Biogeochemistry Science and Education

Part One: Using Non-Traditional Stable Isotopes as Environmental Tracers

Part Two: Identifying and Measuring Undergraduate Misconceptions in Biogeochemistry

by

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A Dissertation Presented in Partial Fulfillment
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ABSTRACT

This dissertation is presented in two sections. First, I explore two methods of using stable isotope analysis to trace environmental and biogeochemical processes. Second, I present two related studies investigating student understanding of the biogeochemical concepts that underlie part one.

Fe and Hg are each biogeochemically important elements in their own way. Fe is a critical nutrient for phytoplankton, while Hg is detrimental to nearly all forms of life. Fe is often a limiting factor in marine phytoplankton growth. The largest source, by mass, of Fe to the open ocean is windblown mineral dust, but other more soluble sources are more bioavailable. To look for evidence of these non-soil dust sources of Fe to the open ocean, I measured the isotopic composition of aerosol samples collected on Bermuda. I found clear evidence in the fine size fraction of a non-soil dust Fe source, which I conclude is most likely from biomass burning.

Widespread adoption of compact fluorescent lamps (CFL) has increased their importance as a source of environmental Hg. Isotope analysis would be a useful tool in quantifying this impact if the isotopic composition of Hg from CFL were known. My measurements show that CFL-Hg is isotopically fractionated, in a unique pattern, during normal operation. This fractionation is large and has a distinctive, mass-independent signature, such that CFL Hg can be uniquely identified from other sources.

Misconceptions research in geology has been a very active area of research, but student thinking regarding the related field of biogeochemistry has not yet been studied in detail. From interviews with 40 undergraduates, I identified over 150 specific misconceptions. I also designed a multiple-choice survey (concept inventory) to measure understanding of these same biogeochemistry concepts. I present statistical evidence, based on the Rasch model, for the reliability and validity of this instrument. This instrument will allow teachers and researchers to easily quantify learning outcomes in biogeochemistry and will complement existing concept inventories in geology, chemistry, and biology.

For Judson Mead

ACKNOWLEDGEMENTS

First and foremost, this dissertation would not exist and would not be of the quality that it is without the contributions of my advisors, Ariel Anbar and Steve Semken. I would also like to acknowledge the contributions of my coauthors on the previously published chapters, Tom Johnson, Jim Lyons, Pierre Herckes, and Brian Majestic, as well as my dissertation committee members for their guidance throughout my time at ASU.

I am a much better scientist as a result of my daily interactions over the past six years with the other graduate students, researchers, and faculty both within SESE and campus-wide. The Anbar and Semken research group members have been invaluable, and I would like to specifically acknowledge Gwyneth Gordon and Steve Romaniello for sharing their time and laboratory insight. I also owe a debt to my colleagues in the ASU IGERT in urban ecology. Through that program, I was able to work directly with a number of social scientists, who helped me make the transition to doing that kind of research myself.

Lastly, I thank my wife, Cherise, for her support and for her willingness to move to Arizona with me in the first place.

TABLE OF CONTENTS

APPENDIX

LIST OF TABLES

LIST OF FIGURES

Chapter 1

A DISCIPLINE-BASED EDUCATION RESEARCH DISSERTATION IN BIOGEOCHEMISTRY

On its face, this dissertation appears very different from the traditional model, but I contend that the difference is superficial. A PhD is widely understood to indicate that the holder is capable of contributing new research to a particular field of study; the dissertation is the evidence of that capability. Commonly this implies both a broad understanding of the relevant supporting fields and a deep knowledge of one facet where the scholar has chosen to carry out his or her new research. However, it is the nature of discipline-based education research (DBER) that the practitioners must have a substantial background in a science discipline so that they can apply that knowledge to their education research. Consequently, the topical diversity of the chapters in this dissertation represents not a lack of specialization, but rather a specialization in a field that requires multiple areas of expertise.

Even if one concedes that a DBER dissertation is appropriate given the nature of that approach, it is still reasonable to ask whether the science research or the science education research is improved by this collocation. In the case of my research, is the science education research made stronger by its proximity to isotope geochemistry research? Is the isotope geochemistry research enhanced by contact with education research? The former is the simpler case to argue. I conducted research identifying scientific misconceptions; immediately prior to the description of that research are two examples of the very topics that students may not grasp without first overcoming those misconceptions. The reverse case is less clear, but there is value in a structure that presents education as an equal partner to science and one that may encourage other scientists to consider the educational applications of their research.

The idea of researchers trained in a traditional scientific discipline conducting rigorous science education research is a relatively new one, but it has been strongly endorsed (Singer, Nielsen, & Schweingruber, 2012). Fundamentally, the goal of all science education research is to improve the quality of science education. Reports like that of the National Research Council (Singer, Nielsen, & Schweingruber, 2012) highlight the value inherent in bringing advanced disciplinary knowledge into the process of education research. Assuming the emphasis on measurable outcomes in education continues, DBER should grow as a priority for science departments. I believe that this dissertation, showing competence in both biogeochemistry research and biogeochemistry education research, positions me well to be one of the researchers to fill that need.

There is a common push and pull regarding interdisciplinarity: we live in a world of interdisciplinary problems needing interdisciplinary approaches to solving them, but researchers across disciplines have trouble talking to each other. Although the wording of DBER may suggest otherwise, it is clearly an interdisciplinary endeavor. For me, specifically, interdisciplinarity has been a constant theme of my research interests. My mercury isotope research ultimately applied a phenomenon understood largely through astronomy and physics to a problem based in environmental science; my iron isotope research brought together terrestrial aerosol emissions and marine biogeochemistry; and, of course, my education research combined the concepts behind both of those projects with education research methods.

In addition to serving as a DBER credential, this dissertation demonstrates my ability to work and communicate across disciplines. It demonstrates my ability to learn the academic standards and values of a social science after years of training as a physical scientist. Importantly, it also represents an effort to communicate that social science understanding back to the physical science community where I remain. In the end, this is an interdisciplinary dissertation for an interdisciplinary world that needs desperately to teach students to operate in all the complexity that implies.

Chapter 2

SOURCE APPORTIONMENT OF AEROSOL IRON IN THE MARINE ENVIRONMENT USING IRON ISOTOPE ANALYSIS[1]

2.1 Introduction

Marine phytoplankton account for roughly half of the photosynthetic activity on Earth (Field, Behrenfeld, Randerson, & Falkowski, 1998; Longhurst, Sathyendranath, Platt, & Caverhill, 2005), but their productivity is limited in a quarter of the global ocean by the scarcity of Fe, an essential nutrient (de Baar et al., 2005; Boyd & Ellwood, 2010; Martin, 1990). These regions of limited productivity, known as high-nutrient, low-chlorophyll areas (HNLC), are characterized by high concentrations of macronutrients, such as nitrate and phosphate, but low levels of chlorophyll, a proxy for photosynthetic activity. Much of the Fe that is available in HNLC areas is dissolved from windblown dust (Falkowski, Barber, & Smetacek, 1998; Jickells et al., 2005; Mahowald et al., 2005). Because of the dominance of aeolian transport, understanding and quantifying the sources of aerosol Fe is very important to our ability to model primary productivity in the ocean and the consequent drawdown of atmospheric CO_2.

Soil dust, produced primarily in large deserts, is the largest source of Fe to the open ocean (Jickells et al., 2005). However, recent studies show that Fe in soil dust is < 1% soluble. This allows for the possibility that sources of highly soluble Fe (some sources have > 80% soluble Fe), while less massive, may contribute significantly to the supply of bioavailable Fe in the open ocean (Oakes et al., 2012; Schroth, Crusius,

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[1] Originally published as Mead, C., Herckes, P., Majestic, B. J., & Anbar, A. D. (2013). Source apportionment of aerosol iron in the marine environment using iron isotope analysis, *Geophysical Research Letters, 40*, 5722–5727.

Sholkovitz, & Bostick, 2009; Sholkovitz, Sedwick, & Church, 2009; Sholkovitz, Sedwick, Church, Baker, & Powell, 2012; Trapp, Millero, & Prospero, 2010). Of particular interest is the idea that anthropogenic aerosol particles, such as combustion byproducts and other industrial pollution, and biomass burning aerosols contribute substantially to the growth of marine phytoplankton (Luo et al., 2008; Sedwick, Sholkovitz, & Church, 2007). In order to explore this possibility, a proxy measurement for non-soil dust aerosol Fe is needed. Previous work demonstrated that Fe isotope analysis can expose some differences in aerosol sourcing in terrestrial environments (Majestic, Anbar, & Herckes, 2009; Majestic, Anbar, & Herckes, 2009). Therefore, Fe isotope composition has the potential to serve as this proxy in marine aerosols.

Bermuda is an ideal natural laboratory for this study. During the summer months it receives a large influx of Saharan dust, while most of the windblown particulate matter the rest of the year originates from North America. This provides a natural comparison between a soil-dust-dominated regime and a mixed regime of anthropogenic, soil-derived, and other sources. In addition to this seasonal contrast, it is known that soil dust particles are larger, on average, than combustion related aerosols (Lighty, Veranth, & Sarofim, 2000; Willeke & Whitby, 1975). By using size-segregated aerosol sampling, the ubiquitous soil-dust signal can be partially separated from other material, improving my ability to detect small isotopic shifts. In previous work measuring the Fe isotope composition of aerosols, including marine aerosols, little or no variation from average crustal rocks was found (Beard, Johnson, Von Damm, & Poulson, 2003; Flament et al., 2008; Waeles, Baker, Jickells, & Hoogewerff, 2007). However, none of these studies reported the isotopic composition of different size fractions. By employing size-segregated sampling at the Bermuda site, I sought to maximize my chance of detecting any Fe isotope variations that exist in marine aerosols.

In this paper I describe the results of Fe isotope analysis of size-segregated aerosol samples collected over a 13-month period on Bermuda and 12 Fe-bearing anthropogenic and natural materials representing potential source materials. I discuss seasonal patterns in the isotope data, the relationships between the isotope data and multi-element concentration data, and possible sources for the Fe reaching Bermuda.

2.2 Methods

Sample collection was done at the Tudor Hill Observatory (Bermuda Institute of Ocean Sciences), located on the Western shore of the Main Island of Bermuda. Samples were collected on 8” x 10” cellulose filters (Whatman 41) at ~1.3 m^3/min using a high-volume total suspended particle sampler with a volumetric flow controller and a single-stage cascade impactor (Tisch Environmental, TE-5170V-FPZ and TE-231). The impactor stage allowed for the collection of fine (< 2.5 μm, also known as $PM_{2.5}$) and coarse (> 2.5 μm) particles simultaneously. Samples were collected between April, 2011 and June, 2012; filters were changed weekly with three exceptions; exact dates for each sample can be found in Table 2.1. Field blanks were collected at the beginning, end, and every 10 weeks during sampling.

Prior to sampling, filters were soaked in 0.5 M HCl (all acids trace metal grade, Fisher) overnight, rinsed with 18MΩ H_2O, and dried prior to use. They were handled with acid-washed Teflon coated tweezers throughout. Following sample collection, filters were stored in a freezer at -20 °C when not in use (Upadhyay, Majestic, Prapaipong, & Herckes, 2009).

Table 2.1. Sample collection periods

	Sample		Sample		Sample		Sample
#[a]	Start Date	#	Start Date	#	Start Date	#	Start Date
2	11-Apr-11	*17*	*25-Jul-11*	31	7-Nov-11	45	19-Mar-12
3	18-Apr-11	*18*	*1-Aug-11*	32	14-Nov-11	46	26-Mar-12
4	25-Apr-11	*19*	*9-Aug-11*	33	21-Nov-11	47	2-Apr-12
5	2-May-11	*20*	*15-Aug-11*	34	14-Dec-11	48	9-Apr-12
6	9-May-11	*21*	*22-Aug-11*	35	9-Jan-12	49	23-Apr-12
7	16-May-11	*22*	*29-Aug-11*	36	16-Jan-12	50	30-Apr-12
9	30-May-11	*23*	*6-Sep-11*	37	24-Jan-12	51	7-May-12
10	6-Jun-11	*24*	*12-Sep-11*	38	30-Jan-12	52	14-May-12
11	14-Jun-11	*25*	*19-Sep-11*	39	6-Feb-12	53	21-May-12
12	21-Jun-11	*26*	*26-Sep-11*	40	13-Feb-12	54	28-May-12
13[b]	*27-Jun-11*	27	3-Oct-11	41	21-Feb-12	55	4-Jun-12
14	*4-Jul-11*	28	17-Oct-11	42	27-Feb-12		
15	*11-Jul-11*	29	26-Oct-11	43	5-Mar-12		
16	*18-Jul-11*	30	31-Oct-11	44	12-Mar-12		

[a] Sample 1 was used to verify sampler operation.

[b] Entries in italics are from the Saharan season.

Table 2.2. Description of source materials analyzed

Sample Name	Description
AZ Test Dust	Arizona soil dust; 0–10 µm[a]
African Buoy Dust	Dust collected from a buoy near the Cape Verde Islands[b]
NIST 2709	San Joaquin Soil
EPA #8	Pittsburgh #8 bituminous coal fly ash
NIST 1633b	Bituminous coal fly ash SRM
NIST 2691	Sub-bituminous coal fly ash SRM
#PM	European heavy-oil fly ash[c]
#PT1	European heavy-oil fly ash[c]
#TV	European heavy-oil fly ash[c]
EPA #5	Fuel oil fly ash
NIST 1650b	Diesel particulate matter SRM
NIST 1649a	Urban dust SRM

[a] Powder Technology Inc.

[b] Eglinton et al. (2002)

[c] Schroth et al. (2009)

A number of potential aerosol source materials were analyzed for Fe isotopes (Table 2.2). References to other studies where those same materials were used are also provided in that table.

Digestion was performed on filter subsections. For the coarse fraction, one of ten impactor strips was used; for the fine fraction, a 25 cm^2 square was cut. Cutting was done using zirconia ceramic blades (Specialty Blades Inc.) on a plastic cutting board—all equipment was washed in 10% HNO_3 prior to use and between samples.

Digestion of the filters and source materials was done by microwave (25 mL MARSXpress vessels, MARS 5, CEM) following a procedure modified from Upadhyay et al. (2009), which is described in the supporting material. The samples were then dried and brought up in 1 mL 7 M HCl for column chromatography (de Jong et al., 2007). The average processed Fe filter blank was 0.50 µg (4.5 µg/g filter) and 0.78 µg (3.4 µg/g filter) for the coarse and fine fractions, respectively. The values differ, because the coarse filter subsections were smaller. These blanks were higher than we anticipated, with the calculated blank for four samples representing greater than 25% of the total Fe. However, the lack of a correlation between Fe concentration and Fe isotope composition strongly suggests that the Fe blank has an isotope composition near the crustal value. A blank of any other composition would be apparent in the coarse fraction, which is consistently crustal throughout the sampling period. Thus the high blanks will have caused some range compression in the lowest concentration samples, but will not lead to any other distortion of the results. Each round of digestion included two reference materials to monitor element recovery (NIST SRMs 1649a and 2709). For all elements reported, recovery was 100% ±20%.

Major and minor element (Na, Mg, Al, P, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Rb, Sr, Zr, Mo, Cs, Ba, Hf, W, Pb, U) concentrations were analyzed using an X-Series quadrupole inductively coupled plasma mass spectrometer (ICP-MS) (Thermo Scientific) following the procedure described in Majestic et al. (2009 a; b). Isotope analysis was performed by multi-collector ICP-MS (Neptune,Thermo Scientific) with mass bias correction done by a combination of sample-standard bracketing and admixed Cu (Arnold, Weyer, & Anbar, 2004; Majestic et al., 2009a, b). Isotope data are reported as δ^{56}Fe, relative to IRMM-014 (Institute for Reference Materials and Measurements) (Eq. 2.1). Accuracy was monitored by the analysis of a gravimetric standard (δ^{56}Fe= −1.00‰) and an in-house marine sediment standard (δ^{56}Fe= −0.86‰). External precision, based on repeated analysis of these two secondary standards was ±0.13‰ (2σ).

$$\delta^{56}\mathrm{Fe} = \frac{^{56}\mathrm{Fe}/^{54}\mathrm{Fe}_{\mathrm{sample}}}{^{56}\mathrm{Fe}/^{54}\mathrm{Fe}_{\mathrm{IRMM\text{-}14}}} - 1 \qquad \text{Eq. 2.1}$$

The soluble phase was analyzed by ion chromatography (NO_3^-, NO_2^-, SO_4^{2-}, Cl^-, Na^+, NH_4^+, and K^+) and ICP-MS (elements as above). The soluble phase was extracted using 18 MΩ H_2O for the elements analyzed by IC and a pH 4.3 5mM acetate buffer for the elements analyzed by ICP-MS. Detailed methods are in the supporting material.

To explore relationships between the trace element concentrations and the isotope data, I calculated the bivariate correlations between the magnitude of the light isotope excursion for each sample (expressed as the difference between the δ^{56}Fe of the fine fraction and the crustal value of 0.09‰) and log-transformed concentrations of each of the elements analyzed and their percent Fe solubility. These correlations were calculated using SPSS v. 20.

2.3 Results

My analysis centers on a comparison between aerosols originating in the Sahara and aerosols originating in North America, thus the sampling periods that represent those two regimes must be identified. From daily back-trajectories calculated using the HYSPLIT model (Draxler & Rolph, 2013; Rolph, 2013), I identified the period between June 27 and October 2 (samples 13–26) as the time during which the majority of sampling days had long-range transport from the West African coast. I will refer to this as the “Saharan” season. During the remainder of the sampling period, Bermuda experienced air masses originating over the US or Canada on a majority of sampling days; I will refer to this time as the “non-Saharan” season. The back-trajectories for all sampling days, color-coded by season, are shown in Fig. 2.1.

Annually, Fe concentrations ranged from 3–281 ng Fe/m^3 (coarse) and 4–212 ng Fe/m^3 (fine), with concentrations reaching a maximum during the Saharan season (Fig. 2.2a). This seasonal pattern closely follows the trend of characteristically crustal elements, such as Al, Ti, and Mn (Appendix A). The Fe concentrations in the two size fractions are roughly equal throughout the year. These concentrations are in the same range as the open ocean studies cited in a synthesis by Sholkovitz et al. (2012). The soluble Fe/total Fe percentage in the coarse and fine fractions (Appendix A) was consistently low during the Saharan season (0.004% and 0.04%, respectively). During the remainder of the year the ratios were more variable, but higher on average (0.02%; 0.07%).

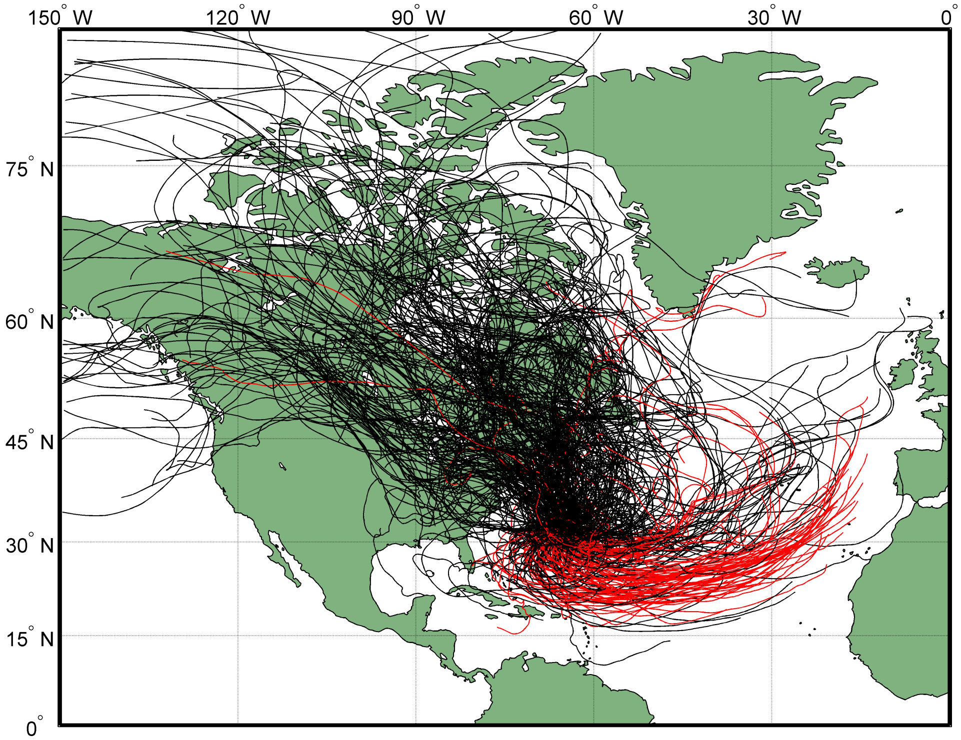

Figure 2.1. HYSPLIT back-trajectories for each sampling day. Days included in the Saharan season are shown in red and days included in the non-Saharan seasons are in black. Because filters were changed weekly, not daily, some trajectories from the West are red and some from the East are black.

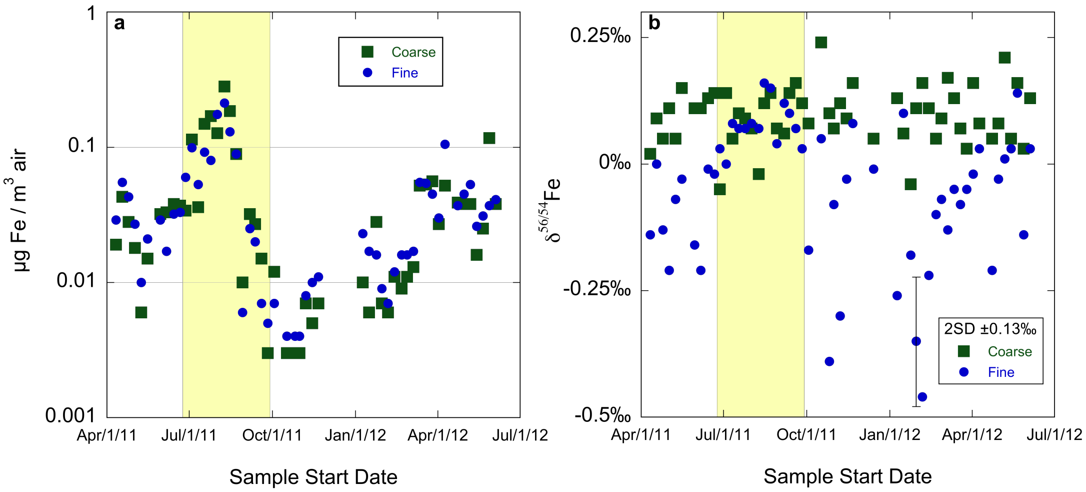

Figure 2.2. (a) Fe concentration by aerosol size and start date. The shaded area (samples 13–26) indicates the period during which air masses with back-trajectories from the East or Southeast made up the majority of sampling days. (b) Isotopic composition of both size fractions from each sampling period. The coarse fraction is consistently similar to crustal Fe, while the fine fraction shows evidence for a non-crustal source during much of the year. In the shaded area, Saharan dust dominates, and both size fractions have crustal isotope values. Outside of this period the coarse and fine samples are statistically different ($p < 0.001$); within it they are indistinguishable ($p = 0.36$).

The Fe isotope composition (δ^{56}Fe) of the coarse fraction (Fig. 2.2b, Table 2.3) shows no seasonal pattern and has an average value of 0.10‰ ±0.11 (2σ), which is well within error of the accepted value for crustal rocks, 0.09‰ (Beard et al., 2003). In contrast, the isotope composition of the fine fraction shows a strong seasonal pattern, with a Saharan season average of 0.08‰ and an average the rest of the year of -0.10‰, with one sample as light as -0.46‰. Statistically, the isotope compositions of the two size fractions are indistinguishable during the Saharan season (*p* = .66), but clearly distinct in the non-Saharan season (*p* < 0.001).

The Fe isotope compositions of the potential aerosol source materials are shown in Fig. 2.3 and Table 2.4. δ^{56}Fe values were not significantly less than 0‰ in any of the aerosol source materials I analyzed. The δ^{56}Fe values of the three materials of crustal origin (i.e., Test Dust, Buoy Dust, San Joaquin Soil) were consistent with previous measurements of crustal materials. The δ^{56}Fe values of oil and coal fly ashes overlapped each other and ranged from 0.10–0.61‰. The diesel particulate matter (NIST 1650b) and urban dust (NIST 1649a) SRMs were both very close to 0‰.

I also examined the filters using scanning electron microscopy (SEM) to explore whether there was a systematic difference between the non-Saharan season samples with and without negative δ^{56}Fe. However, the low particle density of the non-Saharan samples made it impossible to draw conclusions about this question.

