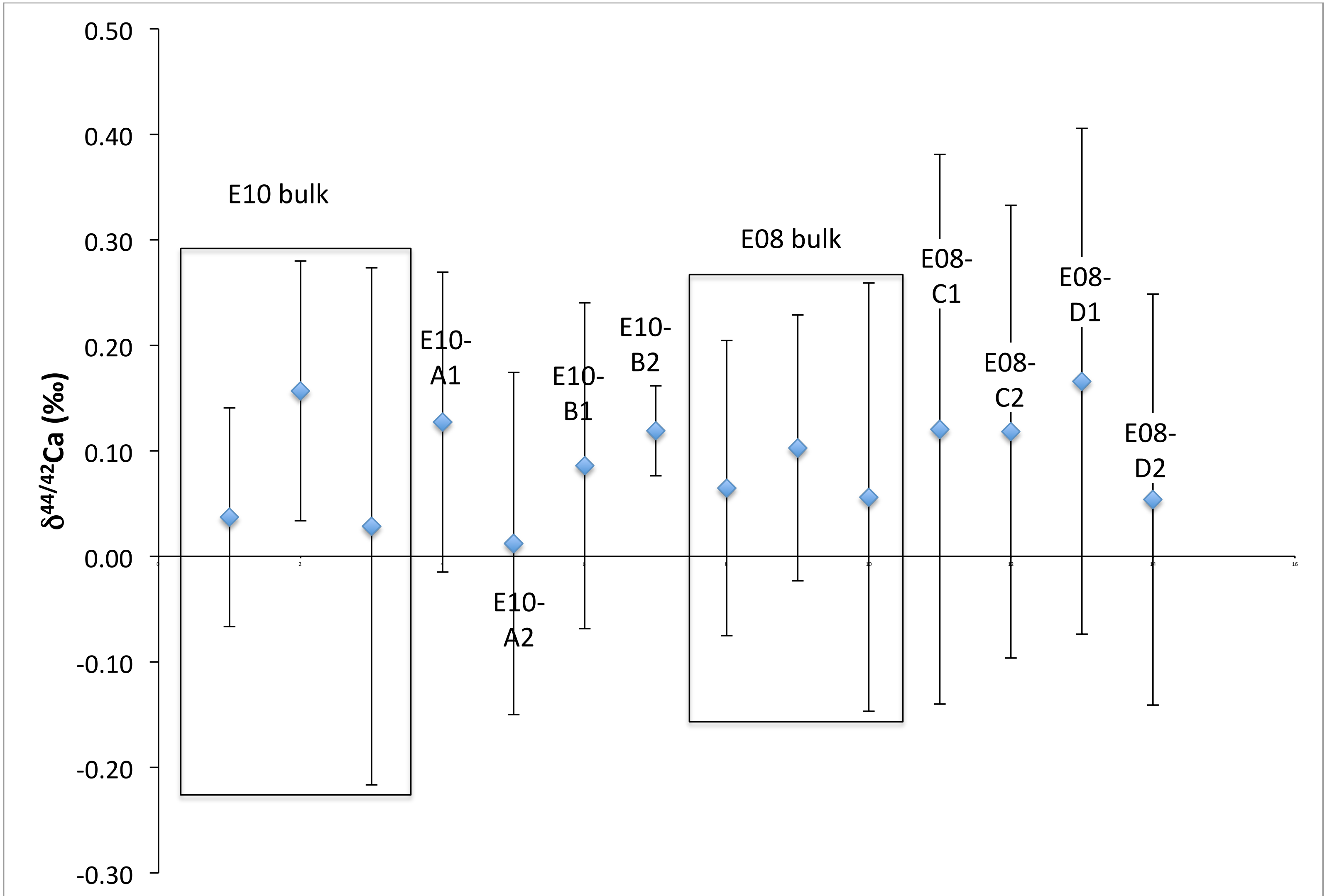




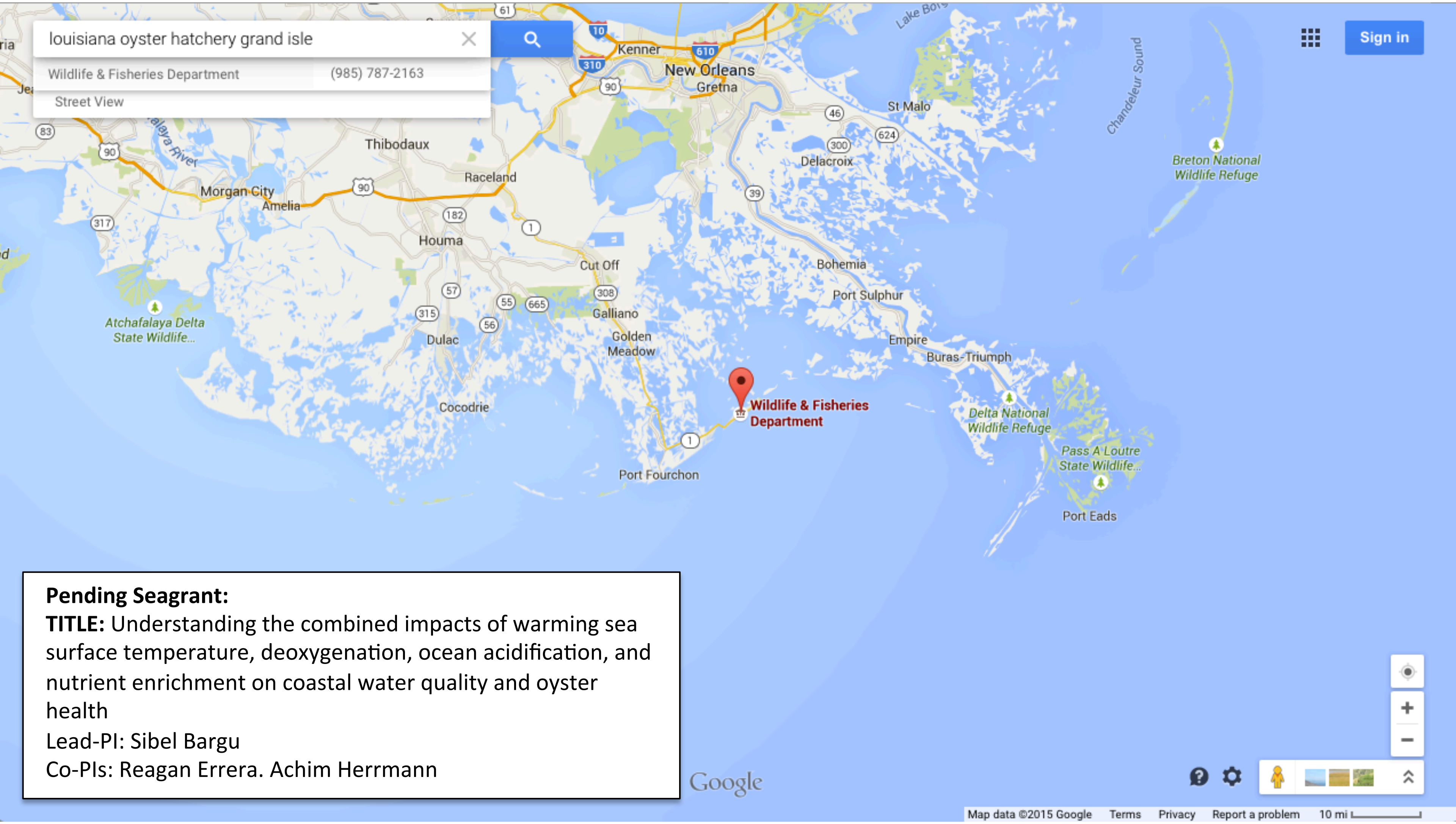
- Thermo Element 2 ICP-MS (low-resolution mode) with a New Wave Research UP-213 laser ablation unit (at the University of California Santa Barbara)
- 30-μm-long by 80-μm-wide line at 40% power, 10 Hz, and 8 μm/s scanning speed
- Solution-based dissolved $CaCO_3$ reference material (OTO), and two solid standards, NIST 612 and USGS MACS3 $CaCO_3$ standard