Table 2.3. Fe isotope composition of size-segregated aerosol samples

Sample[a]	Coarse (‰)		Fine (‰)		Sample[a]	Coarse (‰)		Fine (‰)	
#	δ^{56}Fe	2σ	δ^{56}Fe	2σ	#	δ^{56}Fe	2σ	δ^{56}Fe	2σ
2	0.02	0.11	-0.14	0.08	30	0.07	0.01	n.a.[c]	
3	0.09	0.08	0.00	0.15	31	0.12	0.02	-0.30	0.06
4	0.05	0.01	-0.13	0.02	32	0.09	0.06	-0.03	0.08
5	0.11	0.24	-0.21	0.06	33	0.16	0.10	0.08	0.12
6	0.05	0.06	-0.07	0.09	34	0.05	0.18	-0.08	0.12
7	0.15	0.13	-0.03	0.21	35	0.13	0.02	-0.26	0.05
9	0.11	0.16	-0.16	0.07	36	0.06	0.01	0.10	0.19
10	0.11	0.04	-0.21	0.12	37	-0.04	0.08	-0.18	0.09
11	0.13	0.10	-0.01	0.04	38	0.11	0.02	-0.35	0.03
12	0.14	0.23	-0.02	0.06	39	0.16	0.14	-0.46	0.17
13[b]	*-0.05*	*0.30*	*0.03*	*0.08*	40	0.11	0.10	-0.22	0.01
14	*0.14*	*0.18*	*0.00*	*0.15*	41	0.05	0.03	-0.10	0.15
15	*0.05*	*0.18*	*0.08*	*0.06*	42	0.09	0.22	-0.07	0.08
16	*0.10*	*0.08*	*0.07*	*0.16*	43	0.17	0.09	-0.13	0.14
17	*0.09*	*0.05*	*0.07*	*0.12*	44	0.13	0.19	-0.05	0.02
18	*0.07*	*0.12*	*0.08*	*0.09*	45	0.07	0.08	-0.08	0.28
19	*-0.02*	*0.08*	*0.07*	*0.09*	46	0.03	0.14	-0.05	0.26
20	*0.12*	*0.18*	*0.16*	*0.13*	47	0.16	0.07	-0.02	0.03
21	*0.14*	*0.10*	*0.15*	*0.13*	48	0.08	0.08	0.03	0.06
22	*0.07*	*0.11*	*0.04*	*0.04*	49	0.05	0.07	-0.21	0.01
23	*0.06*	*0.08*	*0.12*	*0.13*	50	0.08	0.01	-0.03	0.10
24	*0.14*	*0.09*	*0.10*	*0.03*	51	0.21	0.20	0.01	0.10
25	*0.16*	*0.13*	*0.07*	*0.06*	52	0.05	0.01	0.03	0.09
26	*0.12*	*0.06*	*0.03*	*0.19*	53	0.16	0.02	0.14	0.20
27	0.08	0.07	-0.17	0.13	54	0.03	0.10	-0.14	0.13
28	0.24	0.22	0.05	0.12	55	0.13	0.15	0.03	0.01
29	0.10	0.16	-0.39	0.02					

[a] Sample 1 was used to verify sampler operation; samples 8 and 34 (fine) were unusable.

[b] Entries in italics are from the Saharan season.

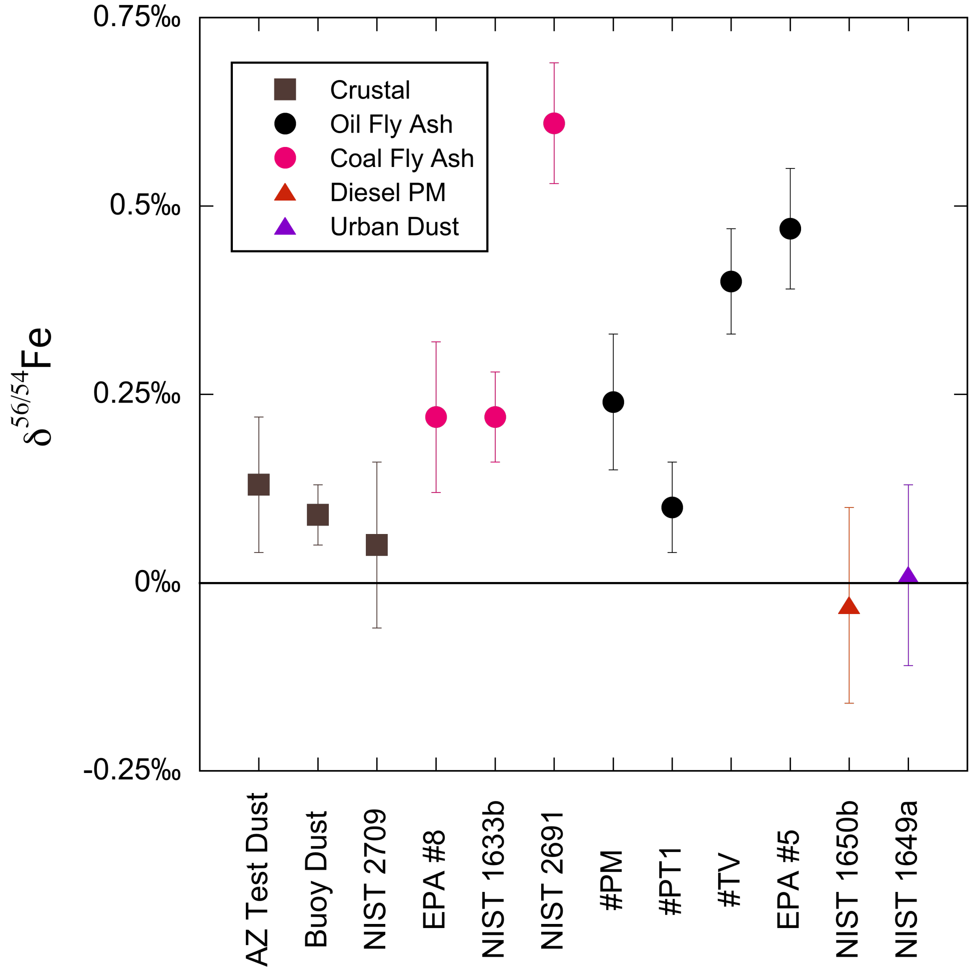

Figure 2.3: Isotopic composition of source samples. Sample descriptions are in Table 2.2

2.4 Discussion

My isotope data show that the Fe isotope composition of the fine fraction is statistically distinct from that of crustal Fe during the non-Saharan season, which is strong evidence for the presence of aerosol Fe from non-crustal sources during that season. In contrast, the δ^{56}Fe values of the fine fraction during the Saharan season are indistinguishable from crustal values, as are those of the coarse fraction in both seasons. In order to account for these data, there must be a source of aerosol Fe with a δ^{56}Fe value less than -0.5‰. In the following, I use my Fe isotope and trace metal concentration data to identify the most likely source of this light Fe.

Table 2.4. Fe Isotope Composition of Source Materials

Material	δ^{56}Fe (‰)	2σ (‰)
AZ Test Dust	0.13	0.09
African Buoy Dust	0.09	0.04
NIST 2709	0.05	0.11
EPA #8	0.22	0.10
NIST 1633b	0.22	0.06
NIST 2691	0.61	0.08
#PM	0.24	0.09
#PT1	0.10	0.06
#TV	0.40	0.07
EPA #5	0.47	0.08
NIST 1650b	-0.03	0.13
NIST 1649a	0.01	0.12

I analyzed 12 aerosol source materials for Fe isotopes (Fig. 2.3), including crustal and anthropogenic sources. None of those samples had δ^{56}Fe values lighter than 0‰, let alone lighter than -0.5‰, so they cannot directly be the source of the isotopically light Fe in Bermuda. Another major source of aerosols globally is sea spray. I was able to rule it out as the source of the light Fe both because direct measurements of δ^{56}Fe in ocean water near Bermuda found it to be approximately 0.3‰ at the surface (John & Adkins, 2012) and because the expected sea spray Fe contribution, using Na concentration as a tracer, is much lower than total Fe in my samples.

Lacking a definitive identification of the source of the light Fe from isotope data alone, I sought to identify it by looking for correlations between the isotope excursion for each sample and its trace metal concentrations and Fe solubility. The back-trajectories and isotope data both demonstrate that the non-Saharan season aerosols are distinct from those of the Saharan season, so the correlation analysis excludes the Saharan season data.

Within the non-Saharan season, I found significant negative correlations between the size of the isotope excursion and V, Fe, Co, and Ni concentrations (V and Fe, $p < 0.01$, Co and Ni, $p < 0.05$). The correlation coefficients were -0.422, -0.428, -0.411, and -0.361, respectively. There was no significant relationship between the isotope excursion and Fe solubility, nor with soluble K^+, a common tracer of biomass burning in aerosols.

The inverse relationship in the non-Saharan season between the isotope excursion and V along with the mismatch between the isotopic compositions of oil fly ash and my samples are surprising given my assumption at the outset of this study that oil fly ash was the primary non-soil dust source of aerosol Fe in Bermuda. This assumption followed from Sholkovitz et al. (2009) who presented evidence that emissions from oil combustion, which are highly enriched in V, are a major source of soluble Fe in the North Atlantic. My isotope data show that oil fly ash cannot be the source of the negative δ^{56}Fe found in the fine particles, but the V data suggest that oil fly ash is an important source of aerosol Fe. The presence of Fe from oil fly ash may explain some of the variability in the δ^{56}Fe values during the non-Saharan season. Consider a scenario in which the aerosol Fe in the fine fraction in Bermuda is a mixture of three sources whose contributions vary in time: soil dust, oil fly ash, and a third source with a δ^{56}Fe value < -0.5‰ that is not enriched in V. In the Saharan season, δ^{56}Fe values will be near crustal, because soil dust is the dominant source. The rest of the year, δ^{56}Fe values will vary from +0.1 to -0.5‰ as the contributions of each source vary, while V will tend to have an inverse relationship with the light isotope excursion.

I suggest three possibilities for the unknown light Fe source: industrial activity (refining, combustion, etc.), isotopic fractionation of soil dust, and biomass burning. Majestic et al. (2009a), with nearly identical size-segregated sampling as my study, observed a similar pattern of light Fe in a suburban site in Arizona (Higley, AZ) to that in Fig. 2.2b and concluded that industrial material was the most likely source. They found δ^{56}Fe values in the $PM_{2.5}$ fraction that were around -0.5‰ and PM_{10} values that were closer to crustal composition. The key difference is that Majestic et al. found that the isotopically light Fe was positively correlated with enrichments in Pb, Cd, V, and Cr, which argued for an industrial source, whereas I did not find any such relationships in the Bermuda samples. Further evidence against an industrial source is that no study to date has identified specific industrial materials that could serve as this source of negative δ^{56}Fe (Flament et al., 2008; Majestic et al., 2009b).

Evidence from other published work shows that it is possible to fractionate Fe during dissolution, but this can only create isotopically light aerosols under very specific conditions. Wiederhold et al. (2006) showed that partial dissolution of goethite produces an isotopically light dissolved phase in the presence of oxalate, a compound known to be important to aerosol chemistry (e.g., Wozniak et al. 2013). But this fractionation alone will not result in an isotopically light aerosol, because the dissolved phase will still be in contact with the undissolved solid and it is very difficult to separate the liquid and solid phases in an aerosol. However, if dissolution and reprecipitation were to yield a distinct phase from the original Fe-bearing mineral (e.g., Shi et al., 2009), the bonding between those two phases could be weak enough to be separated by shattering after a collision with another particle (Kok, 2011; Mouri & Okada, 2007). Reid et al. (2008) showed that the size distribution of dust was not significantly altered after ~1000 km atmospheric transport, arguing that shattering is not a major occurrence in transport. Thus, while it is reasonable to think that isotopically fractionated precipitates form on aerosol particles in transport, the only way such material could be the source of the light Fe in our study is through shattering, which, though possible, is a low probability event.

Finally, the idea of biomass burning as the source is supported by measurements of the Fe isotope composition of plant material showing that the δ^{56}Fe of plant material can be as much as 1.5‰ light relative to soil, making it one of the very few analyzed materials in the same range as the Bermuda data (von Blanckenburg, von Wiren, Guelke, Weiss, & Bullen, 2009). Other such materials include rocks with a chemical origin, such as Fe-Mn nodules and some banded Fe formations (Beard et al., 2003), but exposures of these rocks are relatively rare and would be unlikely aerosol sources. I did not find a relationship between δ^{56}Fe and soluble K^+, a common tracer of biomass burning in aerosols. However, Pachon et al. (2013) and references therein have questioned the reliability of this approach because K is emitted by other common aerosol sources (sea spray, mineral dust) in addition to biomass burning. Especially because combustion aerosols are predominantly in the fine fraction, biomass burning seems the most likely source of the light Fe.

Even the small body of work done previously shows that the Fe isotope compositions of plant materials vary widely. Data from both von Blanckenburg et al. (2009) and Kiczka et al. (2010) show differences greater than 1‰ between different plant species. These variations are attributable to a number of factors including differences in Fe uptake strategies (Römheld & Marschner, 1986) and the mineralogy, nutrient content, and maturity of the soil (Kiczka et al., 2010). This research suggests that grasses, because of their minimally fractionating Fe uptake strategy, are unlikely to have light Fe isotope compositions, but argues that all or most non-grass biomass burning should be isotopically light.

2.5 Conclusions

This work shows that Fe isotope analysis can provide valuable insight into the sources of Fe in marine aerosols. With the present dataset, I have shown that Fe in the coarse fraction is dominantly of crustal origin and does not vary in isotopic composition with season or wind direction. Fe in the fine fraction is of crustal origin only during the Saharan season. In the non-Saharan season, I found that the Fe isotope composition of the fine fraction is variable, which strongly indicates a non-crustal source with a δ^{56}Fe < -0.5‰. Because plant matter is the only likely source material known to be isotopically light, biomass burning appears to be the most likely candidate for this unknown source. Identifying and quantifying this source is an important goal for future research so as to more fully understand the nature of nutrient delivery to the open ocean.

Chapter 3

UNIQUE HG STABLE ISOTOPE SIGNATURES OF COMPACT FLUORESCENT LAMP-SOURCED MERCURY[2]

3.1 Introduction

All fluorescent lamps (FL) use mercury (Hg) and can be a source of Hg to the environment when broken (Johnson et al., 2008). The share of atmospheric anthropogenic Hg emissions represented by FL in the United States is 1–5% (Keating et al., 1998; NESCAUM, 2006, 2011). Only a third of FL are recycled (NESCAUM, 2011). As fluorescent lighting continues to supplant incandescent lighting, and as emissions from large point sources of Hg, such as coal-fired power plants and municipal waste incinerators, are reduced, FL will become an increasingly important source of Hg to the environment (Eckelman, Anastas, & Zimmerman, 2008; NESCAUM, 2011). Therefore, a method to detect and quantify Hg derived from FL would be very useful. Isotope analysis may provide such a method.

Advances in mass spectrometry and interest in geochemical tracers have spurred the discovery of many fractionating processes affecting non-traditional stable isotopes. This is particularly true of Hg, which has been shown to undergo conventional mass-dependent fractionation (MDF) as well as mass-independent fractionation (MIF) (Bergquist & Blum, 2007; Hintelmann & Lu, 2003; Kritee, Blum, Johnson, Bergquist, & Barkay, 2007; Schauble, 2007). MIF of ^{199}Hg and ^{201}Hg can be caused by the nuclear volume effect and/or the magnetic isotope effect, but recent studies have observed MIF of

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[2] Originally published as Mead, C., Lyons, J. R., Johnson, T. M., & Anbar, A. D. (2013). Unique Hg stable isotope signatures of compact fluorescent lamp-sourced Hg. *Environmental Science & Technology, 47*(6), 2542–2547.

^{200}Hg, which cannot be explained by either of these effects (Bergquist & Blum, 2007; Chen, Hintelmann, Feng, & Dimock, 2012; Gratz, Keeler, Blum, & Sherman, 2010; Schauble, 2007).

Based on existing research, I predicted that Hg would undergo distinctive isotope fractionation within FL. Photochemical reactions, which are central to the operation of FL, can induce unusual isotope effects (Bally & Langer, 1982; Bergquist & Blum, 2007). Previous research demonstrated that in addition to producing light, photoexcitation of Hg vapor within FL causes a small fraction of that Hg to become trapped in the glass wall over the lifetime of the lamp (Dang, Frisk, & Grossman, 2002; Dang, Frisk, Grossman, & Peters, 1999; Doughty, Wilson, & Thaler, 1995; Mulder & van Heusden, 1983). This one-way transport preserves the isotopic fractionation between the trapped Hg and the vapor by preventing any re-equilibration.

Hg exists in a number of forms within a FL (Figure 3.1). A Hg amalgam pellet serves as the primary reservoir, with a small amount of Hg vapor present in equilibrium with the amalgam. Less than 1% of the total Hg in the lamp leaves the vapor phase and becomes adsorbed to the interior of the lamp, and a similar amount becomes trapped within the glass wall. Light is generated by exciting the Hg vapor with an electric current. When the Hg atoms return to their ground state, they emit a characteristic UV photon, which is absorbed by the phosphor powder at the lamp wall. The phosphor then re-emits visible light.

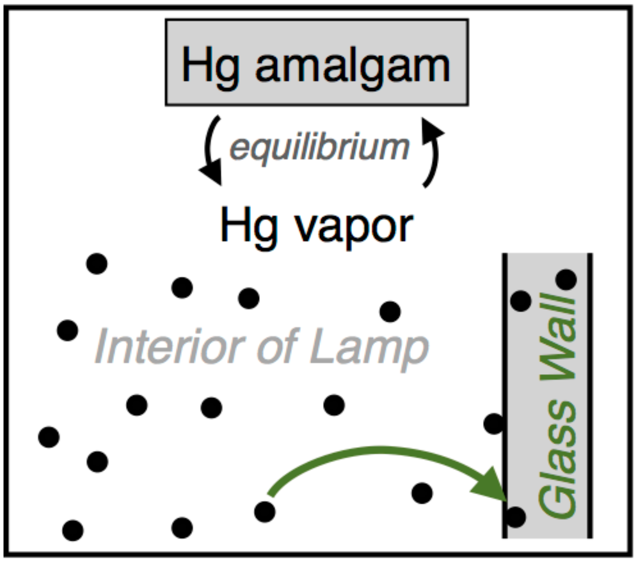

Figure 3.1. Schematic diagram of a fluorescent lamp. The Hg amalgam is located in the base of the lamp and the equilibrium vapor is regulated by the operating temperature. During lamp use, small amounts of Hg becomes trapped within the glass wall.

For this study, I analyzed the Hg isotope composition of compact fluorescent lamps (CFL) used for known numbers of hours to determine whether Hg trapped in their glass walls is isotopically fractionated from the main reservoir of Hg and, if so, whether this fractionation is distinct from that of previously measured sources of environmental Hg. The CFL Hg was divided into two components for analysis: (1) the trapped Hg (i.e., Hg contained within the glass matrix) and (2) the bulk Hg (i.e., the combination of the Hg amalgam pellet, Hg vapor, and adsorbed Hg). I also measured whole-lamp Hg (bulk Hg + trapped Hg), which provides a complete account of all Hg contained within the lamp.

3.2 Materials and Methods

The CFL used in this study were taken from a single box of 14-watt consumer lamps (EcoSmart, Home Depot part #785800). Three were retained in unused condition.

The others were used continuously for 1700, 3600, 10,000 or 16,000 hours. The rated lifetime of the lamps is 10,000 hours. To determine the composition of the trapped Hg, a lamp was broken, the amalgam pellet was removed, and the glass was placed in an HDPE container with 100 mL 10% HNO_3 for one week to remove adsorbed Hg. Then the glass fragments were removed, rinsed with 2% HNO_3 until no phosphor powder was visible, and placed in a second HDPE container. 100 mL of a 1:1 mixture of HNO_3 and HF was added to the glass fragments to extract the Hg from the glass matrix (Thaler, Wilson, Doughty, & Beersb, 1995). For total lamp digestions, an intact lamp was placed in an HDPE container with 100 mL concentrated HNO_3 and 10 mL H_2O_2. The container was sealed and the lamp was then broken, allowing any Hg vapor to oxidize and enter the dissolved phase. After one week a 15 mL aliquot was taken. This aliquot reflects the isotopic composition of the total lamp minus the Hg trapped in glass. 100 mL concentrated HF was then added in order to completely extract the Hg from the lamp. Samples were diluted by a factor of 100 before analysis, so damage from the HF to the glass components of the analytical equipment was minimal. The total blank from these digestions was < 25 ng Hg.

Isotope ratio measurements were made using a Neptune (Thermo Elemental) multicollector inductively coupled plasma mass spectrometer. A custom-made cold vapor system was used for sample introduction (Mead & Johnson, 2010). Briefly, sample Hg(II) is reduced to Hg^0 by $SnCl_2$ and pumped through a small glass chamber with a ground glass frit at the bottom. Ar gas is brought through the frit at 30 mL/min, which strips the Hg^0 from the liquid phase and delivers it directly into the plasma torch. The method sensitivity is ~0.2 V ^{202}Hg/ppb.

Isotope data are reported in permil (‰) relative to NIST SRM-3133 using delta notation: $\delta^{xxx}Hg = (^{xxx}Hg/^{198}Hg_{sample})/(^{xxx}Hg/^{198}Hg_{SRM\text{-}3133}) - 1$, where xxx denotes the mass of each respective isotope. The "cap-delta" notation is defined: $\Delta^{xxx}Hg = ln(\delta^{xxx}Hg + 1) - X\ ln(\delta^{202}Hg + 1)$, where X is -0.5074, 0.2520, 0.5024, 0.7520, or 1.493 for ^{196}Hg, ^{199}Hg, ^{200}Hg, ^{201}Hg, or ^{204}Hg, respectively. This scaling factor is equal to the relative amount of MDF experienced by each isotope pair, such that cap-delta is zero when only MDF is present. The scaling factor for kinetic isotope fractionation was defined in Eq. 21 in Young, Galy, & Nagahara (2002). For $\Delta^{xxx}Hg$ (relative to $^{202}Hg/^{198}Hg$), $X = ln(M_{198Hg}/M_{xxxHg}) / ln(M_{198Hg}/M_{202Hg})$, where M_{xxxHg}, M_{198Hg}, and M_{202Hg} are exact isotope masses.

Mass bias was corrected by sample-standard bracketing using the NIST SRM-3133 standard. Mass bias correction using admixed thallium can provide superior precision on measurements of $\delta^{xxx}Hg$, but sample-standard bracketing was sufficiently precise given the very large delta values measured in this study. Furthermore, $\Delta^{xxx}Hg$ are internally normalized, so the precisions of both methods are comparable. External reproducibilities for each ratio, determined by repeated analysis of the UM-Almadén secondary standard, are shown in Table 3.1.

Due to the large and unusual fractionation that was observed, extensive checks were performed to rule out possible analytical artifacts. Replicate measurements were taken using different faraday cup configurations to check for differences in cup efficiencies. The mass range from 118 to 240 Da was scanned at the 5 mV-level to rule out any isobaric or exotic polyatomic interferences (e.g., ^{196}Pt, ^{198}Pt, $^{118}Sn^{40}Ar^{40}Ar$, ^{204}Pb). No new potentially interfering species were detected. Pb does not pass through the gas-liquid separator. Nonetheless, ^{206}Pb was monitored. Samples from HNO_3:HF extractions were run in a dilute HNO_3:HF matrix, so standards were run in an identical acid matrix to rule out matrix effects. These were found to be indistinguishable from the normal 2% HCl matrix. Finally, a secondary standard was prepared gravimetrically by adding a ^{201}Hg isotope spike (Oak Ridge) to SRM-3133. Multiple analyses of this secondary standard returned the gravimetrically determined value.

To assess whether self-shielding fractionation (see description below) could explain my results, I calculated the patterns of fractionation across all Hg isotopes that would be expected from self-shielding, MDF, and other effects and compared them to my data. MDF was calculated using an exponential fractionation law, $r_i = R_i(M_{xxxHg}/M_{198Hg})^{ß}$, where r_i is the unfractionated isotope ratio, R_i is the fractionated ratio, M_{xxxHg} and M_{198Hg} are isotope masses, and ß is the fractionation factor, which is shared across all ratios. Fractionation factors for self-shielding fractionation were calculated using Hg absorption and emission estimates from a Monte Carlo simulation by Sommerer (1993). The peak absorption and emission intensities for each isotope were normalized to ^{202}Hg, the most abundant isotope, then, the emission/absorption ratio was calculated for each isotope. This ratio represents the degree to which each isotope is less self-shielded than ^{202}Hg, thus the amount of self-shielding fractionation expected relative to ^{202}Hg. These values are 9.3, 2.0, 1.7, 1.2, 1.7, and 1.6 for ^{196}Hg, ^{198}Hg, ^{199}Hg, ^{200}Hg, ^{201}Hg, and ^{204}Hg, respectively. It should be noted that the ^{196}Hg absorption is very weak, so the emission/absorption ratio determined for ^{196}Hg is less precise than those of the other isotopes. The magnetic isotope effect and nuclear volume effect, which produce MIF only of ^{199}Hg and ^{201}Hg, were modeled using ^{199}Hg/^{201}Hg ratios of 1.25 and 1.55, respectively, consistent with Zheng & Hintelmann (2010b).

The array of fractionation factors for each isotope effect was multiplied by a scalar and a best fit for each isotope effect, or combination of effects, was found by minimizing the sum of squared errors between the model isotope effect(s) and a measured sample across all six isotope ratios. Each fractionation type was scaled by a free parameter.

3.3 Results and Discussion

The trapped Hg of used CFL show unusually large isotopic fractionation (Figure 3.2, Table 3.1), the pattern of which is entirely different from that which has been observed in previous Hg isotope research aside from intentional isotope enrichment (Bergquist & Blum, 2007; Biswas, Blum, Bergquist, Keeler, & Xie, 2008; Estrade, Carignan, & Donard, 2011; Estrade, Carignan, Sonke, & Donard, 2009; Gehrke, Blum, & Marvin-Dipasquale, 2011; Ghosh, Xu, Humayun, & Odom, 2008; Jackson, Whittle, Evans, & Muir, 2008; Laffont et al., 2009; Sherman, Blum, Keeler, Demers, & Dvonch, 2012; Sherman et al., 2009; Sonke et al., 2011; Zheng & Hintelmann, 2009, 2010a, 2010b). Most notably, there is no straightforward relationship between extent of fractionation and isotope mass. Thus, while previous studies of MIF of Hg only observed large deviations from mass-dependence in odd mass isotopes, our results clearly show MIF across multiple even mass and odd mass isotopes.

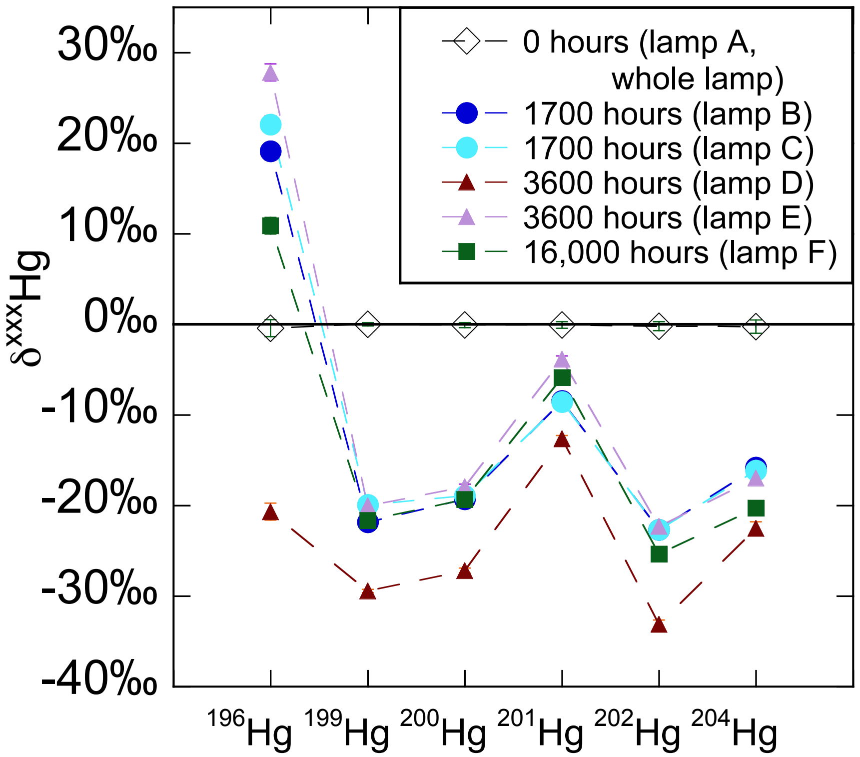

Figure 3.2. Isotope composition of trapped Hg from five CFL of three different ages and of the whole lamp for one unused CFL. I found that all isotopes were enriched relative to ^{202}Hg.

The observed pattern of fractionation is characterized by enrichment in all isotopes relative to ^{202}Hg, the most abundant isotope. This pattern is consistent among the different CFL measured, indicating that there is no systematic trend in the magnitude or pattern of fractionation with time. However, Hg clearly becomes incorporated into the glass with time, because I found no trapped Hg in unused lamps, which is consistent with prior research (Doughty et al., 1995). Further, whole-lamp measurements of used CFL (not shown) are identical within error to those of unused CFL, all of which are within error of 0‰. This is as expected from mass balance and confirms that CFL are a closed system for Hg. The largest deviations from the observed pattern of fractionation are the

Table 3.1. Hg Isotope Composition of CFL Components

Sample Type	Sample Name (hours used)	δ^{196}Hg (‰)	δ^{199}Hg (‰)	δ^{200}Hg (‰)	δ^{201}Hg (‰)	δ^{202}Hg (‰)	δ^{204}Hg (‰)	Δ^{196}Hg (‰)	Δ^{199}Hg (‰)	Δ^{200}Hg (‰)	Δ^{201}Hg (‰)	Δ^{204}Hg (‰)
Whole Lamp	Lamp A (0 hours)	-0.42	0.01	-0.08	-0.06	-0.20	-0.24	-0.52	0.06	0.02	0.09	0.06
	Lamp G (3600 hours)	0.59	-0.08	-0.18	-0.27	-0.38	-0.56	0.52	0.02	0.01	0.01	0.01
Trapped Hg Only	Lamp B (1700 hours)	19.25	-21.92	-19.47	-8.74	-23.04	-16.34	7.25	-16.29	-7.95	8.75	18.32
	Lamp C (1700 hours)	22.09	-19.90	-18.93	-8.58	-22.67	-16.12	10.25	-14.32	-7.59	8.62	17.96
	Lamp D (3600 hours)	-20.68	-29.72	-27.60	-13.14	-33.85	-23.56	-38.00	-21.49	-10.69	12.66	27.57
	Lamp E (3600 hours)	27.82	-20.03	-17.91	-3.86	-22.29	-16.97	16.00	-14.55	-6.74	13.08	16.54
	Lamp F (16,000 hours)	10.90	-21.64	-19.31	-5.89	-25.37	-20.26	-2.20	-15.40	-6.59	13.42	17.90
Bulk Hg Only	Lamp G (3600 hours)	-1.23	0.00	-0.20	-0.41	-0.51	-0.84	-0.58	0.13	0.06	-0.03	-0.08
	Lamp H (10,000 hours)	-1.92	0.60	0.35	-0.07	0.22	-0.09	-1.81	0.54	0.24	-0.24	-0.43
SRM[a]	UM-Almadén	0.43	-0.12	-0.12	-0.09	-0.28	-0.57	0.29	-0.05	0.02	0.12	-0.15
2 SD[b]		0.93	0.18	0.27	0.38	0.48	0.73	0.99	0.06	0.05	0.17	0.12

[a] Standard Reference Material

[b] Standard Deviation

smaller fractionation of ^{196}Hg and the larger fractionation of ^{198}Hg in lamp D. Lamp E, which was used for the same amount of time as lamp D, does not show these offsets. Lamps D and E were aged and processed identically, and I cannot provide an explanation for this inconsistency.

Table 3.2. Masses of Trapped Hg and Whole Lamp Hg

Sample	Number of Hours Used	Mass Hg in Glass (μg)[a]	Mass Hg in Whole Lamp (μg) [a]
Lamp B	1700	4.5	
Lamp C	1700	19	
Lamp D	3600	19	
Lamp E	3600	16	
Lamp F	16,000	100	
Lamp A	0		3300
Lamp G	3600		2200
Lamp H	10,000		3500

[a] The digestion procedure did not allow for analysis of trapped Hg and whole lamp Hg from the same sample.

I interpret these results to indicate that Hg isotopes are fractionated between the trapped pool and the bulk reservoir as a result of CFL operation. Accordingly, I expect to see that the isotope composition of Hg in the bulk reservoir is complementary to that in the glass, reflecting mass balance. The trapped Hg is a small fraction of the total Hg in the lamp; less than 1% of the bulk Hg is incorporated into the glass after 3600 hours (Table 3.2). Therefore, the complementary fractionation in the bulk reservoir should be approximately 100 times smaller than of the trapped Hg. Measurements of these two reservoirs are reported in Figure 3.3, where Figure 3.3a shows the Δ^{xxx}Hg of the trapped Hg, while Figure 3.3b shows the Δ^{xxx}Hg of the bulk Hg. The method of isolating the two reservoirs did not allow analysis of both reservoirs within a single lamp, so the data shown are for multiple lamps spanning a range of hours of use. Δ^{xxx}Hg, which measures the deviation from MDF, is used here because it can be measured at higher precision than δ^{xxx}Hg (Blum & Bergquist, 2007). These measurements conform to the expectation from mass balance; the Δ^{xxx}Hg values of the residual pool (Figure 3.3b) are opposite in sign and roughly 100 times smaller than those of the trapped Hg (Figure 3.3a). Additionally, by comparing lamps of different ages, it is evident that the residual Hg becomes increasingly fractionated through time as more Hg is removed into the glass.

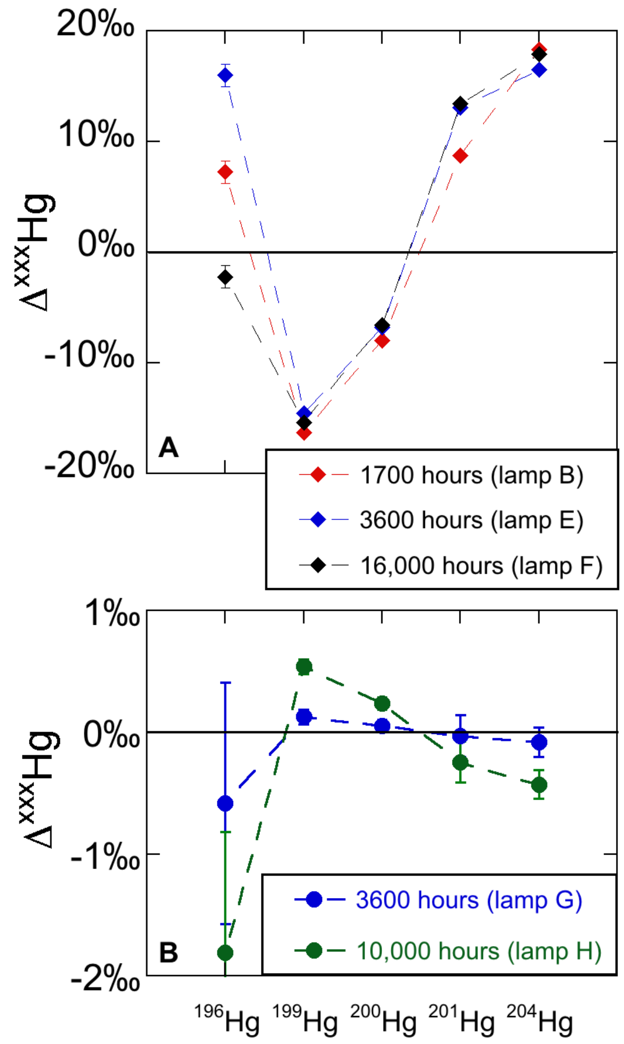

Figure 3.3. (a) Isotope composition, expressed using “cap-delta” notation, of trapped Hg from lamps with three different hours of use. (b) Isotope composition of bulk Hg (all Hg

except trapped Hg) for lamps of two different hours of use. The complementary fractionation of the bulk reservoir reflects the removal of a small amount of highly fractionated Hg with the pattern seen in (a). The increase in fractionation between lamps G and H is caused by greater total Hg removal into the glass, not a change in the isotopic composition of the trapped Hg. The data in (a) and (b) are from different lamps because our method of isolating each Hg reservoir did not allow us to measure the trapped Hg and bulk Hg from the same lamp. Δ^{xxx}Hg are normalized to ^{202}Hg/^{198}Hg, so Δ^{202}Hg is, by definition, zero for all samples.

Previous work describing MIF of Hg has identified two mechanisms of fractionation, the nuclear volume effect and the magnetic isotope effect, both of which produce MIF of ^{199}Hg and ^{201}Hg only (Bergquist & Blum, 2007; Schauble, 2007). Therefore, these effects alone cannot explain the Hg isotope fractionation within CFL. All isotopes in the CFL Hg are enriched relative to ^{202}Hg, the most abundant Hg isotope, suggesting that the effect is modulated by isotope abundance. One such isotope effect, “self-shielding”, known from the oxygen isotope system, has been observed in laboratory conditions and has also been used to explain isotope anomalies in meteorites and molecular clouds (Bally & Langer, 1982; Clayton, 2002; Lyons & Young, 2005; Sander, Loree, Rockwood, & Freund, 1977). Self-shielding effects occur when radiation drives the preferential removal of the less abundant isotopes of an element from an optically thick vapor, because the transmittance of radiation at each isotope-specific absorption line is determined by the abundance of the given isotope. I suggest that differential excitation among Hg isotopes as a result of self-shielding is a key driver of the observed fractionation in CFL.

The proposed self-shielding effect is regulated by the hyperfine structure of the Hg absorption spectrum, specifically that of the 254 nm line. Because of the differences in mass and nuclear spin among the seven Hg isotopes, the Hg absorption line at 254 nm is split into 10 components (Sommerer, 1993). Under CFL conditions, thermal and collisional broadening reduce these to six distinct lines, three of which are mono-isotopic and three of which are composed of multiple isotopic lines (Sommerer, 1993). The transmittances at all lines are very low, but are not identical. The specific transmittance at any given line is a function of the underlying isotopic abundance, so the six components of the 254 nm line will be attenuated in proportion to their respective isotope abundances. This attenuation allows the abundant isotopes to partially "shield" themselves from photoexcitation (see Figure 3.4). As a result, a greater proportion of low abundance isotopes than of high abundance isotopes will be photoexcited, fractionating the excited state relative to the ground state. If the excited pool is preferentially bound into the glass, as earlier research suggests, then the trapped Hg will also be enriched in low abundance isotopes (Dang et al., 2002; Mulder & van Heusden, 1983).

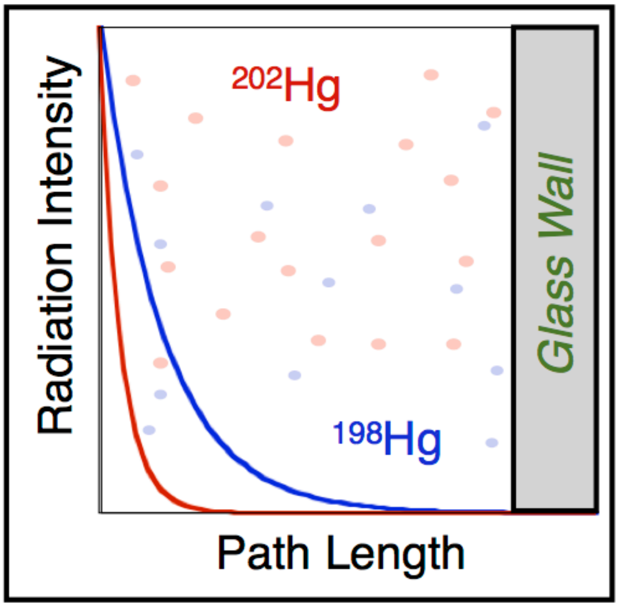

Figure 3.4. Illustration of the self-shielding effect. The greater abundance of ^{202}Hg atoms results in a smaller optical depth for radiation at the ^{202}Hg-specific wavelength than at the absorption wavelength of the less abundant ^{198}Hg. As a result, a greater proportion of ^{198}Hg atoms are susceptible to photo-excitation than ^{202}Hg atoms.

To assess whether self-shielding can account for some or all of the observed fractionation, I estimated the relative fractionation factors for each Hg isotope ratio that would be expected from self-shielding. I then combined these self-shielding fractionation factors with those of other known effects (MDF, nuclear volume effect, magnetic isotope effect) to assess the result of multiple fractionating processes occurring simultaneously. Because the magnitudes of all these potential effects cannot be predicted at present, I attempted to fit the observations with the magnitude of each fractionation effect as an adjustable parameter. Shown in Figure 3.5 are the results of two different models, both compared with measurements of the trapped Hg of lamp E, a lamp chosen to represent the typical isotope composition of CFL in this study.

This exercise demonstrates that a self-shielding effect produces the best match to the observed fractionation among known fractionation mechanisms. A poor qualitative match is found when only MDF is invoked (Figure 3.5A). In contrast, the self-shielding effect fractionation follows the general contour of the measured data (Figure 3.5B). That fit is improved by invoking self-shielding and MDF together (Figure 3.5C), which argues that multiple fractionating processes are occurring in the CFL. Incorporating nuclear volume effect or magnetic isotope components similar to published studies did not significantly improve the fit (Bergquist & Blum, 2007; Zheng & Hintelmann, 2010b). Much of the remaining misfit is on ^{199}Hg and ^{201}Hg, suggesting that the unusual properties of odd mass isotopes contribute to the fractionation in CFL. This hints at an as yet unknown isotope effect among odd mass Hg isotopes.

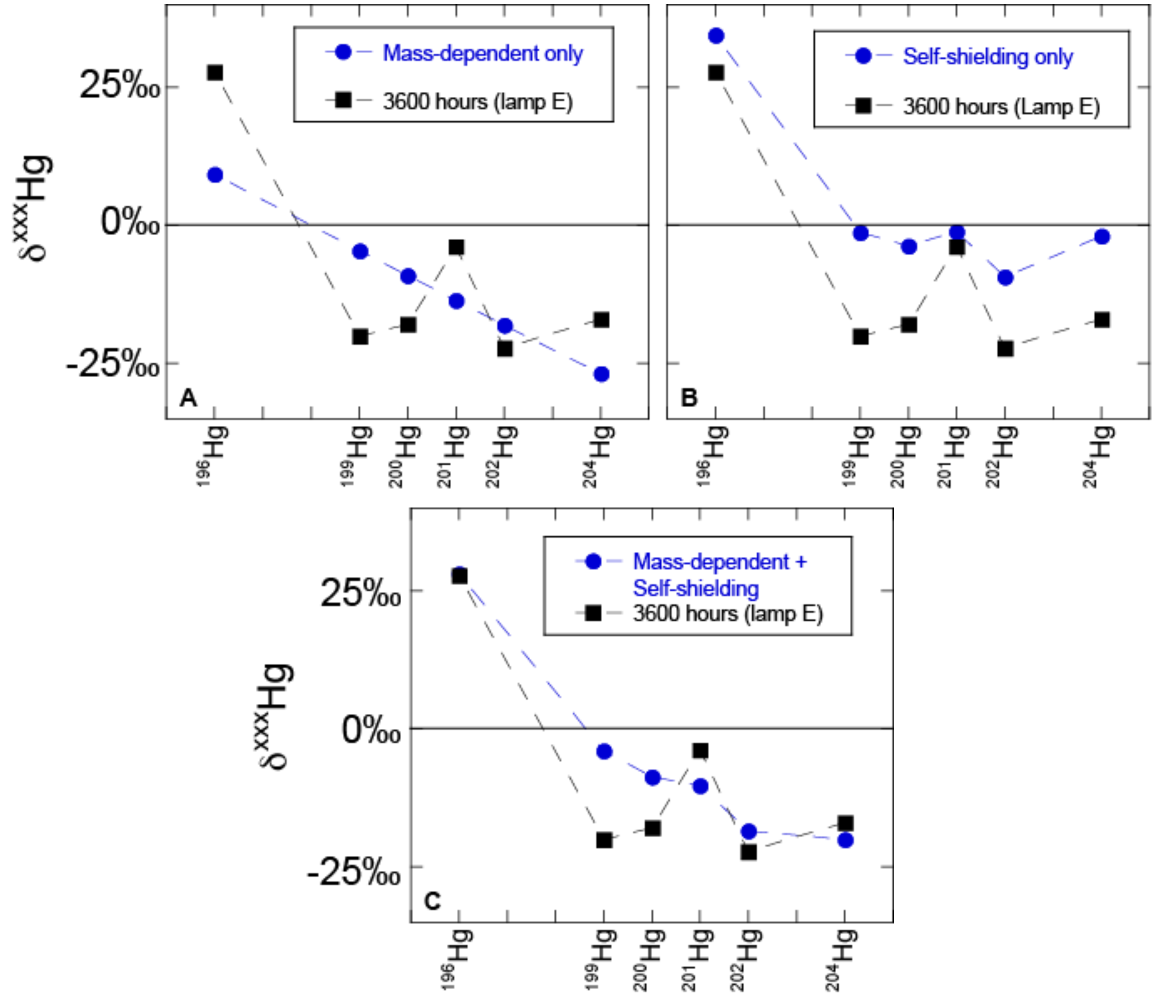

Figure 3.5. Comparison of different fractionation models to data from lamp E. Each model was fit to the data using the least squares method. Error bars on measured data are smaller than the symbols. (a) MDF only. (b) Self-shielding fractionation only. (c) Combination of MDF and self-shielding. The combination is a better fit to the measured data than MDF or self-shielding alone. Incorporating MIF of ^{199}Hg and ^{201}Hg like that produced by the nuclear volume effect or magnetic isotope effect does not improve the fit, because both of those processes fractionate ^{199}Hg and ^{201}Hg in the same direction whereas the mismatch is opposite in sign for the two odd isotopes.

3.4 Environmental Relevance

The most similar isotope measurements to those presented here are of Hg in precipitation, published recently by Chen et al., which show Δ^{200}Hg of up to 1.24‰ (Chen et al., 2012). The findings of Chen et al. are intriguing and may be another example of self-shielding driven fractionation. Although the relative values of Δ^{199}Hg, Δ^{200}Hg, and Δ^{201}Hg in that study do not match either my model of self-shielding fractionation (Figure 3.5b) or my measurements of CFL Hg, it is impossible to rule out self-shielding as the source of fractionation because ^{199}Hg and ^{201}Hg are subject to MIF from other sources and Chen et al. were not able to measure Δ^{204}Hg, which has no other source of MIF. The primary argument against self-shielding fractionation of Hg in the atmosphere is that there is not a sufficient column density of Hg vapor to cause significant differences in the rates of photoexcitation between abundant and rare isotopes. Chen et al. provide evidence that the fractionation occurs in the upper troposphere at high latitude in the winter. The shallow angle through the atmosphere that sunlight must travel to reach the arctic in winter makes the effective column density of Hg much higher than it would be elsewhere on Earth. I estimate the tangential column density of Hg^0 in this scenario to be $5\text{x}10^{17}$ m^{-2} (assuming an average upper troposphere Hg concentration of 750 pg Hg / m^3), which is 17% of the column density over the radius of a CFL ($3\text{x}10^{18}$ m^{-2}). This is more than an order or magnitude greater than the column density experienced by sunlight travelling perpendicular to the Earth's surface. Thus, the self-shielding effect in the arctic winter would be weaker than that seen in CFL, but much stronger than the effect at lower latitudes or in other seasons, which could explain why the MIF of ^{200}Hg was strongest in the winter.

Even including the Chen et al. data, FL Hg displays a unique pattern of fractionation. To apply this information, it is important to consider under what circumstances this pattern could be detected in real-world settings. Because of its distinctive mass-independent signature, the most effective method to detect FL Hg is by measuring Δ^{xxx}Hg. ^{196}Hg makes up only 0.15% of natural Hg, so at environmentally relevant concentrations, Δ^{199}Hg, Δ^{200}Hg, Δ^{201}Hg, and Δ^{204}Hg will be the most useful measurements. Lastly, because the trapped Hg is the least mobile FL component, this analysis will focus on the bulk Hg, which is released through evaporation soon (weeks to months) after breakage (Johnson et al., 2008; Li & Jin, 2011). A mixture between bulk-phase FL Hg, represented by lamp H as shown in Figure 3.3b, and mass-dependently fractionated Hg, will have positive values of Δ^{199}Hg and Δ^{200}Hg and negative values of Δ^{201}Hg and Δ^{204}Hg, though the absolute values depends on the mixture. A 10% mixture of FL Hg would have Δ^{199}Hg, Δ^{200}Hg, Δ^{201}Hg, and Δ^{204}Hg values of 0.05‰, 0.02‰, -0.03‰, and -0.04‰, respectively, while a 20% mixture would have values of 0.10‰, 0.05‰, -0.06‰, and -0.08‰, respectively. At these levels, FL Hg would be detectable based on reported precisions of Δ^{xxx}Hg from previous studies, which range from 0.02‰ to 0.09‰ (Biswas et al., 2008; Estrade et al., 2009; Sonke et al., 2011; Zheng & Hintelmann, 2009). Given that FL Hg is estimated to be 1–5% of overall anthropogenic Hg emissions in the US, a 10–20% concentration of FL Hg may be possible, particularly in landfills, where FL Hg will be relatively more abundant (Keating et al., 1998; NESCAUM, 2006, 2011).

The isotope fractionations reported in this study are unique in the Hg isotope literature and, as a result, have the potential to be a valuable tool in determining the fate of Hg released from FL. Currently it is unclear how mobile FL Hg is within landfills. Isotopic evidence could be a powerful tracer in such future research, especially in the case where FL Hg is not the sole source of Hg. Our data, together with the results of Chen et al., show that there is much yet to be discovered about the mechanisms of Hg isotope fractionation.

Chapter 4

A MIXED-METHODS EXPLORATION OF UNDERGRADUATES' UNDERSTANDING OF IMPORTANT BIOGEOCHEMISTRY CONCEPTS

4.1 Introduction

The traditional introductory geology course seeks to teach students the fundamental processes and materials that shape the world on which they live (e.g., Reynolds, Johnson, Morin, & Carter, 2012). However, much of that world is also shaped by biology, the interaction of which is explained in chemical terms (Wysession et al., 2012). As such, the current body of geoscience education research would be well served by research that studied student thinking in biogeochemistry.

A common approach in science education research is to identify misconceptions—mistaken ideas about scientific topics commonly held by students (see reviews by Bailey & Slater, 2011; Cheek, 2010; Francek, 2013). Learning is an active process in which a student must integrate new information into his or her existing mental framework (Chi, Slotta, & De Leeuw, 1994; Chi & Roscoe, 2002; Posner, Strike, Hewson, & Gertzog, 1982). Depending on the scientific accuracy of this existing framework, new information may be distorted so it aligns with the student's existing misconceptions or the student may reject the new information outright, with both cases resulting in no learning gain (Hake, 1998; Libarkin & Anderson, 2005). Research shows that the most effective instructional strategies force the students to discover the inherent contradictions in their misconceptions, but these strategies require the instructor to know in advance what misconceptions he or she should expect to encounter (Chi & Roscoe, 2002; Kortz, Smay, & Murray, 2008).

Experienced teachers generally have some idea of which concepts are the most difficult for their students. This type of pedagogical content knowledge is a key skill for successful teachers (Shulman, 1986), but in the context of education research, this remains anecdotal information not scientifically derived knowledge. To reach beyond anecdotes, one much take a systematic approach. That is the goal of the research I present here.

There are a number of terms similar to misconception used in the literature, including preconception, alternative conception, intuitive belief, and permutations thereof (e.g., Clement, Brown, & Zietsman, 1989; Nicoll, 2001; Pea, 1993). Among these, the term misconception is sometimes defined narrowly as a scientifically incorrect idea that is resistant to change by instruction (Chi et al., 1994). However, it is also commonly used in the generic sense, meaning simply any scientifically incorrect conception (Francek, 2013; Nicoll, 2001). Because my research did not attempt to track the resistance of these ideas to change through instruction, I have chosen to use the term misconception in this generic sense.

Previous researchers have employed several different methods to identify misconceptions. Osborne & Gilbert (1980) and Posner et al. (1982) used interviews alone. Treagust (1988, 1986) described a procedure that has been referenced by many later studies (Arthurs & Marchitto, 2011; Libarkin & Ward, 2011; Tan, Taber, Goh, & Chia, 2005). In brief, Treagust used interviews initially to explore students' misconceptions. From that interview data, he wrote multiple-choice questions using those misconceptions as distracters. For the initial survey, he included a free-response question after each multiple-choice question for students to explain their answers (i.e., a two-tiered survey). In a subsequent version, this free-response question was changed to a second multiple-choice question with common explanations for students to choose among. Libarkin and Anderson (2005, 2007) followed a similar procedure, but did not make extensive use of the two-tiered multiple-choice format.

Other researchers, such as Nicoll (2001) and Trundle, Atwood, and Christopher (2002), used interviews exclusively to explore misconceptions among undergraduates. They, along with Libarkin and Anderson (2007), point out the power of qualitative methods in misconceptions research. The open-ended approach is particularly useful because it facilitates the discovery of misconceptions that are new to the researcher.