Frieder et al., 2014

MC-ICPMS: Ca Isotopes



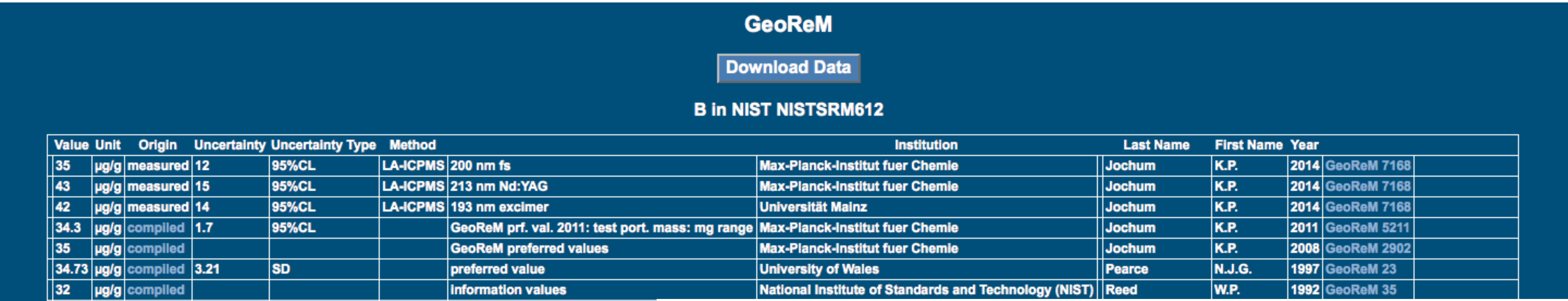
Future directions



Pending Seagrant:
TITLE: Understanding the combined impacts of warming sea surface temperature, deoxygenation, ocean acidification, and nutrient enrichment on coastal water quality and oyster health
Lead-PI: Sibel Bargu
Co-PIs: Reagan Errera. Achim Herrmann

Standards: NIST612

- Commonly used
- Readily available
- Not matrix matched for $CaCO_3$



GeoReM

B in NIST NISTSRM612

Value	Unit	Origin	Uncertainty	Uncertainty Type	Method		Institution	Last Name	First Name	Year	
35	µg/g	measured	12	95%CL	LA-ICPMS	200 nm fs	Max-Planck-Institut fuer Chemie	Jochum	K.P.	2014	GeoReM 7168
43	µg/g	measured	15	95%CL	LA-ICPMS	213 nm Nd:YAG	Max-Planck-Institut fuer Chemie	Jochum	K.P.	2014	GeoReM 7168
42	µg/g	measured	14	95%CL	LA-ICPMS	193 nm excimer	Universität Mainz	Jochum	K.P.	2014	GeoReM 7168
34.3	µg/g	compiled	1.7	95%CL		GeoReM prf. val. 2011: test port. mass: mg range	Max-Planck-Institut fuer Chemie	Jochum	K.P.	2011	GeoReM 5211
35	µg/g	compiled				GeoReM preferred values	Max-Planck-Institut fuer Chemie	Jochum	K.P.	2008	GeoReM 2902
34.73	µg/g	compiled	3.21	SD		preferred value	University of Wales	Pearce	N.J.G.	1997	GeoReM 23
32	µg/g	compiled				information values	National Institute of Standards and Technology (NIST)	Reed	W.P.	1992	GeoReM 35
35	µg/g	measured			ICPAES						
27.2	µg/g	measured	3.7	2SIGMA	LA-ICPMS	Li (mass 6)					
35.6	µg/g	measured	4.3	2SIGMA	LA-ICPMS	Li (mass 6)					
36	µg/g	measured	4	SIGMA		Present data, Nuclear reaction mi					
33	µg/g	measured	4	SIGMA		Microbeam analyses,					
32.08	µg/g	measured	5	RSD(%)	LA-ICPMS						
32	µg/g	compiled				information values					
54	µg/g	measured			LA-ICPMS	calibr. with NIST610, most accura					
33.7	µg/g	measured	0.9	1SIGMA	LA-ICPMS						
32.6	µg/g	measured	0.8	1SIGMA	LA-ICPMS						
37.6	µg/g	measured	1.48	2SIGMA	LA-ICPMS	calibrated with NIST610					
54	µg/g	measured	31	2SIGMA	LA-ICPMS	calibr. with NIST612 and BCR-2G					
33.74	µg/g	measured	2.26	1SIGMA	LA-ICPMS						
35	µg/g	measured			LIMS	calibr. with NIST SRM610					
33.82	µg/g	measured	9	RSD(%)	LA-ICPMS						
34.73	µg/g	measured	1.0043	SD	LA-ICPMS						
34.82	µg/g	measured	5.79	SIGMA	LA-ICPMS						
24.4	µg/g	measured	9	SD	LA-ICPMS						