It is fair to say that one misconception about misconceptions is that they are limited to uneducated people. In fact, as many of these studies have shown, people of all ages have misconceptions about science, from the youngest children in primary school (Driver, Guesne, & Tiberghien, 1985) to preservice teachers (Trundle et al., 2002) to graduate students in chemistry (Bodner, 1991). Thus, one would expect to find a number of misconceptions among undergraduates about the relatively advanced topic of biogeochemistry.

Although there is no previous education research studying biogeochemistry by name, work done in the related fields of biology, geology, chemistry, ecology, and environmental science provides some information about misconceptions in the field.

In chemistry, two groups of researchers have produced general chemistry concept inventories, both known as the Chemistry Concept Inventory (Krause, Birk, Bauer, Jenkins, & Pavelich, 2004; Mulford & Robinson, 2002; Mulford, 1996). These projects showed that students have trouble understanding how dissolved ion concentrations change during evaporation, something that is relevant to the task of understanding ocean chemistry among other areas of biogeochemistry. Students traditionally spend a great deal of time in chemistry courses writing and balancing chemical reactions; however, this research showed that they do not always transfer concepts like the conservation of mass to real-world scenarios. One example found in both Mulford (1996) and Bodner (1991) is the question of whether, and in what way, the mass of a nail changes as it rusts. Even some chemistry graduate students demonstrated misunderstanding of this concept (Bodner, 1991). Another chemistry concept that is essential to understanding how life affects long-term Earth processes is the relationship between reaction rates and thermodynamic favorability. A reaction can be thermodynamically favorable, but occur only very slowly in the absence of a biological intermediary. Krause et al. (2004) found that about a quarter of science majors in a general chemistry course did not understand the basic difference between reaction rate and reaction favorability, saying nothing about misconceptions they may have had about the biogeochemical applications of this concept.

In geology, the Geoscience Concept Inventory (GCI) and the misconceptions research that supports it (Libarkin, Anderson, Dahl, Beilfuss, & Boone, 2005; Libarkin & Anderson, 2005, 2007) provides several misconceptions relevant to biogeochemistry. Many people hold mistaken ideas about the age of the Earth, believing it is much younger than the scientifically accurate age of 4.6 billion years. The GCI research showed that even people who do understand that the Earth is extremely old do not appreciate what kinds of changes have occurred over those billions of years and believe the ancient Earth was quite similar to the modern Earth. This also extended to beliefs about the timing of the origin of life on Earth. Francek (2013) and Dove (1998) each wrote extensive reviews of geoscience misconceptions, though those reviews say very little about biogeochemical concepts.

A number of studies exist concerning misconceptions related to water and life on Earth. Arthurs (2011) and Arthurs and Marchitto (2011) both studied undergraduates' understanding of topics related to oceanography and hydrology. Those studies found that students commonly misunderstood the nature of groundwater and aquifers by thinking of them as similar to surface water. The studies also found that students had difficulty understanding ocean circulation. Munson (1994) reviewed the literature of ecological misconceptions, finding several that are relevant for biogeochemistry as well. Students often do not understand that ecosystems are complex, dynamic systems. As a consequence, they have trouble understanding how resources that are available or plentiful within an ecosystem at present might become limited or entirely depleted in the future. This clearly has implications beyond ecology. Similarly, students have trouble recognizing that two organisms with no direct interactions might be connected indirectly within an ecosystem. Lastly, Brody (1996) investigated the environmental science knowledge of 4th-, 8th-, and 11th-grade students. This study also focused its attention primarily on ocean science. It found that students across all ages studied had a poor understanding of the nature of the Earth's oceans. For example, they thought the ocean had a simple bowl-shape, rather than a complicated profile driven by plate tectonics, and that the bottom was "sandy rock." They believed that seaweed got its nutrients from soil, like land plants, but could also live very deep in the ocean beyond the reach of sunlight. Finally, because many students were aware of the need for fish to breathe oxygen, but unfamiliar with the concept of dissolved gas, they invented the idea that fish could breathe the water molecule itself to get oxygen.

Lastly, the greenhouse effect and climate change have been the subjects of a number of education research studies (as reviewed by Keller, 2006). A majority of those surveyed understood the basic connection between atmospheric CO_2 and the increase in warming. They were also aware of the existence of the greenhouse effect. However, they were not generally able to explain how the greenhouse effect worked. Students very often used the ozone layer hole to explain the warming. They claimed the hole was allowing more sunlight to enter the atmosphere and that the atmosphere was trapping that sunlight, rather than absorbing the re-emitted infrared radiation.

My goal in this research was to provide misconceptions research that is useful for teaching biogeochemistry and related subjects. The breadth of that topic meant that in order to cover the full range of biogeochemistry I would be including some topics that have been previously studied, most notably the greenhouse effect. I think that this is a reasonable choice, because it provides an opportunity to uncover details at the margins of those topics that were outside of the scope of previous, more narrowly defined studies. It also allows for a point of comparison to support the validity of my own work.

In this project, I used semi-structured interviews with undergraduates to determine whether they hold misconceptions about the field of biogeochemistry and to identify which specific misconceptions are common.

4.2. Methods

The concept list for this study relies on expert validation through a modified Delphi method (Dalkey, Brown, & Cochran, 1969). I created the initial list based on my own experience combined with input from textbooks and other content experts. The list was then reviewed and evaluated by eighteen content experts to produce the final concept list (Appendix B). I used those concepts to write my initial interview protocol, which I used for 8 interviews. The preliminary protocol was too long to be covered in an hour-long interview; thus, each interview covered a partially overlapping subset. I considered these interviews to be preliminary and exploratory. The purpose of these preliminary interviews was to make a general assessment of student understanding of biogeochemistry that would guide the remainder of the study. I encountered a wide range of misunderstanding even in this early phase. I also observed that some chemistry-related topics were difficult to discuss due to technical language or other prerequisite knowledge. Where possible, I rephrased these questions in non-technical language for the revised protocol.

In revising the interview protocol, I shortened it so that the same questions could be included in each interview. I also used the preliminary interviews to write a 32 item multiple-choice survey. The revised interview protocol may be found in Appendix C; the survey is reproduced in Appendix D.

The interview protocol and the survey share a common origin in the preliminary interview data. Thus, the results from each method are complementary. However, because I discovered many new misconceptions through interviews using the revised protocol, they are not all included in the survey. Future work will be able to use a revised survey instrument incorporating the misconceptions described in the following sections.

I interviewed 40 students for this study: eight on the initial protocol and an additional 32 using the revised protocol. I administered the survey online to students in three classes, two 100-level general education geology courses and a 300-level chemistry course, as well as to undergraduates solicited outside of specific courses. As a result of these varied recruitment approaches, the study population was academically diverse both in terms of year in school and major. I collected 251 multiple-choice test responses in total.

The respondents were all undergraduates at a major Southwestern US university. In compensation for their time, the interview respondents were given a nominal honorarium. The survey respondents in the three classes were awarded participation points at the instructors' discretion because the surveyed topics were relevant to the course material. Those students solicited outside of those courses were entered in a raffle for a gift certificate. The university's institutional review board approved this study. All participants were issued an information letter informing them of their rights as research subjects.

A person's prior scientific coursework will play a role in determining his or her responses to the interview questions. Because my goal in this study was exploratory, I did not try to control this variable, but instead asked each respondent his or her major, year in school, previous college science coursework generally, and geology or environmental science coursework specifically.

I audio recorded each interview and used a professional service to prepare a full transcript of each interview. Because I knew at the outset of the study which categories I was interested in examining, I used directed content analysis to code the transcripts (Hsieh & Shannon, 2005). The initial coding scheme was simple; I coded statements that were factually untrue and also coded any affective statements, under the assumption that some students would present attitudes that could be counterproductive to learning, but were not strictly true or false. After an initial round of coding it was clear there were a number of quasi-factual statements that did not fit cleanly into my initial scheme. Thus I added a third category I called “speculations” for those statements that are suggestive of an incorrect idea, but are phrased in such a way that they cannot be called incorrect. I coded only 30 affective statements, less than one per interview on average, so I did not include those codes in my analysis. Because coding statements as true or false is a relatively objective process, I did not conduct an inter-rater comparison (cf. Bailey, 2006). Instead I provided the list of 166 statements to another content expert for review. After discussion I removed nine statements (5%) from the initial list.

4.3. Results

In total I identified 157 specific misconceptions in the interviews. Of these, I observed most (118) only one time each throughout the 32 interviews. I attribute this to two related factors. First, the subject area covered by the interview questions is quite broad. Second, the interviews were semi-structured, thus the follow-up questions were not identical across all respondents.

In order to focus the results and discussion on the most prevalent of the 157 statements, I grouped the list into subject categories (e.g., oxygen, humans, etc.) and then examined those sub-categories to identify clusters of statements related to a single concept. I list those clusters and the number of observation of each in Table 1. Of the 157 misconceptions I identified, these clusters account for 64 and include all but one of the misconceptions with more than three occurrences[3]. The remainder of the list will be of interest to some readers, so it is included in Appendix E. In the following sections I describe each of these clusters in more detail and present additional evidence from the survey data where appropriate. I include *p*-values for significance only where comparisons are implied.

Table 4.1. Instances of Misconceptions by Cluster

Cluster Description		Instances (n = 32)
Climate Change	Climate Change Drivers	19
	Greenhouse Effect Mechanisms	8
	Climate Change History	6
Oxygen	O_2 in Ocean Water	23
	Fish Respiration	5
	Source of O_2	19
	Anaerobic Life	6
The pH of Natural Waters	Ocean pH	5
	Rainwater pH	3
	CO_2 Reacting with Water	5
Soil		7
Overstating Human Impacts		6
Stability and Life		7

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[3] Six respondents exhibited the well-known misconception that seasons are caused by the Earth's distance from the sun rather than the tilt of its rotational axis. The topic is not central to biogeochemistry, so I do not discuss it further.

4.3.1. Climate Change

Respondents frequently held misconceptions regarding climate change; two thirds of students I spoke to fell into at least one of these categories. I divided these statements into misconceptions about the ultimate source of the warming, misconceptions about the details of how the greenhouse effect itself functions, and misconceptions about the history of climate change and related effects on Earth. These misconceptions are shown in Table 4.2.

The two ideas that I observed most often were the incorrect linking of the ozone hole and climate change and the idea that internal Earth heating plays a significant role in Earth surface temperatures. The survey data strongly support the ozone connection as a common misconception with 64% of the 100-level students and 52% of the 300-level students selecting that response. Other interview respondents believed that the Earth's distance from the sun was the primary cause of warming or that CO_2 absorption into the ocean caused warming.

The misconceptions regarding the greenhouse effect were varied. Two respondents thought the greenhouse effect was a property of any atmosphere rather than gases with a specific property. Another thought that a chemical reaction was taking place. Others thought the atmosphere was acting like a literal greenhouse. And three respondents stated that the greenhouse effect was a local phenomenon.

Finally, six respondents expressed incorrect ideas regarding the history of climate change on Earth. These varied from those who believed that current CO_2 levels were the highest in Earth history to those who did not think that atmospheric CO_2 had changed at all in previous eras. There are two survey items related to these misconceptions. One showed that 24% of the 100-level students and 14% of the 300-level students ($p = 0.07$) believe the greenhouse effect has only existed for 150 years. A second item showed that 16% and 19% ($p = 0.71$) of 100-level and 300-level students, respectively, believe that humans have not altered the Earth's temperature.

Table 4.2. Climate Change Misconceptions

Respondent Misconceptions about Climate Change Drivers

- The atmosphere is letting more sunlight in, causing warming
- The ozone hole is causing climate change
- Climate change is caused by the Earth moving closer to the sun
- Earth temperatures only change as a result of catastrophic events
- Earth surface temperature is determined by heat escaping from the Earth's interior
- Hot spots and other volcanism are important sources of heat to the ocean
- Humans' primary greenhouse gas emissions are from breathing
- Milankovitch cycles are the only way to change climate
- Plants are a major source of greenhouse gases
- Geologic processes do not affect CO_2
- The process of the ocean absorbing CO_2 causes warming
- Glaciers melting is a cause (not an effect) of climate change

Respondent Misconceptions about Greenhouse Effect Mechanisms

- The atmosphere itself (not greenhouse gases) warms the planet
- The greenhouse effect is caused by chemical reactions that trap heat
- The greenhouse effect is a literal greenhouse
- The greenhouse effect is caused by gas pressure not the properties of specific gases
- Greenhouse gases trap heat because of their density
- O_2 is a greenhouse gas
- CO_2 absorbs reflected light
- The greenhouse effect is a local phenomenon

Respondent Misconceptions about Climate Change History

- Current atmospheric CO_2 levels are the highest ever in Earth history
- Global average ocean temperature has never been below 50°F in Earth history
- Rises in atmospheric CO_2 have not happened in Earth history
- The temperature of Earth has not changed through time
- The temperature of the ocean has not changed through time
- Sea level has not changed through time

4.3.2. Oxygen

Across the entire study, the most common misconceptions I observed related to O_2. Among these, the respondents had particular trouble with dissolved O_2 in the ocean. I divided this group into four subgroups: misconceptions about the abundance of O_2 in ocean water, misconceptions regarding respiration by fish or other ocean life, misconceptions about the sources of O_2, and misconceptions regarding anaerobes. These misconceptions are shown in Table 4.3.

The most common of these were the misconceptions about the abundance of O_2 in ocean water. This cluster of misconceptions appears to arise from the apparent contradiction between the knowledge that O_2 is almost always produced through photosynthesis and the idea of O_2 existing in the deep ocean, far from the sunlight that powers photosynthesis. In fact, several respondents described what is in essence a diffusion-dominated model and concluded that O_2 would be most abundant near the surface and diminish steadily downwards. The survey data are consistent here; 85% of the 100-level students and 68% of the 300-level students failed to identify ocean circulation as the reason there is O_2 available in the deep ocean.

Seventy-five percent of the 100-level students and 44% of the 300-level students chose one of the more exotic explanations, responding that O_2 is either “formed naturally” by seawater or that the oxygen used by fish and other ocean life is taken directly from the H_2O molecule. I observed the O_2 from H_2O misconception specifically in five different interviews.

Table 4.3. Oxygen Misconceptions

Respondent Misconceptions about Dissolved O_2 in Ocean Water

- O_2 in the ocean is primarily transported by diffusion
- There is no O_2 in deep water because the pressure is too high
- There is no O_2 in the deep ocean
- There is no O_2 at deep-sea hydrothermal vents
- There is no O_2 in any water
- O_2 concentration are at their highest at the ocean surface and decrease steadily to zero at the ocean floor
- O_2 settles out or dissipates from water over time

Respondent Misconceptions about Fish Respiration

- Fish get O_2 from the H_2O molecule itself (not from dissolved O_2)

Respondent Misconceptions about Sources of O_2

- Deep-sea vents are a source of O_2
- Abiotic O_2 production has sustained a > 1% O_2 atmosphere at times in Earth history
- O_2 is present in upper crust / mantle
- O_2 was trapped under the Earth prior to its release by biology
- Oxygen is stable as liquid oxygen at the ocean floor
- Anaerobes are a globally important source of O_2 to the oceans
- The atmosphere would have > 1% O_2 in the absence of life

Respondent Misconceptions about Anaerobic Life

- Cannot have life without O_2

The respondents proposed several incorrect theories for how O_2 is produced and how it enters the ocean. Most of these statements reflected the misconception that the Earth could have had an appreciable amount of atmospheric O_2 without life. This was also a common survey response; 71% of the 100-level students and 59% of the 300-level students responded that the Earth's atmosphere has always had at least 1% O_2 (11% and 14%, respectively, said that atmospheric O_2 has been at the present day concentration throughout Earth history). As far as specific mechanisms, six respondents suggested that O_2 is produced geologically or otherwise stored within the Earth. On the survey, this idea was actually more common among the 300-level students (19%) than the 100-level students (11%, $p = 0.06$).

With regard to anaerobic life, six respondents stated that there could be no life without O_2. I found a similar rate of this misconception on the survey with 26% of the 100-level students and 11% of the 300-level students responding that all living things need O_2 to survive.

It is also worth mentioning here that deep-sea hydrothermal vents were a common point of reference for the students I interviewed (17 respondents mentioned vents). The vents were never part of my interview questions, so I found the frequency of this reference surprising. The respondents generally brought up vents at one of two points during the interview: in response to questions about how life affects and is affected by its surroundings and/or in response to questions about places on Earth without O_2 and whether life can survive without O_2. Those responses in the former category were generally accurate, for example, "…there's these vents that take the minerals from the bottom of the ocean and filter them back into the water," (Interview #2012-09). Those in the latter category were generally misconceptions, such as, "…those the deep ocean vents where the hot water comes out because of the lava underneath…the life that live there, I don't think that they get oxygen, do they?" (Interview #2013-08).

4.3.3. pH of Natural Waters

Based on my preliminary interviews, I expected that the respondents would have a generally poor understanding of pH in natural systems. However I also found that respondents' basic chemistry knowledge made it difficult to extract useful information in the interview setting. Thus, pH was not included in the revised interview protocol, but it was a part of several survey items. The subject arose in follow-up questions during several interviews where respondents made incorrect statements about the pH of natural waters, as shown in Table 4.4. The survey results also confirm my preliminary finding that this topic is not well understood.

Three respondents provided variations of the idea that rainwater is “naturally” pure, thus neutral pH, and that rainwater of acidic pH can only occur as a result of human influence. On the surveys, 66% and 60% of the 100-level and 300-level students, respectively, responded that present day rainwater was either neutral or basic pH. Ocean pH came up in interviews more often, with five individuals stating that the ocean is acidic. By comparison, 70% and 42% (100-level and 300-level, respectively) of the survey responses incorrectly identified the pH of the ocean as neutral or acidic.

In an interesting disconnect between abstract and applied chemistry knowledge, 52% of the 100-level students and 78% of the 300-level students correctly answered that CO_2 has an acidifying effect on water. Contrasting the 78% of 300-level students who correctly answered this question to the 40% of that population who correctly specified the pH of rain water, we see that a large number of these students do not understand the relationship between this abstract concept and its real world application.

Table 4.4. pH Misconceptions

Respondent Misconceptions about the pH of Natural Waters
- Ocean pH is acidic
- Acidic rainwater only occurs as a result of human activities
- CO_2 does not react with ocean water
- The ocean does not absorb CO_2

Table 4.5. Soil Misconceptions

Respondent Misconceptions about Soil
- Soil formation is an inevitable consequence of the rock cycle
- Soil formation usually takes millions of years
- Soil can only form from organic rich rocks
- Soil is entirely inorganic
- There is a layer of soil underneath the bedrock layer

4.3.4. Soil

Seven respondents in total had misconceptions regarding soil composition or soil formation, as shown in Table 4.5. Some believed that soil formation was similar to or connected to deep Earth processes. Others significantly overestimated the amount of time it takes soil to form. There was also some confusion about the organic content of soil with one student suggesting that soils have to form from organic rich rocks and another stating that soil was entirely inorganic.

4.3.5. The Impact of Life and Humans on the Earth

The effects that life has on the planet and the ways that the planet affects living things were the focus of the first portion of my interview protocol. I learned in the preliminary interviews that not all students have an accurate sense of the relationship between life and the planet we live on. Predictably, many of these misconceptions involve the role humans play on Earth. I also observed a more unexpected category of misconceptions related to the relative stability of the planet without humans. These misconceptions are shown in Table 4.6.

Several respondents thought ocean life was influenced by trash in unrealistic ways, such as causing fish to live far off shore to avoid human interaction. I found a similar belief among the survey takers, where 30% of 100-level students and 15% of 300-level students said that human activities have cause “most” of the ocean near land to be uninhabited. Other students suggested that humans are causing heat waves (non-climate change) or even altering plate tectonics. In an example of underestimating human impacts, 36% of 100-level students and 24% of 300-level students did not think human activities were changing biological, chemical, or geological systems.

Seven respondents suggested to varying degrees that the planet would be in a state of stasis without humans. This category is closely related to the “speculation” code, which I discuss in section 4.3.6, but unlike the “speculations”, the examples shown in Table 4.6 are definitively inaccurate statements.

Table 4.6. Misconceptions about the Effects of Life on Earth

Respondent Misconceptions about Human Impacts
- Ocean life is substantially limited by trash
- Ocean pH is affected by trash
- The middle of the ocean is most densely populated because it's the furthest away from humans
- Humans have dramatically decreased the O_2 in the atmosphere
- Industrial emissions (non CO_2) cause heat waves
- Humans can affect plate tectonics
- Humans are making the ocean saltier
Respondent Misconceptions about Stability and Life
- Earth would be completely stable without humans
- Ocean temperature would not change through time without humans
- The oceans would not change through time without humans
- Ocean life is unchanging over time

4.3.6. Speculation

The statements I coded as speculation are best described as respondents answering scientific questions with opinions. Because of this, it is less productive to describe them as errors or misconceptions than it is to take them as opinions and consider whether they may lead to any specific instructional obstacles. In total, I identified 17 different statements representing responses from 21 different respondents. Many of these statements are all but identical in terms of content, but I left them separate to emphasize the specific vocabulary chosen by the respondents. As with the misconceptions, I organized these statements into clusters; Table 4.7 shows the full list.

Table 4.7. Student Opinions

Respondent Opinions about Earth Without Life

- Earth would be boring without life
- Earth would be ugly without life
- Earth would be hostile without life

Respondent Opinions about Earth Without Humans

- Earth would be more natural without humans
- Humans are not natural
- Humans produce unnatural waste
- Humans kill lots of things
- Earth would be cleaner without humans
- Humans have trashed the planet
- Humans have degraded
- Earth would be more intact without humans
- Earth would be better without humans
- Earth would be greener without humans
- Humans destroy _______

Respondent Opinions about Natural Balance

- The planet would be more in balance without humans
- Ice ages "balances everything back out"
- CO_2 concentrations want to balance out

In order to force students to consider the changes that life has made to the planet, I asked them what it would be like if life had never existed on Earth. Eight respondents described it as either boring, ugly, or hostile. A similar question asked them to describe what the Earth would be like if humans had never existed. This elicited a range of responses, but 15 of the students used one of the loaded phrases shown in Table 4.7. The most common of these were statements that humans were “not natural” or that the Earth would be more natural without humans. The final cluster involves an imagined "balance to nature." Eight students suggested the idea of a planet in balance and/or the idea that humans have pushed it out of balance.

4.4. Discussion

How do these results relate to the broader question of how undergraduates learn biogeochemistry? I am working under a constructivist model of learning, which is based on the idea that a student's prior understanding and mental framework affect how new information will be learned (Fosnot, 1996; Posner et al., 1982). Under that model, the two central questions are: 1) What mental framework do students have prior to instruction? and 2) How might the instruction be integrated into that pre-existing framework?

4.4.1. Interdisciplinary Concepts and Applied Knowledge

I selected the interview questions to focus on important biogeochemical concepts, so almost by definition they are interdisciplinary concepts. However, I think it is useful to look more closely at the interdisciplinarity of the specific misconceptions shown in the results section.

Regarding climate change and the subject of global surface temperature, very few interview respondents correctly linked internal Earth processes to atmospheric CO_2. At the same time, a third of the respondents suggested instead the erroneous idea that radiated internal heat is responsible for the temperatures we experience at Earth's surface. This is an example of a misconception that is simple and intuitive—the inside of the Earth is very hot; hot things radiate heat—whereas the correct explanation, that this internal heat provides a trivial amount of energy to the surface compared to solar energy, is more complicated.

The concepts connecting O_2 and the ocean are also at the intersection of multiple disciplines—oceanography itself being a subject that requires a sophisticated understanding of chemistry, biology, physics, and geology. Most students knew that fish require O_2 for respiration, reflecting a basic understanding of biology, but their lack of understanding about ocean circulation led them to invent various theories about how O_2 gets into the deep ocean. Others made a chemistry error and proposed that fish could breathe using the oxygen from H_2O instead. Finally, some students described geologically and geochemically impossible origins for atmospheric O_2 wherein the oxygen is trapped in gas pockets or is spontaneously produced from rock. Together these illustrate the web of interdisciplinary knowledge required to understand just one topic within biogeochemistry, and the misconceptions that can emerge from a partial understanding.

Another instance of interdisciplinarity is found where basic chemistry must be applied in real world settings. A number of the misconceptions I have identified serve as examples of a disconnect between abstract and applied knowledge. The clearest of these is the failure of many respondents to connect their understanding of the acidifying effect of CO_2 to the role CO_2 plays in determining the pH of natural waters. Additionally, the "respiration using H_2O" misconception could be rephrased as a basic redox chemistry question. This finding mirrors those of Mulford (1996), Mulford & Robinson (2002), and Krause et al. (2004), who also observed difficulty in applying chemistry to real world examples.

One example of this from my interviews was revealing. Here, to a question about the effect of CO_2 on water, a student who answered most of the other questions correctly talks around the correct answer, but does not quite get to it:

> *"I feel like they* [ocean water and CO_2] *wouldn't—like they're not becoming any kind of acids or anything. It's not like* CO_2 *suddenly becoming a—what's in soda? Oh, okay, no. Yeah, I don't think they really—I feel like they wouldn't be reacting,"* (2013-21).

A question that should be considered alongside the evidence of these misconceptions is: how surprising is it that undergraduates have trouble with interdisciplinary concepts? Should they even be expected to become proficient with such topics at the undergraduate level? Interdisciplinarity is considered to be a valuable skill at the professional level in many fields, so the development of that skill has been the subject of a number of studies (Borrego & Newswander, 2010; Ivanitskaya, Clark, Montgomery, & Primeau, 2002; Jacobson, 2001; Spelt, Biemans, Tobi, Luning, & Mulder, 2009; Tudor, 1992). Most of this research, however, focuses on graduate or professional levels, reflecting the common view that interdisciplinarity is an advanced skill. Research also suggests interdisciplinarity may be a facet of expert knowledge in a field such as biogeochemistry. I cannot determine here the degree to which undergraduates can genuinely learn how to think interdisciplinarily, but this is a question that should be explored further.

4.4.2. Human-scale perspective

One challenge to learning biogeochemistry, as with geosciences generally, is the range of spatial and temporal scales of the important processes. Ocean circulation is a global scale process occurring on a millennial scale. The rise of atmospheric oxygen was a global process that took place billions of years ago in a world nearly unrecognizable to a contemporary resident of planet Earth. Researchers studying how students learn about geologic time have found that the difference in scale compared to everyday human experience is a key obstacle in understanding that subject, and failing to grasp geologic time will make it very difficult to understand many other aspects of geology (Ault, 1982; Dodick & Orion, 2003; Libarkin, Kurdziel, & Anderson, 2007; Piburn, Kraft, & Pacheco, 2011; Trend, 2000). Kortz & Murray (2009) identified both deep time and large spatial scales as important conceptual barriers in their study. The misconceptions in my work that best exemplify problems with a human-scale perspective are the climate change history cluster, climate change drivers, and O_2 in ocean water.

4.4.3. Student Opinions and Biases

I observed many interesting responses related to human activity; this topic was the source of most of the “speculation” codes as well as the misconceptions included in Table 4.6. Similar to the scientifically accurate view that human activity is changing the world and affecting life around us is the misconception that the world’s events are almost entirely determined by human activities. The former idea is important to understanding and making decisions about environmental policy, but the latter would logically lead a person to believe that we can reverse previous environmental damage as quickly as we once caused it. This view of the way human technology can alter the Earth system does not take into account the concept of the Earth as a complex system (Raia, 2008; Steffen et al., 2004).

A number of respondents had trouble relating to a planet without life. The Earth was “boring,” “ugly,” or “hostile” without life. Those responses, though not scientific, do not seem to represent attitudes that would impede scientific thinking. The images of the Earth without humans, however, present a different challenge. The Earth would be “more natural,” “more intact,” “greener,” or just “better” without humans. These convey the idea of a pastoral, pre-human Earth.

> *“Pretty much we’re just un-naturalizing the Earth, and we’re kind of just – we’re destroying it; we’re just headed towards a brick wall pretty much,”* (Interview #2012-05).

These ideas, combined with the “stability” misconceptions suggest that some students imagine the world before humans as a still life—they think of a world that was a certain way and would have continued to be that same way forever. This idea is not only incorrect, but also symptomatic of a simplistic, non-process-based view of the Earth system (Libarkin & Kurdziel, 2006). The natural versus unnatural language also separates humans from the Earth in a way that can lead to “all or nothing” positions on environmental policy issues (see Cronon, 1996; Siipi, 2004).

4.4.4. Validity and Reliability

Although this research relies largely on qualitative data, the fundamental concerns about data quality are the same as for quantitative data: Do the data support the conclusions, and would another researcher reach similar conclusions if the study were repeated? I present evidence supporting the validity and reliability of my study in the form of triangulation, including consistency with other published research, and expert agreement.

Where there is subject matter overlap with previous studies, most significantly on the subject of climate change, my results are aligned with those previous studies. Gautier et al. (2006) and studies cited by Keller (2006) noted the same conflation of the ozone layer hole and the greenhouse effect that I observed. Brody (1996) observed the same "respiration using H_2O" misconception in middle- and high-school students. These similarities support the validity of my coding method. They also suggests my interview population was not dramatically outside the norm.

I consulted content experts at two points in this project. First, through the Delphi method (see Section 4.2), I was able to ensure the concepts included in the interviews were fundamental to the field of biogeochemistry and in line with the content of interest for instructors. Second, I had a content expert review my initial list of misconceptions. After discussion, we agreed on 95% of the misconceptions I identified, which provides additional support to the validity of my coding.

I also used a mixed-methods approach, combining qualitative data with quantitative survey data. Mixed-methods is a common technique, because the strengths of quantitative methods (larger populations leading to better generalizability) tend to be weaknesses of qualitative methods, while the strengths of qualitative methods (open-ended questions and detailed description) are weaknesses of quantitative methods (Creswell, 2003). The combination of methods also allowed me to compare two independent populations. I found that the survey data supported my interview findings.

The total number of respondents was appropriate for a qualitative study whose goal was the exploration of student conceptions and identification of common misconceptions. I arrived at the number of 32, not counting the eight people interviewed in the preliminary round, by reviewing similar studies and through discussion with other researchers. The number of interviews I conducted is also consistent with the studies referenced throughout this work (Anderson, Fisher, & Norman, 2002; Gautier et al., 2006; Kortz & Murray, 2009; Libarkin & Anderson, 2007; Nicoll, 2001; Osborne & Gilbert, 1980). Finally, I can report that by the end of the interview process I was mostly hearing statements similar or identical to statements heard in prior interviews, which suggests that additional interviews would have resulted in diminishing returns.

4.4.5. Limitations

One notable limitation of this study, as noted in the introduction, is that it was not intended to measure the extent to which these student conceptions are resistant to change through instruction. It is possible that some or even many of these statements are merely preconceptions stemming from a lack of previous experience with this subject matter. In that case, when students are presented with the accurate concepts they will readily adjust their thinking, and learning in biogeochemistry will not be impeded. This will have to be addressed by a future study. My work is nevertheless an important contribution because it lays the groundwork for such future research to conduct pre- and post-instruction interviews or surveys to determine the resistance to change of these misconceptions. In addition, it is difficult to imagine how even the most weakly held misconceptions will change for the large majority of students who never receive any instruction in biogeochemistry.

Owing to the respondents' unfamiliarity with the subject matter, many of the responses I received were vague and seldom included technical or scientific wording.

Sometimes I was able to capture this type of response with the “speculation” code, but in other instances the statements were not specific enough to conclude whether or not the respondent had made an inaccurate statement. In a related limitation, I did not attempt to count errors of omission. The semi-structured interview format, as compared to a structured interview, does not lend itself to that type of interpretation, because respondents are not asked exactly the same questions. Both this and the problem of vague responses suggest the numbers I report in the results section are a lower limit on the frequency of these misconceptions.

Finally, the population interviewed consisted predominantly of life science, physical science, and engineering majors (29 of 32). I decided to only recruit science majors for this study after my first two interviews with non-science majors. I found non-science majors in those initial interviews had difficulty answering the questions in a way that revealed any misconceptions. In particular, they had trouble speculating on topics they were unfamiliar with. This led to terse answers or “I don’t know,” even after follow-up questions. Previous misconceptions research supports the idea that certain epistemologies and ontologies may impede progress in learning science (Libarkin & Kurdziel, 2006; Rebich & Gautier, 2005). It is possible that some non-science majors will require more structured interview questions in order to provide useful responses. It should be noted that although I was unable to interview non-science majors extensively, they did make up the majority of the survey population.

4.5. Conclusions

It is clear from my findings that many important biogeochemical concepts are unfamiliar to undergraduates, even those majoring in science. Respondents had particular difficulty explaining the nature of the greenhouse effect and climate change, describing the source(s) and distribution of O_2 in the ocean, and identifying the pH of natural waters. They also exhibited an interesting array of opinions and misconceptions about the effects of humans on Earth systems.

What is also clear from my experiences in carrying out this project is that this subject is deserving of more research. There were concepts I would have liked to include in my revised protocol that proved to be too difficult to discuss given the existing knowledge of the respondents. These include: how the rock cycle is connected to atmospheric CO_2 and climate, and how organisms are affected by the chemistry and element availability of their surroundings. I am optimistic that this could be accomplished in a research study integrated with either an undergraduate course or perhaps a self-contained tutorial. One of my goals in pursuing this line of research is to increase the likelihood that some of the ideas central to biogeochemistry will be taught in general-education survey courses. Certainly much of the field is well beyond that audience, but I think the subject at its most reductionist level—that there is a connection between the biosphere and the geosphere, and that together they form a unified system whose dynamics explain so much about the world we live in—can be communicated even in a survey course. However, that proposition is another direction for future research. Particularly in the context of the question of how novices learn interdisciplinarity, it would be useful to discover what level of biogeochemistry can truly be taught at the survey level.

This catalog of misconceptions will be useful for instructors teaching biogeochemistry and to education researchers interested in studying biogeochemistry. Because it is often useful in both teaching and research to have a quantitative instrument to assess misconceptions, I present a validated biogeochemistry concept inventory in Chapter 5. Together these two tools will give educators a means of identifying extant misconceptions as well as insight into the student thinking behind them.

Chapter 5

DEVELOPMENT OF A VALID AND RELIABLE BIOGEOCHEMISTRY CONCEPT INVENTORY USING THE RASCH MODEL

5.1. Introduction

Biogeochemistry is a field of great relevance in today's world, both as means of understanding Earth systems generally and as a critical area of knowledge relating to climate change and its potential effects (Bonan, 2008; Jickells et al., 2005; Schlesinger & Bernhardt, 2013). As biogeochemistry is a highly interdisciplinary field, students learning about it are likely to begin instruction with a range of different majors and background knowledge. This variation in preexisting knowledge not only increases the amount of review that is necessary, but also increases the potential number of misconceptions that must be corrected. Teaching biogeochemistry will always be a challenging task, but it is one that would be made easier if there were an assessment tool to easily identify misconceptions in a group of students (Hestenes, Wells, & Swackhamer, 1992).

Certainly, any instructor could create a knowledge survey to use instead of a research-backed instrument, but a validated instrument supported by research has advantages (Libarkin, 2008). Misconceptions grounded in student responses should better encompass the range of incorrect thinking (Libarkin & Anderson, 2007). In addition, non-validated surveys have the potential to produce spurious results either through confusing wording or by unknowingly measuring an area of knowledge separate from the intended focus (American Educational Research Association [AERA], American Psychological Association [APA], & National Council on Measurement in Education

[NCME], 1999). Finally, use of a published, publicly available instrument provides opportunities for comparisons between courses and a meaningful benchmark for achievement or learning gains (Hake, 1998; Libarkin & Anderson, 2005).

The idea of a concept inventory (CI), a test designed to measure students' comprehension and key misunderstandings of the fundamental concepts of a field, dates to Hestenes et al. (1992) and the "Force Concept Inventory," which tests conceptual knowledge of Newtonian physics. Although a CI is useful as an achievement test, its principal benefit is the identification of specific misconceptions held by students (Hestenes et al., 1992). Teaching that fails to address misconceptions can lead students to reject the scientific conception in favor of their original understanding, which will ultimately limit their success in that and future classes (Chi et al., 1994; Posner et al., 1982). Therefore, the CI is a tool that can be used at the beginning of a course to identify misconceptions that should be addressed. It may also be used at the end of a course to assess conceptual change through the course. At present, validated concept inventories exist for physics (Hestenes et al., 1992), basic chemistry (Krause et al., 2004; Mulford & Robinson, 2002), biology (Klymkowsky, Underwood, & Garvin-Doxas, 2010), solid-Earth geoscience (Libarkin & Anderson, 2005), astronomy (Bailey, 2007), and the greenhouse effect (Keller, 2006). These instruments cover a large number of discipline-specific concepts, but biogeochemistry, geochemistry, and related environmental science topics are not represented. In this work I demonstrate that the CI I have developed for biogeochemistry is a valid and reliable instrument to measure proficiency in that field as well as to identify misconceptions that may impede learning.

5.1.1. Instrument Design

The field of psychometrics is concerned with making meaningful measurements of a person’s mental state, commonly referred to as latent traits or constructs (AERA et al., 1999). Consequently, there is a large body of research in psychometrics describing ways to measure and evaluate instrument (test) performance (Cronbach, 1951; Guttman, 1945; Novick, 1966; Spearman, 1904). At its core, instrument design is concerned with the question of “What do the responses to instrument items (questions) say about the respondents themselves?” This is systematized through the use of the terms validity and reliability (AERA et al., 1999).

Reliability is the more straightforward term; a reliable instrument is one that produces the same result each time the same measurement is made. This property can be computed (AERA et al., 1999). In contrast, validity is multifaceted and, rather than a simple calculation, it is supported by multiple lines of evidence. Researchers formerly described multiple independent types of validity, but now regard validity as a unitary concept (AERA et al., 1999; Geisinger, 1992; Goodwin & Leech, 2003). The previous “types” of validity do remain a useful way to approach the validity argument, however. Of these, construct validity is the broadest and asks whether the instrument actually measures the latent trait that it is purported to measure. Does a greater or lesser score represent a greater or less amount of “biogeochemistry ability,” for example? Content validity asks, more narrowly, whether the items are relevant to the trait being measured, whether they are complete in their coverage of that trait, and whether they are accurate. Criterion validity considers external points of reference and relates to the agreement between the instrument and other instruments or metrics that assess the same trait. Finally, an instrument must be reliable to be valid; it must be both to be useful.

Historically instrument design was guided by what is now called classical test theory (CTT; Novick, 1966). The basic assumption of CTT is that the observed score (i.e., the number of items correctly answered by a respondent) is better understood as a combination of a true score and an error score, where true score is the idealized value of the trait and error score is the sum total of the effects of all other factors. Thus, the goal of an instrument designer is to minimize the magnitude of the error score and to ensure the errors between items are uncorrelated. CTT has three important disadvantages as compared to item response theory (IRT), which has supplanted CTT in many psychometric applications (DeMars, 2010; Libarkin & Anderson, 2010). First, reliability in CTT is determined by a comparison of parallel forms, meaning the instrument must be administered twice to the same population, two equivalent instruments must be administered, or the instrument must be divided in half and compared internally; each of these methods has its challenges (Cronbach & Shavelson, 2004; Cronbach, 1951; Guttman, 1945). Second, the determination of an instrument's properties is not separable from the population studied. Finally, instrument parameters are determined at the instrument level, so the individual items are also not separable (Bond & Fox, 2007; DeMars, 2010; Wright, 1977).

In contrast, IRT and Rasch are based on the idea that a person's likelihood of correctly answering any one item is determined by a relationship between his or her proficiency and the difficulty of the item (Bond & Fox, 2007; Rasch, 1960). With a large sample of respondents, the functional relationship can be examined for each item.

Deviations from the expected model represent items where something other than proficiency is influencing success and failure. In other words, there is a reliability and/or validity issue with that item. Thus, analyzed at the item level, instruments constructed from a validated item pool can produce scores that are comparable on a single construct axis (DeMars, 2010; Libarkin & Anderson, 2010).

The Rasch model was developed independently of IRT, but arrived at a similar formulation (Rasch, 1960). It is mathematically equivalent to the one-parameter logistic model in IRT, though there are disagreements about the extent to which IRT and Rasch are the same in practice (Andrich, 2004; DeMars, 2010). The fundamental equation for the Rasch model is shown in Eq. 5.1. It defines the probability, for each item i, that a person of proficiency θ will answer correctly, given a difficulty b_i (using dichotomous, right or wrong, scoring). This produces a function with an upper asymptote approaching 1 as the proficiency exceeds the difficulty and a lower asymptote approaching 0 for the converse. The comparison between proficiencies and difficulties also emphasizes that in the Rasch model and in IRT those properties are expressed in identical units.

$$\mathrm{P}_i(\theta) = \frac{\mathrm{e}^{(\theta - b_i)}}{1+\mathrm{e}^{(\theta - b_i)}} \qquad \text{Eq. 5.1}$$

The process of instrument validation with the Rasch model requires the designer to demonstrate that the instrument fits this mathematical model to an acceptable degree. In practice, this means one must demonstrate that the instrument is unidimensional, that the items are locally independent, and that each item fits the specific functional form of Eq. 5.1 (DeMars, 2010; Rasch, 1960). Unidimensionality means that a person's likelihood of success is affected by a single latent trait; thus, if an instrument is unidimensional (and reliable), a person’s score can be attributed entirely to that one trait. Local independence is related to unidimensionality and means that each item is only related to the other items through the latent trait.

To produce a biogeochemistry CI (BGC-CI), I have followed the procedures described by Libarkin & Anderson (2005, 2007) in creating and validating the now widely used Geoscience Concept Inventory. The initial steps of identifying key concepts and conducting interviews are described in Chapter 3. This chapter focuses on the instrument design and validation process. I have based my analysis on responses from 251 undergraduates, both science and non-science majors ranging from freshman to senior level. I performed an item response theory analysis, using a statistical model developed by Rasch (1960), on the survey data to support my argument that the BGC-CI thus developed is both valid and reliable.

5.2. Methods

The concept list for this study relies on expert validation through a modified Delphi method (Dalkey et al., 1969). I created the initial list based on my own experience combined with input from textbooks and other content experts. The list was then reviewed and evaluated by 18 content experts to produce the final concept list (Appendix B). This process supports the content validity of the instrument. I used those concepts to write an interview protocol to identify misconceptions about those concepts (Libarkin & Anderson, 2007; Nicoll, 2001; Osborne & Gilbert, 1980; Posner & Gertzog, 1982; Trundle et al., 2002). I interviewed eight undergraduates, who provided a wide range of misconceptions.

I wrote the incorrect response options (distractors) for the CI items using the misconceptions derived from these interviews. I wrote the stems, correct answers, and distractors using non-technical language as much as possible. This involves a trade-off in that content experts could consider certain imprecisely worded items to be flawed, but the more accurately written item would be difficult for non-experts to interpret and thus diminish the reliability of that item (Libarkin & Anderson, 2007; Libarkin & Ward, 2011; Libarkin, 2008).

The initial version of the survey contained 18 two-tiered items and used a true-false format. I administered that version to one upper-division oceanography class at a large Southwestern US research university (n = 62) and used those responses to guide my revisions. The revised version contained 32 items and used a multiple-choice format. I administered this version online to students in three classes at the same institution: two introductory geology courses and an upper-division chemistry course. I also administered the revised version to undergraduates solicited outside of specific courses. The study population was academically diverse both in terms of year in school and major. I collected 251 multiple-choice responses in total.

These responses were evaluated for their goodness of fit to the Rasch model using several statistical software packages. I used the Extended Rasch Modeling (eRm) package and the "psych" package for R (Mair & Hatzinger, 2007; Revelle, 2012). I also used the NOHARM software package, version 4 (Fraser, McDonald, & Vandermeulen, 2012; Fraser & Mcdonald, 1988).

5.3. Results and Discussion

5.3.1. Individual Item Fit

The model fit of each item can be evaluated individually. This evaluation is based on two parameters: infit and outfit (Bond & Fox, 2007; DeMars, 2010). Outfit is the mean of squared standardized Rasch residuals for each item across the survey population. The residuals are the difference between the expected and observed results, so the largest residuals come from unexpected responses far from a person's ability, where $\theta >> b$ or $\theta << b$ (see eq. 5.1). Thus outfit is most strongly influenced by those results. Infit is calculated the same way as outfit, except the residuals are weighted so that items close to the person's ability ($\theta \approx b$) dominate the statistic.

Both infit and outfit are chi-squared (χ^2) statistics. In Rasch analysis, their fit is commonly evaluated using both mean squared values (χ^2/df) and standardized values (t-statistics). Using both methods of evaluation tempers the effect of large sample sizes, which tend to hide errors in mean squared values and exaggerate errors in t-statistics (Bond & Fox, 2007). Wright et al. (1994) and Bond and Fox (2007) recommend that items on low-stakes instruments have outfit and infit values between 0.7 and 1.3 or between -2.0 and 2.0 for mean squared values and t-statistics, respectively. Items outside of those ranges are describes as either underfit or overfit. Items with values greater than the upper value are said to be underfit, in other words, they fall too far from the model to be useful. These items may be poorly written or may be measuring a distinct trait. Items with values less than the lower value are overfit, meaning they are closer to the model than probability would predict. These items may be redundant with other items. The item fit statistics are shown in Table 5.1. Infit and outfit values can also be plotted against item difficulty to illustrate the quality of fit for multiple items within any given difficulty range. These are referred to as Bond and Fox pathways maps (Bond & Fox, 2007) and are shown in Figure 5.1. The calculated person parameters (proficiencies, θ) for each of the 251 respondents are shown with the item parameters (difficulties, b) in Figure 5.2. Based on these results, item 7 is underfit and item 15 is overfit, and both should be removed or revised as appropriate.

Table 5.1. Item Fit Statistics

Item	χ^2	d.f.[a]	p-value	Outfit MSQ[b,c]	Infit MSQ[c]	Outfit t[c]	Infit t[c]
1	244.082	249	0.576	0.976	0.975	-0.23	-0.47
2	262.552	249	0.266	1.050	0.980	0.55	-0.25
3	231.947	249	0.774	0.928	0.962	-0.49	-0.46
4	259.219	249	0.315	1.037	1.065	0.48	1.46
5	166.334	179	0.742	0.924	0.960	-0.85	-0.78
6	257.097	249	0.349	1.028	1.037	0.44	0.78
7	512.924	248	0.000	**2.060**	1.160	**9.80**	**3.31**
8	252.277	247	0.395	1.017	0.990	0.21	-0.11
9	257.590	249	0.341	1.030	0.993	0.35	-0.07
10	249.944	249	0.471	1.000	1.014	0.02	0.39
11	235.563	248	0.705	0.946	0.960	-0.43	-0.43
12	195.211	249	0.995	0.781	0.881	-1.34	-0.92
13	248.647	249	0.494	0.995	1.010	-0.04	0.25
14	292.225	250	0.034	1.164	1.035	1.31	0.40
15	217.479	250	0.932	0.866	0.897	**-2.27**	**-2.71**
16	256.318	250	0.378	1.021	1.019	0.31	0.37
17	235.936	250	0.729	0.940	0.971	-0.78	-0.67
18	236.542	249	0.705	0.946	0.981	-0.82	-0.40
19	253.516	250	0.426	1.010	0.998	0.16	-0.03
20	219.190	250	0.921	0.873	0.918	-1.65	-1.90
21	244.747	248	0.546	0.983	0.941	-0.24	-1.55
22	246.360	250	0.553	0.982	0.986	-0.16	-0.24
23	266.541	249	0.212	1.066	1.051	0.66	0.89
24	268.067	250	0.206	1.068	1.026	0.51	0.34
25	210.680	249	0.963	0.843	0.935	-1.19	-0.83
26	205.942	249	0.978	0.824	0.924	-0.91	-0.63
27	249.791	250	0.492	0.995	0.993	-0.02	-0.07
28	234.850	250	0.746	0.936	0.952	-0.83	-1.12
29	202.575	250	0.988	0.807	0.874	-1.76	-2.00
30	264.099	250	0.258	1.052	1.021	0.74	0.53
31	257.987	250	0.351	1.028	1.029	0.38	0.68
32	221.905	250	0.899	0.884	0.945	-0.74	-0.60

[a] d.f., degrees of freedom. These vary due to skipped items in the responses

[b] Items in boldface are outside of the acceptable range

[c] MSQ, mean squared values

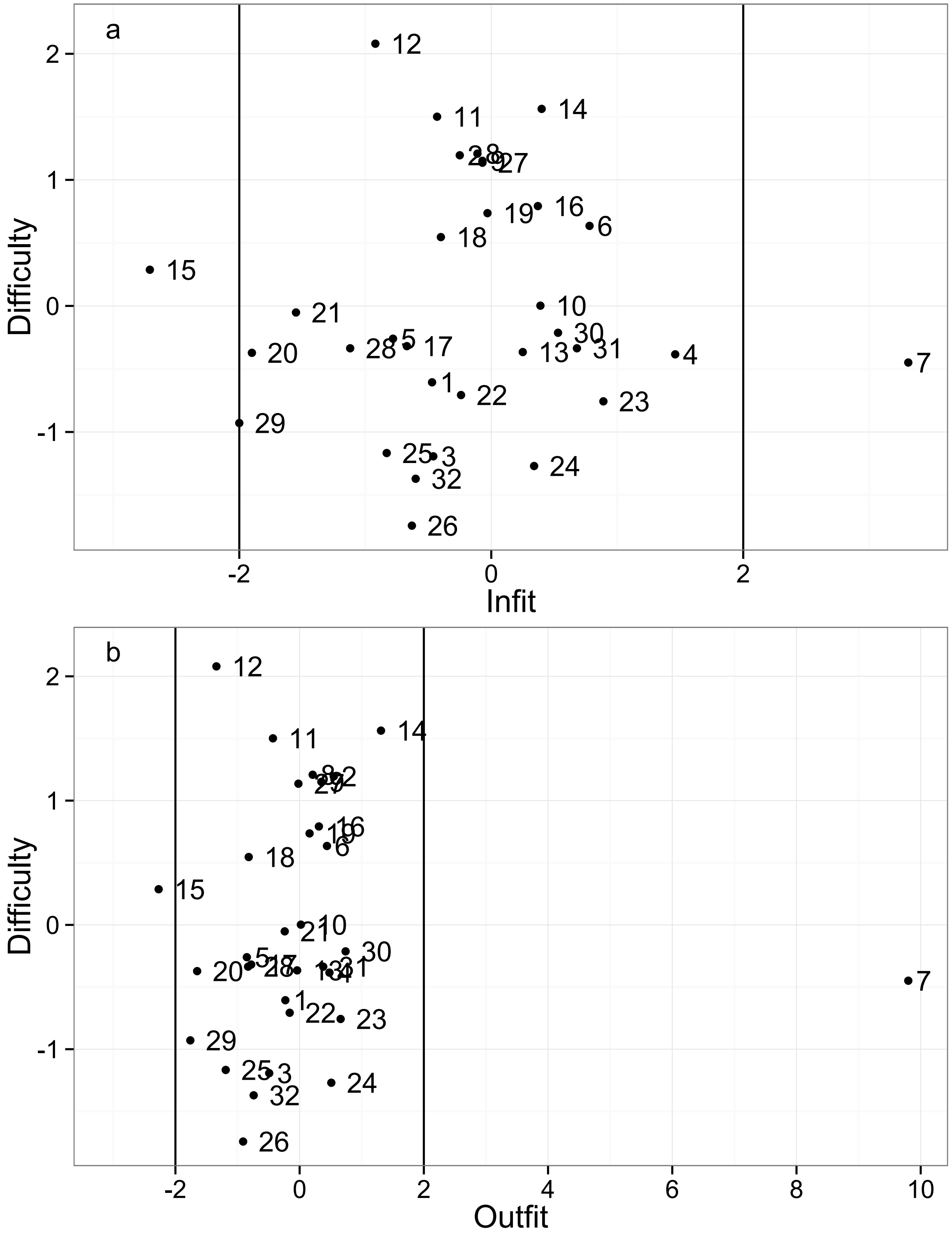

Figure 5.1. Items are plotted as difficulty vs. infit (a) or outfit (b). Vertical lines at -2 and +2 define the range of acceptable values.