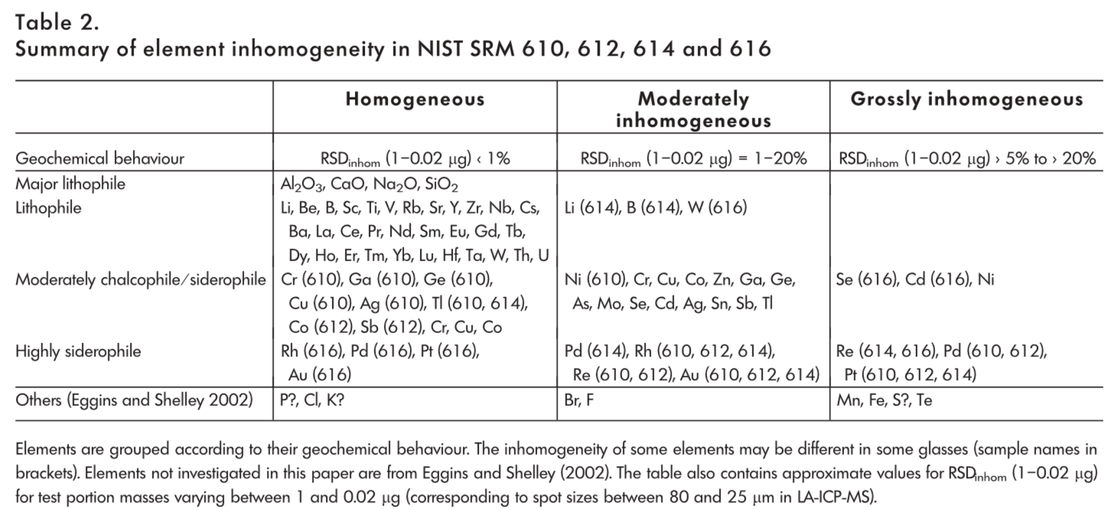


Table 2.
Summary of element inhomogeneity in NIST SRM 610, 612, 614 and 616

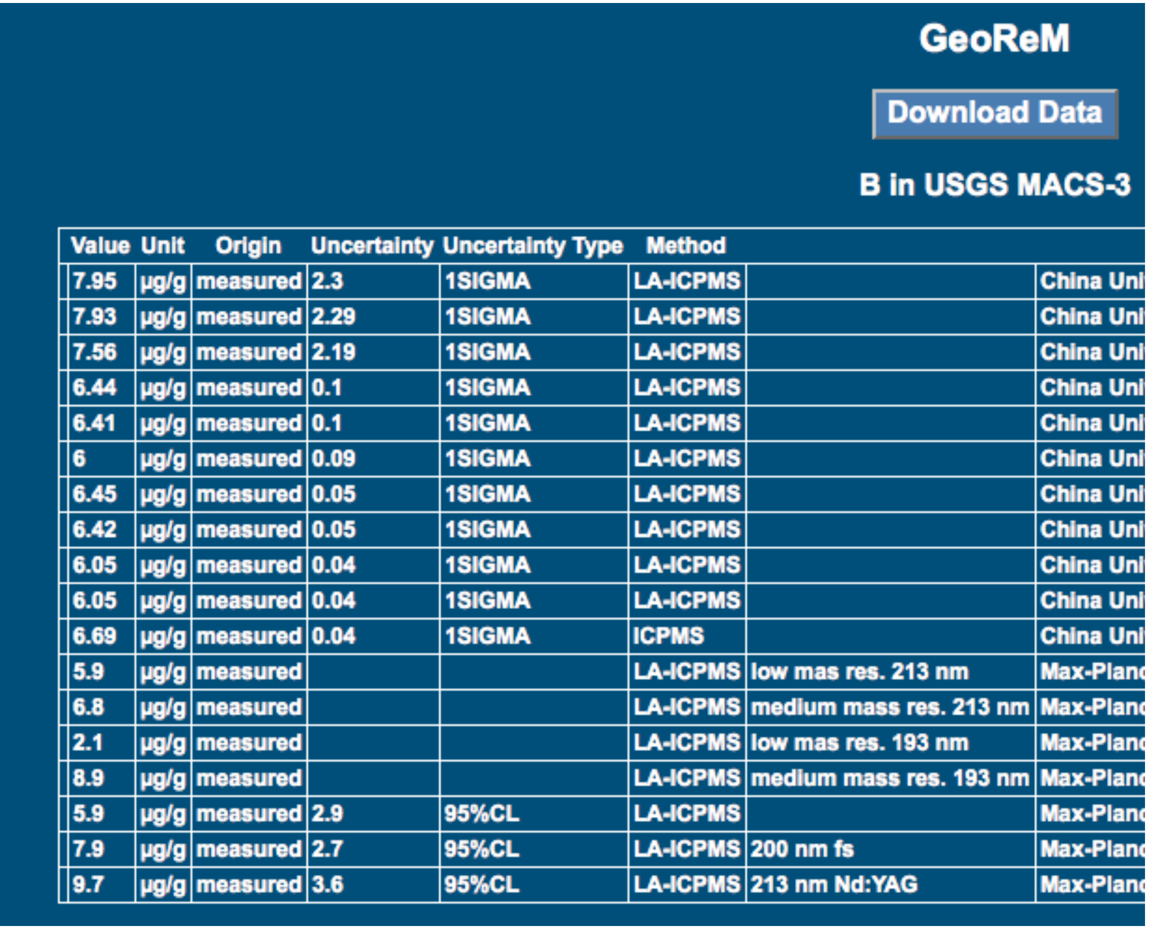
	Homogeneous	Moderately inhomogeneous	Grossly inhomogeneous
Geochemical behaviour	$\mathrm{RSD}_{\mathrm{inhom}}$ (1−0.02 µg) < 1%	$\mathrm{RSD}_{\mathrm{inhom}}$ (1−0.02 µg) = 1−20%	$\mathrm{RSD}_{\mathrm{inhom}}$ (1−0.02 µg) > 5% to > 20%
Major lithophile	Al_2O_3, CaO, Na_2O, SiO_2		
Lithophile	Li, Be, B, Sc, Ti, V, Rb, Sr, Y, Zr, Nb, Cs, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Ta, W, Th, U	Li (614), B (614), W (616)	
Moderately chalcophile/siderophile	Cr (610), Ga (610), Ge (610), Cu (610), Ag (610), Tl (610, 614), Co (612), Sb (612), Cr, Cu, Co	Ni (610), Cr, Cu, Co, Zn, Ga, Ge, As, Mo, Se, Cd, Ag, Sn, Sb, Tl	Se (616), Cd (616), Ni
Highly siderophile	Rh (616), Pd (616), Pt (616), Au (616)	Pd (614), Rh (610, 612, 614), Re (610, 612), Au (610, 612, 614)	Re (614, 616), Pd (610, 612), Pt (610, 612, 614)
Others (Eggins and Shelley 2002)	P?, Cl, K?	Br, F	Mn, Fe, S?, Te