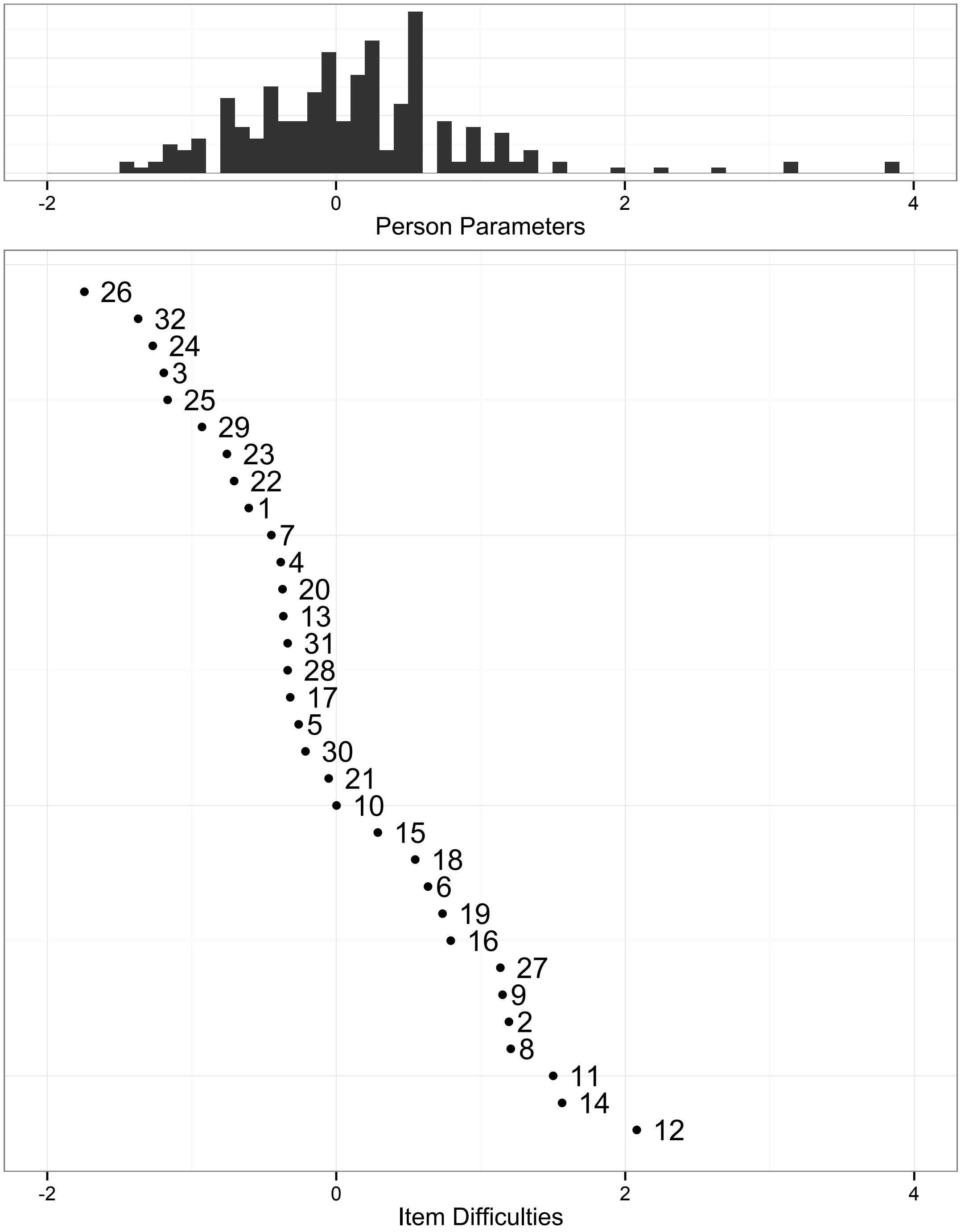

Figure 5.2. Person-item map. The top panel shows the distribution of scores (person parameters, θ). The bottom panel shows the sorted item difficulties (b).

5.3.2. Overall Model Fit

In addition to the fit of individual items, the Rasch model fit of the whole instrument can be evaluated. One method for determining overall model fit is by using Andersen's likelihood ratio test (Andersen, 1973; Baker, 1992). The Andersen test is designed to detect alternatives to the Rasch model, such as the two-parameter logistic model (Baker, 1992). This test is similar to a split-half reliability test, in which item difficulties are calculated twice. Here I used the median score as the split criterion; the y-axes on Figures 5.3 and 5.4 show the difficulties calculated using the responses of respondents above the median trait score while the x-axes show them calculated using the responses of those below the median trait score. For a well-functioning instrument, the difficulties should be the same for both groups and should plot along a 1:1 line. The goodness of fit relative to that ideal is evaluated using a chi-squared test. The results of this test and the other model fit metrics are shown in Table 5.2.

Table 5.2. Goodness of Fit Indicators

Instrument Version	Andersen LR Test	χ^2_{GD}		Tanaka Goodness of Fit Index		Eigenvalue of First Residuals Component
		1 D	2 D	1 D	2 D	
Full	Accept (*p=0.11*)	Reject (*p<0.001*)	Accept (*p=0.87*)	Accept (GoF = 0.90)	Accept (GoF = 0.92)	2.1
Alternative Version A[a]	Reject (*p=0.02*)	Reject (*p<0.001*)	Accept (*p<0.77*)	Accept (GoF = 0.90)	Accept (GoF = 0.93)	2.1
Alternative Version B[b]	Accept (*p=0.86*)	Reject (*p<0.001*)	Accept (*p<0.56*)	Accept (GoF = 0.91)	Accept (GoF = 0.93)	2.0

[a] Includes all items except item 7

[b] Includes all items except items 7, 12, 14, 15, 24, and 29

When the analysis was run using all 32 items, the null hypothesis for the Andersen test (that the BGC-CI fits the Rasch model) was not rejected (*p=0.11*). Because the infit and outfit statistics indicated that item 7 is misfitting, I also ran the Andersen test without item 7 (Alternative Version A). For that instrument version, the null hypothesis was rejected (*p=0.02*). In addition to overall model fit, the Andersen test yields information about item fit, which can be used to diagnose the reason(s) the instrument has failed the Andersen test. Based on the results shown on Figure 5.3, items 7, 12, and 29 are beyond 2SE from the 1:1 line and should be considered outliers. In an iterative process, I recalculated the model until there were no outliers, ultimately removing items 7, 12, 14, 15, 24, and 29 (Alternative Version B, Figure 5.4). The Andersen test could not reject the null hypothesis for this final, 26-item version (*p=0.86*). I previously identified item 7 for removal based on the infit and outfit statistics. The other five items identified here should be revised in future versions of the BGC-CI.

The Andersen test failure for Alternative Version A, following the removal of a strongly misfitting item, is surprising. Although removing additional items brought the instrument back to an acceptable model fit, a more likely explanation for the model fit problem is the bimodal distribution of science ability in the study population. When a 100-level (general education) student group is combined with a 300-level (science major) student group, the item-to-item discrimination may vary. This is a deviation from the Rasch model, which assumes all items have the same discrimination. It is also the specific problem the Andersen test is designed to identify. I recalculated the Andersen test with the two populations kept separate and obtained an acceptable model fit for both subpopulations (100-level: *p=0.78*; 300-level: *p=0.42*).

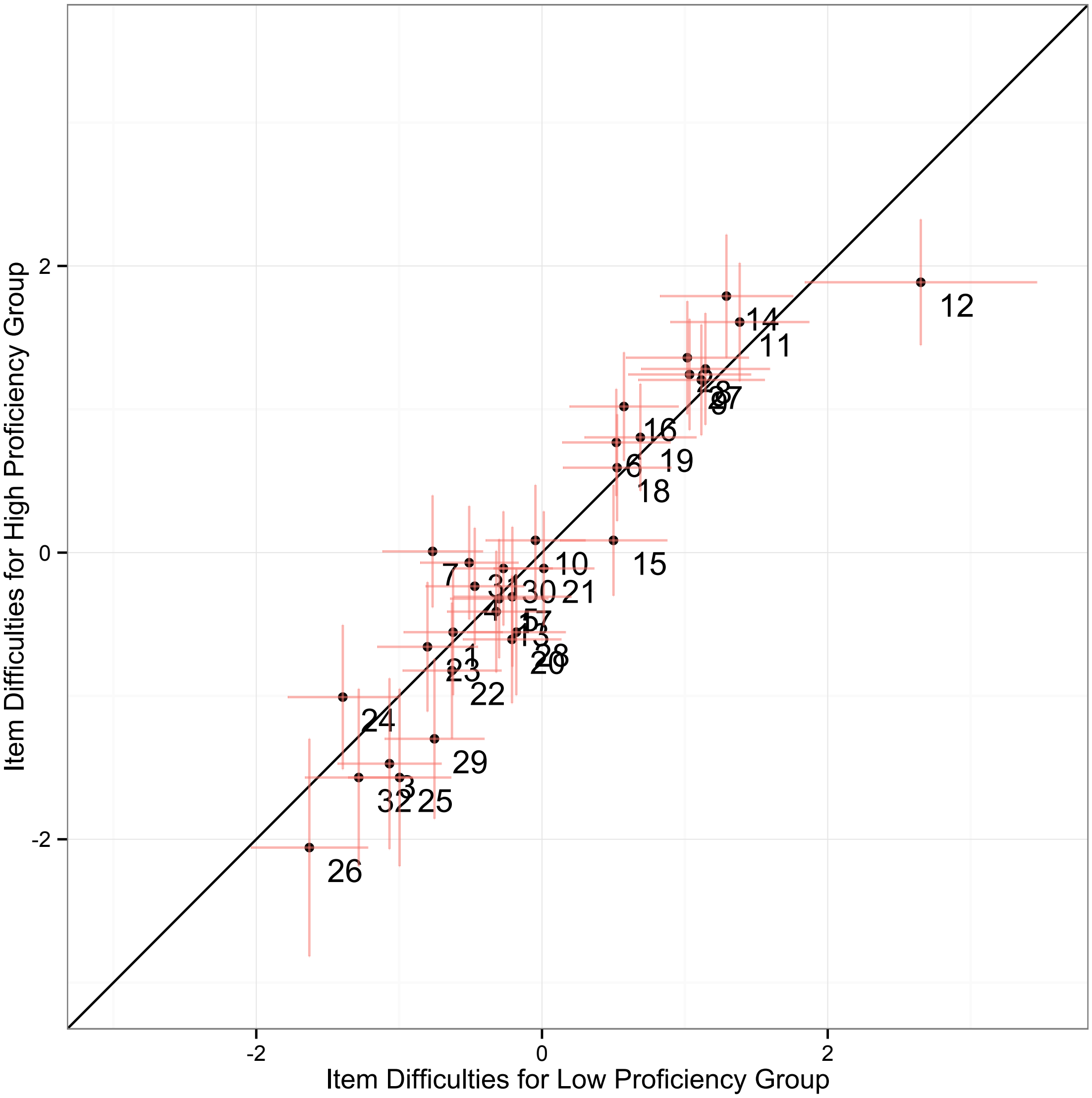

Figure 5.3. Andersen likelihood ratio test for all items. Error bars are 2SE.

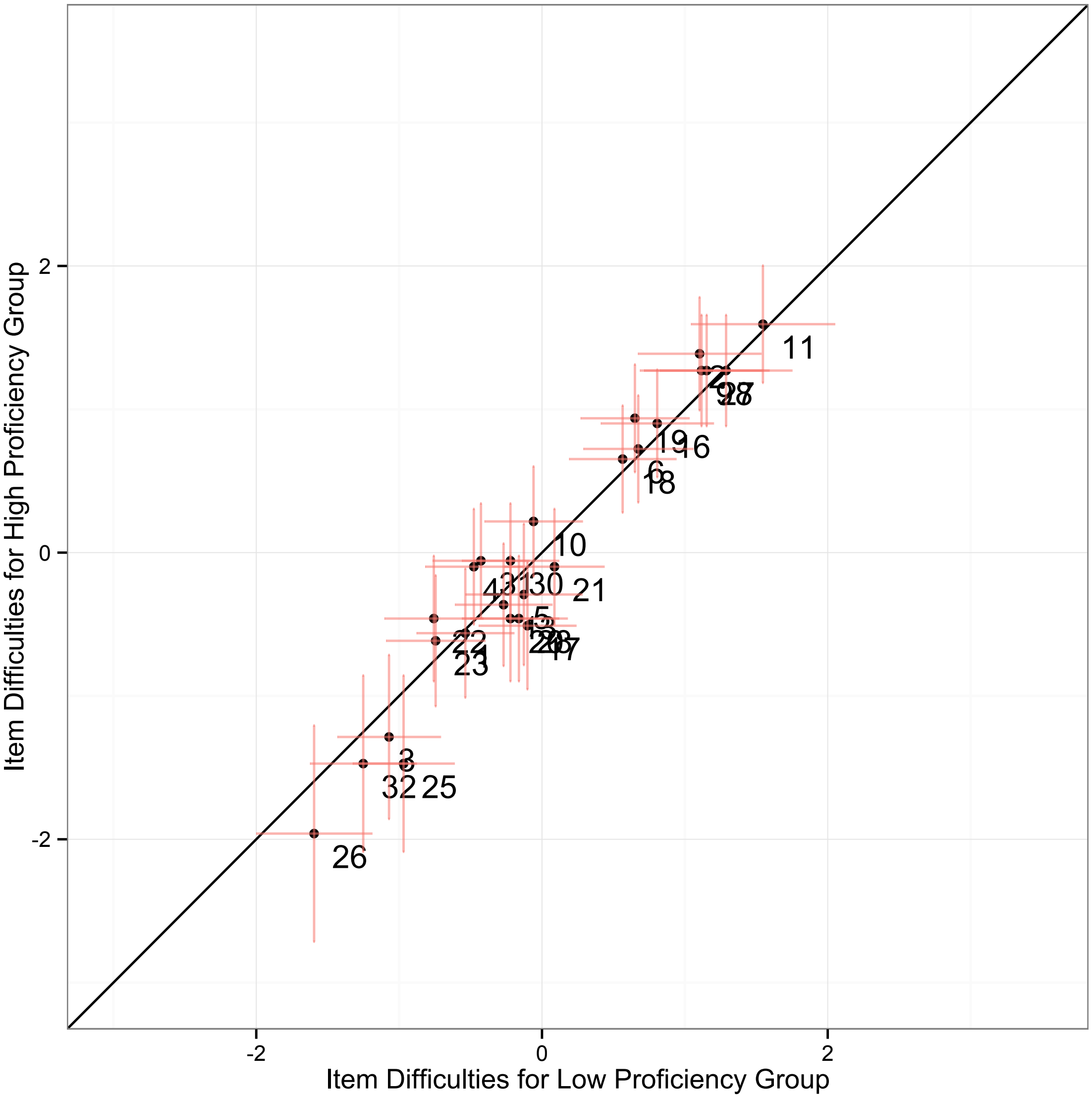

Figure 5.4. Andersen likelihood ratio test with outliers (items 7, 12, 14, 15, 24, and 29) removed (Alternative Version B). Error bars are 2SE.

5.3.3. Unidimensionality

As described in the introduction, unidimensionality means a person's likelihood of success is affected by only a single latent trait. This is the fundamental assumption of the Rasch model. For the purposes of a CI, there is an important difference between biogeochemistry and geology, which is the fact that students beginning in geology either have some knowledge of geology or they do not, whereas students beginning in biogeochemistry may have knowledge of some relevant concepts but not all (e.g., knowledge of geology, but not chemistry or biology). This means that the assumption that the BGC-CI is unidimensional may not be justified.

The Rasch model assumes unidimensionality, so this question also has a bearing on instrument validity. One method of evaluating unidimensionality is to use the NOHARM statistical package (De Ayala, 2009; DeMars, 2010; Fraser et al., 2012). The NOHARM test calculates a matrix of residuals for all items by comparing the actual and expected response patterns. Unidimensionality is then evaluated based on the degree of covariation among the test items, which is expressed through the Tanaka goodness-of-fit index and Gessaroli and De Champlain's approximate chi-square statistic, χ^2_{GD} (Gessaroli & De Champlain, 1996; Tanaka, 1993). I evaluated the BGC-CI as both a unidimensional instrument and as a two-dimensional instrument. The results of these analyses are shown in Table 5.2. The instrument is considered acceptably unidimensional according to the Tanaka index, but the χ^2_{GD} rejected the unidimensional model (Ayala, 2012; DeMars, 2010).

Another method for evaluating unidimensionality is to use principal component analysis (PCA; DeMars, 2010). PCA can be performed on the full dichotomous response matrix, but such analyses can be confounded by components related to item difficulty. Instead, I have used the Rasch model residuals as the basis for the PCA (Chou & Wang, 2010; Raîche, 2005). By starting with the residuals, the primary dimension should be removed from the data, thus any remaining components represent an unmodeled dimension.

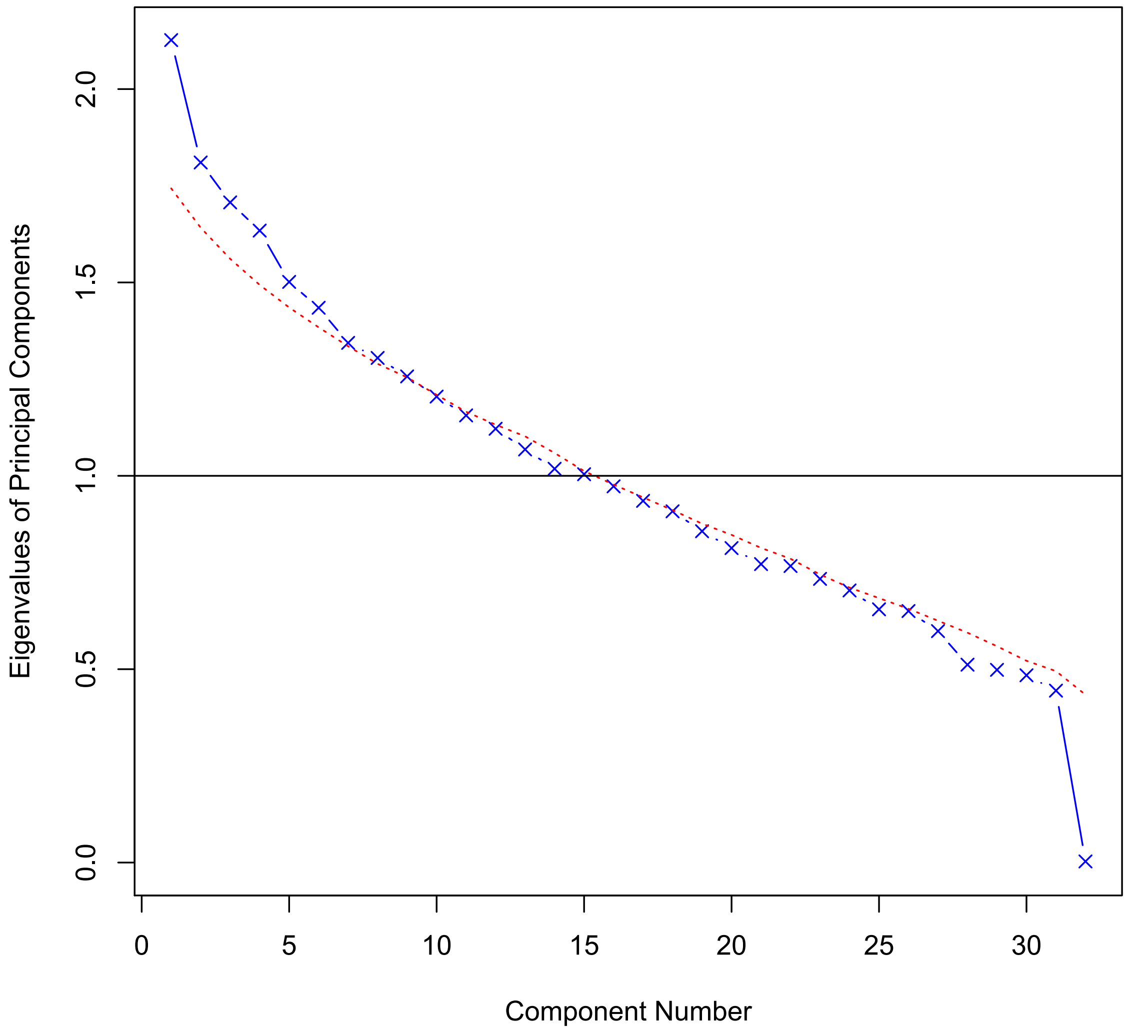

Figure 5.5. Scree plot of PCA of Rasch residuals for all items. The dotted line shows a parallel analysis.

The key value to report from PCA of residuals is the eigenvalue of the first component. Chou and Wang (2010) note that the critical threshold for unidimensionality varies based on the ratio of population size to number of items. Based on Chou and Wang's simulations, the expected value of the first eigenvalue should be less than

1.8±0.2. As shown in Table 5.2 and Figure 5.5, the first component eigenvalue for the full BGC-CI is 2.1, which falls outside of that range.

The item loadings from the PCA of residuals provide some insight into the nature of the possible second dimension. There are two notable trends in these data. First, the item loadings have a moderate negative correlation with item difficulty (Pearson's r = -0.38, *p=0.03*). Second, items near the end of the instrument (items 25, 28, 29, 31, and 32) have the five strongest loadings on the second dimension. Thus, one explanation for the second dimension is test fatigue. Respondents who give these final questions less careful consideration may score higher and exhibit fewer misconceptions by employing metacognitive (test-taking skills) than more careful respondents who answer more authentically. A second explanation is that this unmodeled dimension is caused by the same bimodal distribution of science ability that affected the Andersen test.

In light of differences among people of different science ability, the BGC-CI needs additional study with a larger population of more evenly distributed ability. The dimensionality metrics based on this dataset suggest that some of the item response behavior is not explained by a single trait. A multidimensional Rasch model may be necessary, but such a model would require a larger study population. This is recommended for future study.

To conclude, although the Tanaka goodness-of-fit index rates the BGC-CI as acceptably unidimensional, the other metrics suggest that a two-dimensional model may be more appropriate. Given that biogeochemistry is an interdisciplinary subject and that the respondents to this survey had not had previous instruction in the subject, it is not entirely unexpected that there would be multiple dimensions. Given the otherwise acceptable model fit, I suggest that the BGC-CI should be considered acceptable for use, but that the use of unidimensional instruments to measure learning in interdisciplinary fields should be investigated specifically in future research.

5.3.4. Instrument Revision

The calculated item fit parameters for the BGC-CI showed that item 7 is underfit with respect to both infit and outfit, while item 15 is overfit by both metrics (Table 5.1). The Andersen likelihood ratio test identified items 7, 12, and 29 as outliers in the initial calculation and items 14, 15, and 24 as outliers in subsequent recalculations.

Item 7 is about enzymes, so its poor fit suggests it is measuring a different area of knowledge from the other items; it should be removed. Item 12 is a complex, two-part question and the most difficult of the 32 items. The correct answers to items 14, 15, and 29 are each “all of the above” style options, and more sophisticated test-takers know that these are likely correct answers. Items 12, 14, 15, and 29 could each be revised to address these specific problems. Finally, item 24 is very simply worded and among the easier items on the CI. It is possible the more advanced respondents are essentially “over thinking” it, but additional feedback will be needed to determine how that item should be revised. Similarly, based on the PCA results, it would be beneficial to examine all items for instances where test-taking ability may distort misconceptions measurement.

5.4. Conclusions

The conclusion from my evaluation of the BGC-CI is that, although my analysis shows one item that should be removed and several others that should be revised in future test versions, the test is sufficiently reliable for use. This is particularly true given that it is intended as a low-stakes test. The concepts used on the instrument were chosen through a process that included review by external content experts, which argues that the subject matter is accurate, relevant, and complete. I found the overall model fit to be within accepted parameters, which, based on the properties of the Rasch model, supports the construct validity of the instrument. Taken together, this supports the proposition that scores on the BGC-CI can be interpreted to represent proficiency in the field of biogeochemistry.

This instrument was developed with misconceptions from a small population (eight interviews). In parallel to its development, I have conducted a larger qualitative study of biogeochemistry misconceptions, which now provides a larger pool of misconceptions. The future development of the BGC-CI will certainly take advantage of this new resource, but a major benefit of Rasch analysis is that it is compatible with the use of multiple test forms constructed from a shared item pool, so the development work described here will be applicable to any expanded version of the BGC-CI.

My findings regarding the dimensionality of the instrument suggest a direction for future research investigating the nature of interdisciplinary learning. Existing concept inventories are more disciplinary (geology, astronomy, chemistry, etc.), so this may not have been a significant obstacle to the effective use of those instruments. The capability to think interdisciplinarily is valued in the sciences (Frodeman, Klein, & Mitcham, 2010; NSF, n.d.), so such research would be of considerable interest.

These findings also raise questions about the way interdisciplinary topics should be taught. Although the issue of instrument dimensionality is esoteric on its face, it is interesting to consider what it represents by analogy in a course context. Should an interdisciplinary course strive to be “unidimensional” in the sense of teaching students one topic? Or, is it acceptable to teach multiple related topics in parallel, essentially a multidisciplinary approach? This is one of the many possible applications for the BGC-CI and it is the focus of my final chapter, “Learning an Interdisciplinary Science.”

Chapter 6

LEARNING AN INTERDISCIPLINARY SCIENCE

A theme that each of the preceding chapters share is interdisciplinarity, whether by highlighting its benefits to scientific understanding, as in Chapters 2 and 3, or in demonstrating its importance in science education, as in Chapters 4 and 5. In light of the evident value of interdisciplinary thinking, I posit that one of the most important future directions stemming from my education research is exploring how thinking in an important area of interdisciplinary science is learned at the undergraduate level. At issue is whether, or to what degree, interdisciplinary learning is different from disciplinary learning, and, by extension, whether interdisciplinary courses need to be taught differently.

There is existing research on interdisciplinary education (e.g., Cooper et al., 2001; Hoerrner et al., 2008; Ivanitskaya et al., 2002; Sales et al., 2006). Of these, Sales et al. (2006), which described a course designed to bring an interdisciplinary approach to an introductory general studies course, is the closest to my area of research. In that study, the authors note improvements in attitudes toward science, and in understanding of the nature of science, but do not discuss changes in content knowledge. Thus, although there is some research, there has not yet been a study focused on measuring content-based learning gains or an analysis of how those gains differ between disciplinary and interdisciplinary courses. To argue, as some do (e.g., Goldsmith, 2012), for an increase in the number of interdisciplinary courses at the undergraduate level, there must be research results to support the claim that such courses are more effective than conventional disciplinary courses.

Concept inventories (CI) are an ideal tool for this problem. They provide a quick assessment of conceptual knowledge within a given field, which allows for the calculation of learning gains as a result of instruction (e.g., Hake, 1998). Focusing on biogeochemistry specifically, CIs exist for geology (GCI, Libarkin & Anderson, 2005), biology (BCI, Klymkowski et al., 2010), and chemistry (CCI, Mulford & Robinson, 2002), in addition to my own biogeochemistry CI (BGC-CI), making biogeochemistry an excellent initial test case for comparative research.

For this work, I propose studying learning of declarative interdisciplinary knowledge both at the general education level and at the science major level. Interdisciplinarity is considered to be an advanced skill (Borrego & Newswander, 2010; Ivanitskaya, Clark, Montgomery, & Primeau, 2002; Jacobson, 2001; Spelt, Biemans, Tobi, Luning, & Mulder, 2009; Tudor, 1992), so there may well be a difference in results even among undergraduates. Both interdisciplinary and disciplinary courses appropriate to each student level should be identified. At the general education level, disciplinary courses would include introductory geology, chemistry, or biology; while examples of interdisciplinary courses include introductory Earth system science, oceanography, or climate science. At the science major level, there would be a wide range of appropriate disciplinary and interdisciplinary courses to choose from. After the courses have been selected, pre- and post-course measurements should be made using each CI.

There are many possible results from this study, but I would like to consider the implications of only a few of those possible outcomes. Of primary interest is the question of whether students in disciplinary courses will show learning gains on the interdisciplinary CI (BGC-CI). Conversely, it will be interesting to see whether students in interdisciplinary courses demonstrate disciplinary learning (i.e., learning gains on the GCI, BCI, and/or CCI). As stated in the introduction, the question here is whether learning biogeochemistry is distinct from learning the disciplines that compose it. Thus, is interdisciplinary knowledge simply some compilation of all relevant disciplinary knowledge or does interdisciplinary synthesis impart its own set of unique characteristics? The more the learning gains shown by students in interdisciplinary courses match the gains shown by students in disciplinary courses, the more likely it is that interdisciplinary learning is a "sum of parts" activity. The less those gains match, the more likely it is that interdisciplinary learning is a "thing apart." Finally, it is also possible that no students, regardless of course type, will show learning gains on the BGC-CI. Such an outcome might indicate that the teaching methods employed are ineffective for interdisciplinary learning or that the material is too difficult.

There are known obstacles to the proposed work. One of the most significant is highlighted by the work of Hake (1998) and Libarkin & Anderson (2005), who observed no significant learning gains in many introductory science courses. Knowing that, it is possible the overall dearth of learning gains will mask any differences in learning between disciplinary and interdisciplinary courses. The best strategy for combating this problem is to target disciplinary and interdisciplinary courses that employ reformed teaching strategies (e.g., Sawada et al., 2002), which have been found to produce greater learning gains (Mora, 2008; Hake, 1998; Kortz et al., 1998). As a quasi-experimental study, another concern is spurious correlations related to uncontrolled variables (e.g., prior coursework or instructional strategy). As much as possible, these populations and course characteristics should be identified during data collection so that they can be considered during analysis.

In conclusion, this proposed research would not only benefit course and curriculum designers who teach interdisciplinary science, but would also help clarify what is meant by interdisciplinary teaching. It is the nature of the word, but something that is interdisciplinary is delineated by the disciplines that compose it. Taken one way, that implies a field is interdisciplinary until it is established enough to be considered a discipline unto itself—it is, essentially, a social and historical construction. If this is true, and there is nothing fundamentally different between fields we call interdisciplinary and fields we call disciplinary, then there is a relatively low barrier to teaching interdisciplinary subjects in introductory science classes. If, however, there is something cognitively distinct about thinking and learning in a field such as biogeochemistry, that would demand a very different approach to teaching it to undergraduates. Certainly, this is a complicated issue, but the instrument I have developed here provides a reasonable approach for beginning to address it.

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APPENDIX A

SUPPLEMENTAL AEROSOL DATA

Table A.1. Elemental Concentrations ($\mu g/m^3$) and Soluble Fe for the Coarse Fraction.[a]

Sample Number	Sample Collection Start (m/d/y)[b]	Na	Mg	Al	P	K	Ca
2	4/11/11	3.3E+00	3.3E-01	2.7E-02	3.6E-03	1.1E-01	1.7E-01
3	4/18/11	2.8E+00	2.8E-01	4.9E-02	4.6E-03	9.7E-02	2.1E-01
4	4/25/11	3.3E+00	3.2E-01	3.4E-02	5.3E-03	1.1E-01	1.9E-01
5	5/2/11	3.8E+00	3.7E-01	1.8E-02	3.8E-03	1.2E-01	2.1E-01
6	5/9/11	4.2E+00	4.0E-01	1.6E-02	1.9E-03	1.2E-01	1.9E-01
7	5/16/11	2.3E+00	2.2E-01	2.5E-02	5.2E-03	7.6E-02	1.3E-01
9	5/30/11	2.9E+00	2.9E-01	3.3E-02	6.1E-03	1.0E-01	1.7E-01
10	6/6/11	1.4E+00	3.4E-01	5.9E-02	5.7E-03	n.a.	1.7E-02
11	6/14/11	1.6E+00	3.7E-01	7.6E-02	6.5E-03	n.a.	2.6E-02
12	6/21/11	1.4E+00	2.6E-01	8.4E-02	4.6E-03	n.a.	3.3E-02
13	6/27/11	1.2E+00	2.5E-01	6.7E-02	1.0E-02	n.a.	2.1E-02
14	7/4/11	1.4E+00	2.7E-01	2.0E-01	6.3E-03	n.a.	1.2E-01
15	7/11/11	2.1E+00	3.8E-01	8.1E-02	6.4E-03	n.a.	2.3E-02
16	7/18/11	1.6E+00	3.3E-01	2.7E-01	2.2E-02	n.a.	1.1E-01
17	7/25/11	2.2E+00	4.5E-01	2.3E-01	8.6E-03	n.a.	1.7E-01
18	8/1/11	2.0E+00	8.8E-01	1.5E-01	7.1E-03	n.a.	3.4E-02
19	8/9/11	1.7E+00	2.4E-01	3.1E-01	1.1E-02	n.a.	1.5E-01
20	8/15/11	8.6E-01	1.6E-01	3.5E-01	1.1E-02	1.3E-01	1.7E-01
21	8/22/11	1.1E+00	1.6E-01	1.7E-01	1.3E-02	9.5E-02	1.4E-01
22	8/29/11	1.3E+00	1.4E-01	3.2E-02	2.1E-02	8.6E-02	6.5E-02
23	9/6/11	1.6E+00	1.8E-01	6.9E-02	5.3E-03	8.5E-02	1.1E-01
24	9/12/11	6.9E-01	9.9E-02	7.9E-02	3.0E-02	1.0E-01	5.6E-02
25	9/19/11	4.6E-01	6.2E-02	3.3E-02	1.6E-02	6.0E-02	4.7E-02
26	9/26/11	5.0E-01	6.2E-02	8.6E-03	1.3E-02	5.3E-02	4.4E-02
27	10/3/11	9.0E-01	9.7E-02	2.2E-02	1.6E-02	6.2E-02	7.9E-02
28	10/17/11	5.3E-01	6.1E-02	6.4E-03	1.7E-02	4.8E-02	4.3E-02
29	10/26/11	2.3E+00	2.3E-01	6.3E-03	1.5E-02	1.1E-01	1.1E-01
30	10/31/11	3.0E+00	3.4E-01	3.8E-03	4.9E-03	1.1E-01	1.8E-01
31	11/7/11	3.5E+00	4.2E-01	8.5E-03	1.1E-02	1.6E-01	2.0E-01
32	11/14/11	2.5E+00	3.0E-01	1.7E-02	6.6E-03	1.1E-01	1.4E-01
33	11/21/11	3.3E+00	4.0E-01	9.9E-03	6.3E-03	1.3E-01	1.8E-01
34	12/14/11	3.1E+00	4.0E-01	1.1E-02	2.1E-03	1.2E-01	6.8E-02
35	1/9/12	5.0E+00	6.0E-01	8.7E-02	8.4E-03	2.0E-01	2.7E-01
36	1/16/12	3.0E+00	3.6E-01	1.5E-02	2.6E-03	1.2E-01	1.3E-01
37	1/24/12	2.3E+00	2.8E-01	5.4E-02	5.3E-03	1.1E-01	1.2E-01
38	1/30/12	2.9E+00	3.5E-01	1.1E-02	1.1E-03	1.1E-01	1.7E-01
39	2/6/12	4.0E+00	4.7E-01	9.3E-03	6.1E-03	1.6E-01	1.9E-01
40	2/13/12	4.1E+00	4.8E-01	1.9E-02	4.0E-03	1.6E-01	2.1E-01
41	2/21/12	3.9E+00	4.7E-01	1.1E-02	2.6E-03	1.5E-01	1.8E-01
42	2/27/12	3.2E+00	3.8E-01	1.4E-02	4.6E-03	1.3E-01	1.7E-01
43	3/5/12	3.3E+00	4.0E-01	1.9E-02	2.3E-03	1.4E-01	1.9E-01
44	3/12/12	1.3E+00	1.8E-01	8.4E-02	4.3E-03	8.5E-02	1.7E-01
45	3/19/12	2.5E+00	3.3E-01	9.1E-02	3.8E-03	1.3E-01	2.4E-01
46	3/26/12	5.6E+00	6.9E-01	9.4E-02	3.9E-03	2.5E-01	3.5E-01
47	4/2/12	7.2E+00	8.7E-01	4.7E-02	4.1E-03	3.0E-01	3.6E-01
48	4/9/12	2.5E+00	3.2E-01	8.2E-02	3.3E-03	1.2E-01	2.3E-01
49	4/23/12	3.1E+00	3.8E-01	7.0E-02	4.5E-03	1.4E-01	2.4E-01
50	4/30/12	2.3E+00	2.9E-01	7.1E-02	3.6E-03	1.1E-01	1.8E-01
51	5/7/12	3.2E+00	4.0E-01	6.2E-02	7.7E-03	1.6E-01	2.6E-01
52	5/14/12	2.3E+00	2.8E-01	2.4E-02	5.7E-03	1.0E-01	1.5E-01
53	5/21/12	1.4E+00	1.7E-01	1.0E-01	2.2E-02	9.9E-02	8.4E-02
54	5/28/12	2.7E+00	3.5E-01	2.3E-01	1.4E-02	1.7E-01	1.9E-01
55	6/4/12	2.7E+00	3.3E-01	6.8E-02	1.7E-02	1.5E-01	1.6E-01

Table A.1 (cont.)

Sample Number	Ti	V	Cr	Mn	Fe	Co	Ni
2	2.0E-03	8.1E-05	9.8E-05	3.9E-04	1.9E-02	8.1E-06	6.6E-04
3	4.3E-03	1.4E-04	1.8E-04	7.3E-04	4.3E-02	1.5E-05	9.2E-05
4	3.0E-03	9.4E-05	1.4E-04	5.4E-04	2.8E-02	1.0E-05	2.6E-05
5	2.1E-03	1.5E-04	9.4E-05	3.7E-04	1.8E-02	8.3E-06	5.1E-05
6	8.0E-04	3.1E-05	6.4E-05	1.3E-04	6.3E-03	4.9E-06	1.2E-04
7	1.8E-03	6.7E-05	9.2E-05	3.3E-04	1.5E-02	6.3E-06	3.0E-05
9	3.8E-03	1.8E-04	1.3E-04	7.9E-04	3.2E-02	1.2E-05	7.6E-05
10	1.6E-03	1.0E-04	1.2E-04	7.0E-04	3.3E-02	2.9E-06	1.1E-04
11	2.0E-03	7.1E-05	1.5E-04	7.1E-04	3.8E-02	6.2E-06	7.4E-05
12	2.2E-03	7.3E-05	1.6E-04	7.1E-04	3.7E-02	7.8E-06	1.4E-04
13	1.2E-03	6.5E-05	1.5E-04	5.9E-04	3.4E-02	3.3E-06	3.8E-05
14	5.7E-03	2.4E-04	3.5E-04	1.8E-03	1.1E-01	3.9E-05	9.9E-05
15	1.8E-03	6.3E-05	2.7E-04	5.6E-04	3.6E-02	1.4E-06	b.d.
16	7.7E-03	3.1E-04	4.3E-04	2.5E-03	1.5E-01	4.6E-05	6.2E-05
17	7.0E-03	3.7E-04	6.9E-04	2.7E-03	1.7E-01	5.9E-05	2.2E-04
18	6.0E-03	2.7E-04	3.3E-04	3.5E-03	1.3E-01	5.2E-05	4.8E-04
19	1.3E-02	6.6E-04	7.8E-04	4.5E-03	2.8E-01	9.9E-05	2.4E-04
20	2.1E-02	5.0E-04	3.8E-04	2.8E-03	1.8E-01	8.0E-05	2.5E-04
21	1.0E-02	2.4E-04	2.1E-04	1.4E-03	8.9E-02	3.7E-05	9.5E-05
22	9.5E-04	5.7E-05	5.3E-05	2.6E-04	9.8E-03	4.3E-06	1.9E-05
23	4.2E-03	1.3E-04	8.5E-05	5.8E-04	3.2E-02	1.6E-05	4.2E-05
24	3.4E-03	1.1E-04	1.2E-04	5.2E-04	2.7E-02	1.1E-05	7.8E-05
25	1.7E-03	1.0E-04	6.9E-05	3.1E-04	1.5E-02	7.5E-06	5.4E-05
26	6.0E-04	5.1E-05	4.9E-05	1.1E-04	3.5E-03	1.8E-06	2.1E-05
27	1.2E-03	8.9E-05	7.6E-05	3.7E-04	1.2E-02	5.7E-06	5.2E-05
28	3.3E-04	7.1E-05	6.4E-05	8.3E-05	2.8E-03	1.3E-06	3.5E-05
29	2.7E-04	7.1E-05	2.9E-05	1.1E-04	3.1E-03	7.0E-07	1.3E-05
30	5.0E-04	2.9E-04	8.9E-05	1.1E-04	3.3E-03	3.8E-06	7.7E-05
31	1.1E-03	5.9E-05	1.1E-04	2.8E-04	6.9E-03	4.8E-06	1.8E-04
32	1.0E-03	1.0E-04	1.0E-04	1.9E-04	4.7E-03	5.0E-06	7.5E-05
33	9.7E-04	1.1E-04	1.1E-04	2.3E-04	7.1E-03	5.2E-06	3.4E-05
34	5.6E-04	2.7E-05	4.4E-05	1.6E-04	4.7E-03	3.4E-06	1.4E-04
35	1.2E-03	8.4E-05	2.3E-04	2.9E-04	9.8E-03	7.9E-06	1.3E-04
36	8.7E-04	6.4E-05	1.2E-04	1.6E-04	6.1E-03	5.5E-06	1.5E-04
37	2.2E-03	1.7E-04	1.7E-04	4.2E-04	2.8E-02	1.0E-05	3.7E-05
38	5.5E-04	5.7E-05	1.2E-04	1.4E-04	6.8E-03	5.2E-06	3.5E-06
39	4.7E-04	7.2E-05	1.2E-04	1.5E-04	5.9E-03	3.8E-06	8.8E-05
40	1.4E-03	8.8E-05	1.3E-04	2.5E-04	1.1E-02	7.7E-06	7.6E-05
41	8.2E-04	2.4E-04	3.7E-04	1.6E-04	9.3E-03	3.2E-06	4.7E-05
42	1.2E-03	2.4E-04	3.1E-04	2.0E-04	1.1E-02	3.3E-06	8.3E-05
43	1.2E-03	2.7E-04	4.3E-04	2.7E-04	1.3E-02	5.0E-06	5.5E-05
44	4.7E-03	3.7E-04	5.2E-04	9.7E-04	5.2E-02	2.1E-05	1.7E-04
45	5.0E-03	4.0E-04	5.2E-04	1.2E-03	5.3E-02	2.2E-05	9.8E-05
46	5.0E-03	3.7E-04	5.2E-04	1.1E-03	5.6E-02	2.4E-05	2.5E-04
47	2.5E-03	3.0E-04	4.6E-04	6.3E-04	2.7E-02	1.3E-05	1.5E-04
48	4.6E-03	2.6E-04	3.3E-04	8.8E-04	5.2E-02	2.1E-05	1.3E-04
49	4.6E-03	3.5E-04	5.9E-04	8.0E-04	3.9E-02	1.5E-05	9.5E-04
50	3.7E-03	4.4E-04	4.8E-04	7.5E-04	3.8E-02	1.5E-05	1.2E-04
51	3.5E-03	3.5E-04	4.9E-04	9.5E-04	3.8E-02	1.6E-05	1.3E-04
52	1.5E-03	2.7E-04	4.1E-04	3.4E-04	1.6E-02	6.3E-06	4.8E-05
53	2.9E-03	3.7E-04	5.4E-04	5.4E-04	2.5E-02	9.4E-06	8.3E-05
54	1.3E-02	5.7E-04	6.4E-04	2.1E-03	1.2E-01	4.8E-05	2.3E-04
55	4.0E-03	4.8E-04	5.0E-04	8.1E-04	3.8E-02	1.6E-05	1.7E-04

Table A.1 (cont.)

Sample Number	Cu	Zn	Rb	Sr	Zr	Mo
2	1.4E-04	7.1E-04	2.7E-05	2.3E-03	7.9E-04	1.2E-05
3	2.1E-04	4.4E-04	4.3E-05	2.5E-03	2.3E-03	1.7E-05
4	1.3E-04	3.6E-04	3.3E-05	2.7E-03	1.2E-03	1.3E-05
5	2.2E-04	4.1E-04	2.4E-05	3.0E-03	9.8E-04	1.9E-05
6	7.0E-05	1.6E-04	2.0E-05	3.3E-03	2.9E-04	1.7E-05
7	1.3E-04	3.2E-04	2.0E-05	1.7E-03	7.1E-04	1.1E-05
9	2.1E-04	6.3E-04	3.4E-05	2.1E-03	1.3E-03	2.5E-05
10	1.9E-04	5.7E-04	1.4E-04	2.0E-03	6.1E-05	1.4E-05
11	8.6E-05	4.5E-04	1.4E-04	2.3E-03	8.1E-05	8.6E-06
12	1.5E-04	4.7E-04	1.4E-04	1.5E-03	5.1E-05	1.3E-05
13	5.5E-05	3.7E-04	1.4E-04	1.7E-03	5.6E-05	8.4E-06
14	8.5E-05	4.8E-04	3.1E-04	3.2E-03	2.6E-04	6.6E-06
15	7.0E-05	3.9E-04	1.2E-04	2.4E-03	6.1E-05	5.5E-06
16	1.0E-04	7.7E-04	4.1E-04	3.9E-03	3.2E-04	4.8E-06
17	2.0E-04	7.7E-04	4.6E-04	6.1E-03	3.7E-04	1.6E-05
18	2.2E-04	1.5E-03	4.3E-04	4.9E-03	2.3E-04	6.6E-06
19	2.0E-04	1.0E-03	7.3E-04	5.2E-03	6.0E-04	9.5E-06
20	1.7E-04	5.1E-04	3.5E-04	1.8E-03	7.5E-02	6.2E-06
21	9.5E-05	2.6E-04	1.9E-04	1.6E-03	3.6E-02	6.1E-06
22	4.7E-05	2.8E-04	4.5E-05	1.0E-03	4.3E-03	2.7E-06
23	4.2E-05	7.7E-05	8.6E-05	1.5E-03	1.5E-02	3.0E-06
24	1.0E-04	4.4E-04	9.4E-05	8.9E-04	1.2E-02	4.2E-06
25	1.1E-04	3.0E-04	4.7E-05	5.9E-04	7.1E-03	3.3E-06
26	5.3E-05	1.8E-04	2.4E-05	5.9E-04	2.0E-03	2.8E-06
27	9.0E-05	3.3E-04	4.8E-05	8.8E-04	5.6E-03	5.0E-06
28	4.8E-05	1.7E-04	1.8E-05	6.1E-04	1.7E-03	4.5E-06
29	6.3E-05	9.6E-05	2.6E-05	1.6E-03	2.3E-03	3.2E-06
30	3.8E-06	1.2E-04	4.5E-05	2.9E-03	2.2E-03	1.5E-05
31	5.8E-05	2.4E-04	9.1E-05	3.2E-03	5.5E-03	1.5E-05
32	4.0E-05	1.9E-04	4.7E-05	2.0E-03	3.1E-03	8.6E-06
33	7.2E-05	2.3E-04	5.3E-05	2.5E-03	5.3E-03	1.2E-05
34	6.2E-05	2.6E-04	5.3E-05	1.5E-03	3.1E-03	7.6E-06
35	4.0E-05	2.7E-04	8.8E-05	4.4E-03	6.7E-03	2.3E-05
36	1.6E-05	2.0E-04	5.1E-05	2.2E-03	3.8E-03	1.0E-05
37	b.d.	6.4E-05	9.8E-05	1.9E-03	1.5E-02	1.3E-05
38	b.d.	8.4E-05	5.3E-05	2.7E-03	4.0E-03	8.5E-06
39	1.5E-05	1.4E-04	6.3E-05	3.2E-03	4.1E-03	1.2E-05
40	6.3E-05	2.5E-04	7.6E-05	3.5E-03	6.7E-03	1.5E-05
41	5.2E-05	9.4E-05	5.7E-05	2.8E-03	1.2E-05	2.7E-06
42	7.5E-05	1.9E-04	5.5E-05	2.6E-03	2.4E-05	7.5E-06
43	1.0E-04	2.8E-04	6.5E-05	2.7E-03	2.6E-05	6.9E-06
44	2.5E-04	5.0E-04	1.4E-04	1.7E-03	9.4E-05	1.8E-05
45	2.2E-04	5.6E-04	1.6E-04	2.5E-03	1.1E-04	1.8E-05
46	2.1E-04	5.4E-04	1.9E-04	4.9E-03	1.0E-04	1.1E-05
47	1.5E-04	3.8E-04	1.4E-04	5.4E-03	5.4E-05	8.8E-06
48	1.8E-04	5.1E-04	1.4E-04	2.8E-03	9.4E-05	9.3E-06
49	1.6E-04	4.9E-04	1.2E-04	2.8E-03	8.4E-05	9.8E-06
50	1.9E-04	3.7E-04	1.1E-04	2.0E-03	7.6E-05	1.5E-05
51	2.2E-04	5.1E-04	1.2E-04	3.0E-03	8.8E-05	1.4E-05
52	1.1E-04	3.2E-04	5.6E-05	1.9E-03	3.2E-05	1.9E-06
53	1.6E-04	6.0E-04	6.5E-05	1.1E-03	5.7E-05	8.8E-06
54	2.8E-04	7.2E-04	2.5E-04	2.4E-03	2.5E-04	2.9E-05
55	2.0E-04	6.5E-04	1.0E-04	2.1E-03	8.3E-05	1.1E-05

Table A.1 (cont.)