Elements are grouped according to their geochemical behaviour. The inhomogeneity of some elements may be different in some glasses (sample names in brackets). Elements not investigated in this paper are from Eggins and Shelley (2002). The table also contains approximate values for $\mathrm{RSD}_{\mathrm{inhom}}$ (1−0.02 µg) for test portion masses varying between 1 and 0.02 µg (corresponding to spot sizes between 80 and 25 µm in LA-ICP-MS).

Jochum et al., 2011

Standards: MACS-3

- “Matrix matched”
- Low boron concentration
- Heterogeneous

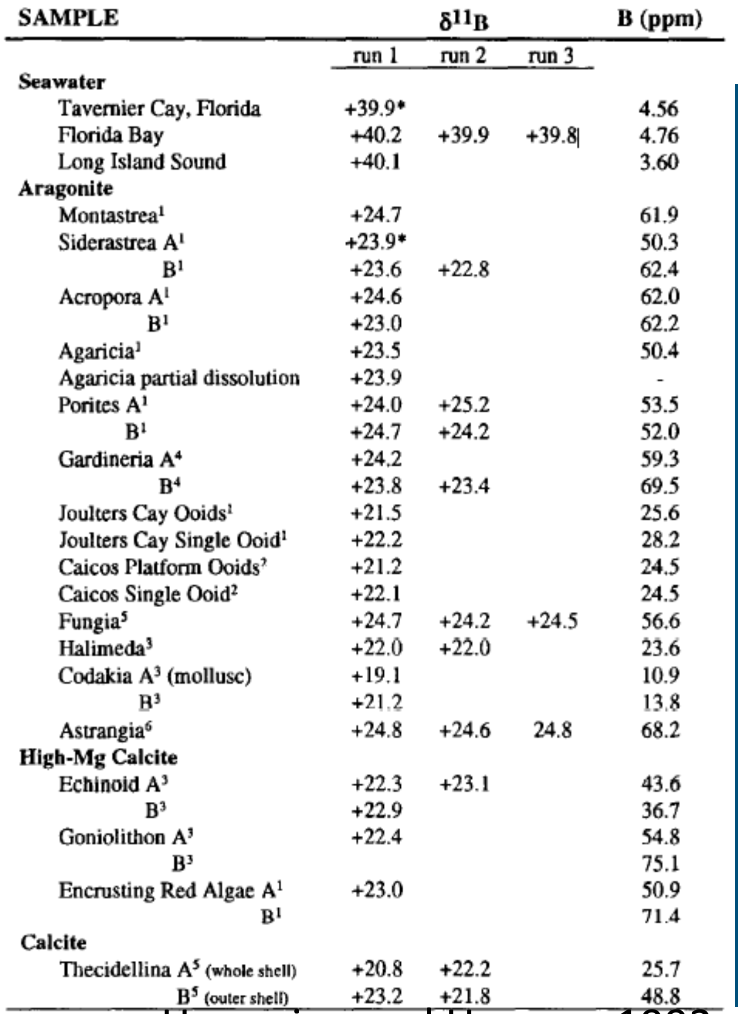


GeoReM

Download Data

B in USGS MACS-3

Value	Unit	Origin	Uncertainty	Uncertainty Type	Method		
7.95	µg/g	measured	2.3	1SIGMA	LA-ICPMS		China Uni
7.93	µg/g	measured	2.29	1SIGMA	LA-ICPMS		China Uni
7.56	µg/g	measured	2.19	1SIGMA	LA-ICPMS		China Uni
6.44	µg/g	measured	0.1	1SIGMA	LA-ICPMS		China Uni
6.41	µg/g	measured	0.1	1SIGMA	LA-ICPMS		China Uni
6	µg/g	measured	0.09	1SIGMA	LA-ICPMS		China Uni
6.45	µg/g	measured	0.05	1SIGMA	LA-ICPMS		China Uni
6.42	µg/g	measured	0.05	1SIGMA	LA-ICPMS		China Uni
6.05	µg/g	measured	0.04	1SIGMA	LA-ICPMS		China Uni
6.05	µg/g	measured	0.04	1SIGMA	LA-ICPMS		China Uni
6.69	µg/g	measured	0.04	1SIGMA	ICPMS		China Uni
5.9	µg/g	measured			LA-ICPMS	low mas res. 213 nm	Max-Planc
6.8	µg/g	measured			LA-ICPMS	medium mass res. 213 nm	Max-Planc
2.1	µg/g	measured			LA-ICPMS	low mas res. 193 nm	Max-Planc
8.9	µg/g	measured			LA-ICPMS	medium mass res. 193 nm	Max-Planc
5.9	µg/g	measured	2.9	95%CL	LA-ICPMS		Max-Planc
7.9	µg/g	measured	2.7	95%CL	LA-ICPMS	200 nm fs	Max-Planc
9.7	µg/g	measured	3.6	95%CL	LA-ICPMS	213 nm Nd:YAG	Max-Planc



SAMPLE	$\delta^{11}B$			B (ppm)
	run 1	run 2	run 3	
Seawater				
Tavernier Cay, Florida	+39.9*			4.56
Florida Bay	+40.2	+39.9	+39.8	4.76
Long Island Sound	+40.1			3.60
Aragonite				
Montastrea[1]	+24.7			61.9
Siderastrea A[1]	+23.9*			50.3
B[1]	+23.6	+22.8		62.4
Acropora A[1]	+24.6			62.0
B[1]	+23.0			62.2
Agaricia[1]	+23.5			50.4
Agaricia partial dissolution	+23.9			-
Porites A[1]	+24.0	+25.2		53.5
B[1]	+24.7	+24.2		52.0
Gardineria A[4]	+24.2			59.3
B[4]	+23.8	+23.4		69.5
Joulters Cay Ooids[1]	+21.5			25.6
Joulters Cay Single Ooid[1]	+22.2			28.2
Caicos Platform Ooids[2]	+21.2			24.5
Caicos Single Ooid[2]	+22.1			24.5
Fungia[5]	+24.7	+24.2	+24.5	56.6
Halimeda[3]	+22.0	+22.0		23.6
Codakia A[3] (mollusc)	+19.1			10.9
B[3]	+21.2			13.8
Astrangia[6]	+24.8	+24.6	24.8	68.2
High-Mg Calcite				
Echinoid A[3]	+22.3	+23.1		43.6
B[3]	+22.9			36.7
Goniolithon A[3]	+22.4			54.8
B[3]				75.1
Encrusting Red Algae A[1]	+23.0			50.9
B[1]				71.4
Calcite				
Thecidellina A[5] (whole shell)	+20.8	+22.2		25.7
B[5] (outer shell)	+23.2	+21.8		48.8

Hemming and Hanson, 1992

Conclusions

- Progress: LA-ICPMS can be used for the analysis of (some) trace elements in single shell bivalve larvae to trace pH exposure history (esp. U)
- Pitfalls: B and Ca isotopes do not work
- Future directions: Comparative, multi-stressor studies needed across different taxa
- Future directions: Ecosystem response using "deep time" studies
- (Progress needed: Appropriate, readily available standards are needed)

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