Sample Number	Cs	Ba	Hf	W	Pb	U	Soluble Fe
2	7.6E-06	2.8E-04	1.9E-06	4.9E-06	1.3E-04	8.2E-06	0.042%
3	1.6E-05	5.6E-04	5.2E-06	7.4E-06	2.2E-04	1.6E-05	0.0096%
4	9.8E-06	4.1E-04	2.9E-06	6.1E-06	1.6E-04	9.2E-06	0.039%
5	4.9E-06	3.2E-04	2.2E-06	7.3E-06	1.5E-04	2.6E-05	0.093%
6	2.6E-06	9.4E-05	8.5E-07	5.2E-06	4.0E-05	6.1E-06	0.064%
7	4.7E-06	2.4E-04	8.6E-06	4.6E-06	8.3E-05	6.7E-06	0.081%
9	7.0E-06	4.9E-04	3.3E-06	1.1E-05	1.9E-04	1.4E-05	0.039%
10	4.7E-06	8.0E-04	8.2E-07	6.3E-06	6.1E-05	4.0E-06	0.050%
11	4.5E-06	6.7E-04	1.8E-06	5.3E-06	4.1E-05	4.4E-06	0.019%
12	4.7E-06	7.7E-04	9.0E-07	3.7E-06	5.7E-05	3.2E-06	0.041%
13	5.6E-06	5.9E-04	7.3E-07	2.3E-06	3.0E-05	3.4E-06	0.0081%
14	1.3E-05	1.7E-03	6.4E-06	2.1E-06	6.2E-05	8.4E-06	0.0028%
15	3.0E-06	5.9E-04	8.8E-07	2.1E-06	3.8E-05	3.6E-06	0.0063%
16	1.5E-05	2.1E-03	6.3E-06	2.5E-06	6.6E-05	1.2E-05	0.0014%
17	1.8E-05	2.4E-03	9.7E-06	1.0E-06	9.8E-05	1.4E-05	0.014%
18	1.4E-05	1.9E-03	6.4E-06	1.7E-06	9.6E-05	1.0E-05	0.0017%
19	2.8E-05	4.0E-03	1.5E-05	1.0E-06	1.4E-04	2.1E-05	0.0015%
20	1.7E-05	1.8E-03	1.1E-05	4.4E-06	1.0E-04	1.1E-05	0.0016%
21	8.7E-06	9.8E-04	5.3E-06	1.7E-06	5.6E-05	5.7E-06	0.0013%
22	1.3E-06	1.2E-04	7.0E-07	b.d.	1.3E-05	1.3E-06	0.0037%
23	3.4E-06	3.7E-04	2.5E-06	b.d.	2.9E-05	3.2E-06	0.0036%
24	3.3E-06	3.3E-04	1.9E-06	b.d.	2.9E-05	2.2E-06	0.0014%
25	2.1E-06	2.0E-04	1.3E-06	b.d.	2.5E-05	2.1E-06	b.d.
26	7.0E-07	4.6E-05	3.0E-07	b.d.	1.4E-05	5.4E-07	b.d.
27	1.5E-06	2.4E-04	9.3E-07	6.7E-08	3.3E-05	1.2E-06	0.0053%
28	6.4E-07	6.0E-05	2.5E-07	b.d.	1.3E-05	4.7E-07	b.d.
29	3.8E-07	9.0E-05	2.9E-07	b.d.	2.1E-05	1.0E-06	b.d.
30	4.7E-07	6.0E-05	3.6E-07	3.9E-07	3.1E-05	1.5E-06	b.d.
31	1.0E-06	1.4E-04	7.9E-07	8.2E-07	3.3E-05	1.7E-06	b.d.
32	1.1E-06	1.0E-04	6.5E-07	6.1E-07	2.4E-05	1.1E-06	b.d.
33	1.6E-06	1.6E-04	1.0E-06	5.6E-07	3.8E-05	1.4E-06	0.0010%
34	2.1E-06	9.2E-05	5.6E-07	5.8E-07	2.9E-05	1.1E-06	0.026%
35	2.8E-06	2.6E-04	1.2E-06	2.7E-06	3.7E-05	2.8E-06	b.d.
36	1.6E-06	1.3E-04	6.7E-07	1.4E-06	2.0E-05	1.5E-06	0.011%
37	5.1E-06	4.1E-04	2.9E-06	2.2E-06	5.7E-05	2.6E-06	0.020%
38	3.0E-06	1.3E-04	7.5E-07	8.8E-07	2.8E-05	2.8E-06	0.013%
39	1.5E-06	1.3E-04	7.9E-07	6.3E-07	2.7E-05	1.7E-06	b.d.
40	4.4E-06	2.3E-04	1.2E-06	1.3E-06	3.5E-05	2.5E-06	0.031%
41	2.2E-06	1.4E-04	2.4E-07	b.d.	2.5E-05	7.3E-07	0.010%
42	2.1E-06	1.7E-04	8.3E-07	b.d.	2.4E-05	6.3E-07	0.017%
43	3.8E-06	2.8E-04	6.3E-07	4.2E-07	4.9E-05	1.0E-06	0.014%
44	1.4E-05	8.2E-04	3.1E-06	3.5E-06	9.5E-05	1.9E-06	0.015%
45	1.7E-05	8.3E-04	3.5E-06	2.9E-06	1.2E-04	2.3E-06	0.0048%
46	1.3E-05	7.0E-04	3.1E-06	2.9E-06	1.0E-04	2.7E-06	0.0060%
47	6.5E-06	4.0E-04	1.7E-06	1.7E-06	6.2E-05	1.7E-06	0.0021%
48	9.8E-06	6.5E-04	2.9E-06	3.9E-06	9.3E-05	2.5E-06	0.0022%
49	7.7E-06	6.0E-04	2.7E-06	4.4E-06	1.3E-04	2.3E-06	0.010%
50	6.7E-06	5.7E-04	2.5E-06	2.3E-06	8.5E-05	1.7E-06	0.0044%
51	6.5E-06	5.6E-04	2.5E-06	2.5E-06	8.7E-05	1.9E-06	0.0016%
52	2.9E-06	2.6E-04	8.3E-07	b.d.	4.6E-05	1.0E-06	0.0011%
53	2.5E-06	3.1E-04	1.9E-06	b.d.	3.7E-05	8.3E-07	0.0011%
54	1.1E-05	1.4E-03	7.7E-06	5.4E-06	1.2E-04	3.3E-06	0.0038%
55	4.2E-06	5.6E-04	2.7E-06	1.7E-06	6.4E-05	1.5E-06	b.d.

[a] n.a., not analyzed; b.d., below detection limit

Table A.2. Elemental concentrations (μg/m^3) and soluble Fe for the fine fraction.[a]

Sample Number	Sample Collection Start (m/d/y)[b]	Na	Mg	Al	P	K	Ca
2	4/11/11	1.0E+00	1.1E-01	3.0E-02	1.3E-02	5.0E-02	1.3E-01
3	4/18/11	9.3E-01	1.1E-01	6.2E-02	1.5E-02	6.0E-02	2.6E-01
4	4/25/11	7.7E-01	8.7E-02	4.7E-02	1.8E-02	5.9E-02	2.4E-01
5	5/2/11	1.3E+00	1.4E-01	2.6E-02	9.5E-03	5.6E-02	1.8E-01
6	5/9/11	1.2E+00	1.3E-01	9.7E-03	4.4E-03	4.4E-02	5.2E-02
7	5/16/11	5.2E-01	5.9E-02	2.4E-02	1.4E-02	3.7E-02	1.1E-01
9	5/30/11	5.6E-01	6.3E-02	3.7E-02	1.0E-02	4.4E-02	1.4E-01
10	6/6/11	3.2E-01	4.6E-02	3.1E-02	2.1E-03	n.a.	4.7E-03
11	6/14/11	4.3E-01	6.3E-02	5.5E-02	4.3E-03	n.a.	4.7E-03
12	6/21/11	4.7E-01	7.0E-02	5.9E-02	3.1E-03	n.a.	5.8E-03
13	6/27/11	5.0E-01	7.2E-02	7.2E-02	1.4E-02	n.a.	1.0E-02
14	7/4/11	4.6E-01	8.3E-02	1.9E-01	9.3E-03	n.a.	1.5E-02
15	7/11/11	6.2E-01	9.2E-02	9.4E-02	1.6E-02	n.a.	2.3E-02
16	7/18/11	3.6E-01	6.7E-02	1.8E-01	7.7E-03	n.a.	8.5E-03
17	7/25/11	3.6E-01	6.8E-02	1.6E-01	3.0E-03	n.a.	4.5E-03
18	8/1/11	7.2E-01	1.4E-01	3.3E-01	7.3E-03	n.a.	1.5E-02
19	8/9/11	6.7E-01	1.4E-01	4.1E-01	1.2E-02	n.a.	1.3E-02
20	8/15/11	1.8E-01	6.0E-02	2.8E-01	1.1E-02	9.1E-02	7.9E-02
21	8/22/11	2.3E-01	5.4E-02	1.9E-01	6.7E-03	7.9E-02	7.1E-02
22	8/29/11	1.5E-01	1.8E-02	1.4E-02	3.4E-03	4.0E-02	1.3E-02
23	9/6/11	4.1E-01	5.5E-02	5.3E-02	7.7E-03	6.9E-02	4.0E-02
24	9/12/11	1.9E-01	3.0E-02	4.4E-02	b.d.	6.2E-02	3.6E-02
25	9/19/11	6.1E-02	9.4E-03	1.9E-02	1.2E-02	4.6E-02	2.2E-02
26	9/26/11	1.3E-01	1.7E-02	9.7E-03	2.7E-04	4.1E-02	1.4E-02
27	10/3/11	1.4E-01	1.8E-02	1.4E-02	4.9E-03	3.7E-02	2.8E-02
28	10/17/11	2.1E-01	2.6E-02	7.0E-03	1.5E-02	5.2E-02	2.3E-02
29	10/26/11	3.4E-01	4.1E-02	8.8E-03	1.9E-02	7.5E-02	4.9E-02
30	10/31/11	8.0E-01	9.3E-02	7.4E-03	1.5E-02	5.5E-02	7.5E-02
31	11/7/11	9.6E-01	1.2E-01	1.3E-02	4.5E-02	1.0E-01	1.0E-01
32	11/14/11	6.7E-01	8.1E-02	2.7E-02	2.1E-02	4.7E-02	1.2E-01
33	11/21/11	5.7E-01	6.7E-02	2.1E-02	9.8E-03	3.1E-02	1.3E-01
34	12/14/11	1.2E+00	1.3E-01	2.0E-02	7.7E-04	5.9E-02	7.1E-02
35	1/9/12	4.2E+00	5.0E-01	7.9E-03	3.3E-03	1.7E-01	2.1E-01
36	1/16/12	6.4E-01	7.3E-02	3.6E-02	2.6E-03	4.1E-02	6.3E-02
37	1/24/12	8.8E-01	1.0E-01	3.5E-02	5.6E-03	4.1E-02	8.9E-02
38	1/30/12	8.2E-01	9.8E-02	9.7E-03	2.3E-03	3.6E-02	7.5E-02
39	2/6/12	8.2E-01	1.0E-01	6.0E-02	5.1E-03	4.3E-02	9.2E-02
40	2/13/12	1.6E+00	1.9E-01	3.5E-02	9.1E-03	8.6E-02	1.6E-01
41	2/21/12	1.1E+00	1.3E-01	1.4E-02	4.3E-03	6.7E-02	6.6E-02
42	2/27/12	9.6E-01	1.1E-01	2.6E-02	6.4E-03	4.7E-02	1.2E-01
43	3/5/12	3.3E-01	6.3E-02	1.3E-01	1.8E-02	8.2E-02	2.1E-01
44	3/12/12	6.4E-01	7.7E-02	1.1E-01	2.0E-02	9.7E-02	1.9E-01
45	3/19/12	1.3E+00	1.7E-01	7.7E-02	7.1E-03	9.2E-02	1.1E-01
46	3/26/12	1.4E+00	1.8E-01	4.6E-02	4.7E-03	8.4E-02	1.0E-01
47	4/2/12	2.8E+00	3.5E-01	7.1E-02	8.6E-03	1.5E-01	2.4E-01
48	4/9/12	8.0E-01	1.0E-01	1.5E-01	7.9E-03	7.9E-02	1.0E-01
49	4/23/12	4.9E-01	6.9E-02	7.8E-02	7.8E-03	6.7E-02	1.5E-01
50	4/30/12	7.2E-01	1.1E-01	1.1E-01	1.6E-02	7.9E-02	2.7E-01
51	5/7/12	7.2E-01	9.8E-02	3.8E-02	8.4E-03	4.9E-02	1.3E-01
52	5/14/12	5.6E-01	7.1E-02	6.8E-02	9.7E-03	4.7E-02	9.5E-02
53	5/21/12	2.7E-01	3.6E-02	7.2E-02	9.7E-03	4.8E-02	4.0E-02
54	5/28/12	7.2E-01	9.7E-02	9.9E-02	9.9E-03	7.6E-02	8.5E-02
55	6/4/12	1.0E+00	1.1E-01	3.0E-02	1.3E-02	5.0E-02	1.3E-01

Table A.2 (cont.)

Sample Number	Ti	V	Cr	Mn	Fe	Co	Ni
2	3.0E-03	5.4E-04	2.6E-04	7.5E-04	2.9E-02	1.4E-05	2.3E-04
3	5.5E-03	9.6E-04	3.4E-04	1.2E-03	5.5E-02	2.5E-05	4.7E-04
4	4.6E-03	7.6E-04	4.9E-04	1.0E-03	4.3E-02	1.9E-05	3.6E-04
5	5.1E-03	2.4E-03	2.5E-04	7.0E-04	2.7E-02	2.5E-05	1.0E-03
6	1.2E-03	2.7E-04	1.4E-04	2.3E-04	1.0E-02	5.7E-06	6.4E-05
7	2.6E-03	8.1E-04	2.1E-04	4.7E-04	2.1E-02	1.2E-05	3.6E-04
9	3.3E-03	1.6E-03	3.3E-04	8.6E-04	2.9E-02	2.4E-05	8.5E-04
10	1.4E-03	1.0E-03	2.0E-04	5.7E-04	1.7E-02	b.d.	2.5E-04
11	3.2E-03	8.2E-04	2.0E-04	6.7E-04	3.2E-02	b.d.	1.4E-04
12	3.5E-03	8.6E-04	1.6E-04	6.4E-04	3.3E-02	b.d.	9.3E-05
13	3.2E-03	9.7E-04	4.5E-03	1.1E-03	6.0E-02	2.0E-05	3.2E-03
14	1.0E-02	4.5E-04	3.2E-04	1.5E-03	9.9E-02	1.4E-05	3.9E-04
15	4.9E-03	8.5E-04	1.0E-03	9.7E-04	5.4E-02	9.9E-06	1.4E-03
16	7.7E-03	5.3E-04	3.4E-04	1.4E-03	9.2E-02	1.0E-05	4.3E-04
17	8.7E-03	4.2E-04	2.8E-04	1.2E-03	8.0E-02	b.d.	1.1E-04
18	1.8E-02	7.0E-04	6.7E-04	2.8E-03	1.7E-01	4.9E-05	3.6E-04
19	2.1E-02	1.4E-03	1.4E-03	3.4E-03	2.1E-01	4.2E-05	8.3E-04
20	1.6E-02	7.7E-04	3.8E-04	2.3E-03	1.3E-01	6.0E-05	3.1E-04
21	1.1E-02	4.7E-04	2.5E-04	1.5E-03	8.9E-02	4.0E-05	1.5E-04
22	6.6E-04	1.5E-04	6.0E-05	1.3E-04	5.8E-03	2.7E-06	3.0E-05
23	3.1E-03	3.3E-04	9.9E-05	4.7E-04	2.5E-02	1.3E-05	1.0E-04
24	2.5E-03	3.1E-04	1.3E-04	3.6E-04	2.0E-02	1.2E-05	1.1E-04
25	9.5E-04	4.1E-04	1.8E-04	1.6E-04	6.9E-03	5.3E-06	1.4E-04
26	9.2E-04	5.3E-04	1.0E-04	9.6E-05	4.6E-03	3.1E-06	1.7E-04
27	8.0E-04	8.4E-04	1.0E-04	2.9E-04	7.4E-03	7.5E-06	3.3E-04
28	2.1E-04	7.6E-04	1.2E-04	1.0E-04	3.5E-03	5.0E-06	3.3E-04
29	5.3E-04	2.4E-04	1.1E-04	2.0E-04	4.3E-03	3.1E-06	8.1E-05
30	7.1E-05	4.7E-03	2.9E-04	1.4E-04	3.9E-03	2.5E-05	1.9E-03
31	9.5E-04	3.7E-04	3.8E-04	3.1E-04	8.4E-03	1.0E-05	1.5E-04
32	1.0E-03	2.1E-03	3.5E-04	2.6E-04	1.0E-02	1.4E-05	7.0E-04
33	1.3E-03	1.9E-03	3.2E-04	2.9E-04	1.1E-02	2.0E-05	6.8E-04
34	3.3E-04	5.0E-04	3.2E-03	6.9E-04	2.3E-02	2.6E-05	2.2E-03
35	5.6E-04	3.5E-04	2.5E-03	3.8E-04	1.7E-02	2.0E-05	1.3E-03
36	2.4E-03	7.5E-04	4.8E-04	5.9E-04	1.6E-02	1.5E-05	3.0E-04
37	1.4E-03	2.5E-04	3.9E-04	3.3E-04	8.5E-03	1.1E-05	2.0E-04
38	6.9E-04	5.1E-04	2.8E-04	2.0E-04	6.5E-03	9.4E-06	1.5E-04
39	1.3E-03	5.2E-04	4.0E-04	3.4E-04	1.2E-02	1.2E-05	2.7E-04
40	1.7E-03	1.1E-03	1.2E-03	5.0E-04	1.6E-02	1.1E-05	4.1E-04
41	1.1E-03	1.0E-03	9.6E-04	4.0E-04	1.6E-02	9.0E-06	3.4E-04
42	1.8E-03	1.4E-03	9.0E-04	5.3E-04	1.7E-02	1.5E-05	5.4E-04
43	5.4E-03	1.3E-03	1.1E-03	1.4E-03	5.5E-02	2.9E-05	6.3E-04
44	5.1E-03	1.2E-03	1.6E-03	1.4E-03	5.4E-02	3.0E-05	7.4E-04
45	5.4E-03	8.1E-04	1.4E-03	1.0E-03	4.5E-02	2.3E-05	1.7E-03
46	2.9E-03	7.6E-04	1.3E-03	7.3E-04	3.0E-02	1.5E-05	4.6E-04
47	4.1E-03	6.5E-04	1.4E-02	1.8E-03	b.d.	9.1E-05	6.5E-03
48	4.4E-03	1.1E-03	1.3E-03	1.2E-03	3.7E-02	2.1E-05	7.9E-04
49	7.4E-03	2.3E-03	1.1E-03	1.1E-03	4.5E-02	3.3E-05	1.1E-03
50	5.2E-03	1.0E-03	1.1E-03	1.4E-03	5.3E-02	2.3E-05	3.5E-04
51	2.4E-03	7.3E-04	1.1E-03	6.8E-04	2.6E-02	1.2E-05	2.6E-04
52	3.6E-03	1.8E-03	1.3E-03	7.1E-04	3.1E-02	2.5E-05	8.9E-04
53	4.2E-03	1.6E-03	1.1E-03	7.8E-04	3.7E-02	2.2E-05	6.7E-04
54	5.0E-03	2.1E-03	1.2E-03	9.0E-04	4.1E-02	2.6E-05	1.1E-03
55	3.0E-03	5.4E-04	2.6E-04	7.5E-04	2.9E-02	1.4E-05	2.3E-04

Table A.2 (cont.)

Sample Number	Cu	Zn	Rb	Sr	Zr	Mo
2	2.3E-04	2.0E-03	3.4E-05	1.3E-03	9.8E-04	2.1E-05
3	4.1E-04	2.2E-03	4.8E-05	2.3E-03	2.0E-03	3.4E-05
4	3.9E-04	2.5E-03	4.2E-05	2.1E-03	1.7E-03	3.5E-05
5	4.7E-04	2.4E-03	2.8E-05	1.7E-03	2.0E-03	8.1E-05
6	1.2E-04	6.5E-04	1.4E-05	8.3E-04	6.0E-04	1.5E-05
7	2.9E-04	1.3E-03	2.1E-05	1.0E-03	1.2E-03	2.7E-05
9	3.7E-04	3.2E-03	3.0E-05	1.2E-03	1.3E-03	4.8E-05
10	9.4E-05	1.9E-03	8.0E-05	5.8E-04	3.3E-05	3.1E-05
11	3.2E-05	1.8E-03	1.5E-04	7.1E-04	7.3E-05	2.0E-05
12	b.d.	1.6E-03	1.3E-04	9.9E-04	9.1E-05	9.8E-06
13	3.8E-04	1.9E-03	1.8E-04	1.0E-03	9.9E-05	b.d.
14	8.8E-05	1.6E-03	2.5E-04	1.4E-03	2.2E-04	b.d.
15	1.6E-04	1.6E-03	1.4E-04	1.8E-03	1.0E-04	1.2E-05
16	b.d.	7.7E-04	2.2E-04	1.1E-03	1.8E-04	b.d.
17	1.8E-05	1.3E-03	1.8E-04	9.9E-04	1.8E-04	3.9E-06
18	4.6E-05	1.7E-03	3.8E-04	1.9E-03	4.8E-04	6.0E-07
19	1.4E-05	1.8E-03	4.7E-04	2.2E-03	4.4E-04	1.8E-05
20	1.5E-04	6.6E-04	2.5E-04	1.1E-03	5.8E-02	7.2E-06
21	8.0E-05	4.7E-04	1.8E-04	9.3E-04	4.1E-02	4.6E-06
22	3.1E-05	2.3E-04	1.7E-05	1.7E-04	2.6E-03	1.0E-06
23	2.9E-05	2.6E-04	6.0E-05	5.5E-04	1.3E-02	4.0E-06
24	5.5E-05	4.9E-04	6.1E-05	3.7E-04	9.8E-03	3.3E-06
25	9.9E-05	6.4E-04	2.5E-05	2.5E-04	3.2E-03	3.0E-06
26	2.0E-05	3.6E-05	1.3E-05	1.7E-04	2.7E-03	1.9E-06
27	9.4E-05	7.6E-04	3.9E-05	3.0E-04	3.9E-03	9.9E-06
28	4.9E-05	3.3E-04	2.1E-05	2.7E-04	2.1E-03	6.4E-06
29	1.0E-04	1.1E-03	3.2E-05	5.7E-04	3.1E-03	1.2E-05
30	b.d.	5.0E-04	5.9E-05	7.7E-04	2.2E-03	2.5E-05
31	b.d.	1.5E-03	1.3E-04	1.0E-03	5.4E-03	2.8E-05
32	b.d.	1.3E-03	5.6E-05	1.0E-03	5.2E-03	2.4E-05
33	b.d.	1.4E-03	4.1E-05	9.9E-04	5.8E-03	1.9E-05
34	2.1E-04	2.9E-03	6.8E-05	8.8E-04	4.6E-03	2.3E-05
35	9.3E-05	2.9E-04	7.0E-05	3.4E-03	3.5E-03	3.5E-05
36	b.d.	2.3E-03	8.2E-05	6.6E-04	1.0E-02	4.1E-05
37	2.7E-05	1.2E-03	5.6E-05	9.2E-04	5.7E-03	2.8E-05
38	b.d.	9.3E-04	3.9E-05	8.9E-04	3.4E-03	1.4E-05
39	b.d.	1.3E-03	5.6E-05	1.0E-03	5.6E-03	2.9E-05
40	2.4E-04	1.7E-03	6.1E-05	1.8E-03	5.6E-05	2.5E-05
41	2.5E-04	1.8E-03	4.9E-05	8.9E-04	3.7E-05	2.0E-05
42	2.0E-04	1.7E-03	6.1E-05	1.2E-03	4.2E-05	2.5E-05
43	5.8E-04	6.0E-03	1.5E-04	1.8E-03	1.1E-04	4.0E-05
44	5.0E-04	3.2E-03	1.8E-04	1.7E-03	1.3E-04	4.2E-05
45	2.7E-04	2.5E-03	1.3E-04	1.4E-03	7.9E-05	2.5E-05
46	2.3E-04	1.7E-03	9.2E-05	1.3E-03	6.1E-05	1.2E-05
47	7.5E-04	1.1E-03	1.3E-04	2.8E-03	9.2E-05	9.3E-05
48	4.6E-04	4.8E-03	1.3E-04	1.1E-03	8.1E-05	2.5E-05
49	3.6E-04	2.5E-03	1.3E-04	1.3E-03	9.8E-05	4.4E-05
50	4.1E-04	2.6E-03	1.3E-04	2.2E-03	1.1E-04	2.7E-05
51	2.3E-04	1.9E-03	7.6E-05	1.2E-03	4.0E-05	9.9E-06
52	3.3E-04	5.8E-03	7.2E-05	1.3E-03	5.7E-05	2.7E-05
53	2.9E-04	1.7E-03	8.8E-05	4.4E-04	1.0E-04	4.2E-05
54	3.7E-04	3.4E-03	9.3E-05	9.3E-04	9.7E-05	3.3E-05
55	2.3E-04	2.0E-03	3.4E-05	1.3E-03	9.8E-04	2.1E-05

Table A.2 (cont.)

Sample Number	Cs	Ba	Hf	W	Pb	U	Soluble Fe
2	1.7E-05	4.2E-04	2.4E-06	1.6E-05	1.6E-03	8.0E-06	0.081%
3	2.1E-05	5.6E-04	4.0E-06	1.2E-05	1.6E-03	1.2E-05	0.13%
4	1.7E-05	5.2E-04	3.8E-06	1.3E-05	1.7E-03	2.3E-05	0.049%
5	1.1E-05	4.4E-04	4.1E-06	1.6E-05	1.6E-03	5.4E-05	0.050%
6	3.8E-06	1.4E-04	1.3E-06	6.6E-06	4.2E-04	3.2E-06	0.096%
7	7.1E-06	2.6E-04	2.6E-06	1.1E-05	5.8E-04	2.3E-05	0.10%
9	9.4E-06	4.1E-04	3.0E-06	1.6E-05	8.8E-04	1.5E-05	0.072%
10	2.0E-06	4.0E-04	b.d.	8.2E-06	5.3E-04	7.9E-07	0.20%
11	4.6E-06	5.5E-04	6.9E-07	4.8E-06	3.7E-04	2.1E-06	0.13%
12	1.1E-06	6.9E-04	b.d.	2.0E-06	4.1E-04	1.3E-06	0.11%
13	5.4E-06	5.9E-04	1.0E-06	9.0E-07	2.9E-04	1.8E-06	0.051%
14	9.5E-06	1.4E-03	4.3E-06	2.0E-06	1.9E-04	6.0E-06	0.022%
15	3.3E-06	8.2E-04	1.4E-06	1.7E-06	1.9E-04	2.5E-06	0.058%
16	7.6E-06	1.4E-03	4.3E-06	b.d.	1.2E-04	5.3E-06	0.021%
17	4.8E-06	1.2E-03	3.3E-06	2.4E-06	2.4E-04	4.5E-06	0.054%
18	1.4E-05	2.5E-03	1.1E-05	2.3E-06	2.8E-04	1.1E-05	0.032%
19	1.7E-05	3.0E-03	9.4E-06	1.5E-06	3.2E-04	1.2E-05	0.030%
20	1.3E-05	1.6E-03	9.3E-06	7.2E-07	2.5E-04	8.5E-06	0.0066%
21	1.1E-05	1.1E-03	6.2E-06	b.d.	1.2E-04	6.0E-06	0.0063%
22	9.7E-07	7.6E-05	4.5E-07	b.d.	3.6E-05	5.1E-07	0.053%
23	3.1E-06	3.1E-04	2.1E-06	b.d.	7.3E-05	1.8E-06	0.026%
24	2.1E-06	2.4E-04	1.7E-06	b.d.	5.5E-05	1.8E-06	0.021%
25	9.9E-07	8.3E-05	5.2E-07	b.d.	4.4E-05	8.2E-07	0.054%
26	6.9E-07	5.8E-05	4.9E-07	b.d.	2.8E-05	5.3E-07	0.087%
27	2.8E-06	1.6E-04	5.2E-07	8.3E-07	3.0E-04	7.2E-07	0.18%
28	7.7E-07	8.6E-05	2.6E-07	b.d.	8.2E-05	4.8E-07	0.18%
29	1.6E-06	8.4E-05	5.1E-07	b.d.	2.3E-04	1.2E-06	0.23%
30	1.4E-06	5.2E-05	3.8E-07	2.9E-07	1.5E-04	4.7E-07	0.061%
31	2.6E-06	1.3E-04	8.8E-07	1.5E-06	3.1E-04	7.4E-07	0.046%
32	2.1E-06	1.9E-04	9.7E-07	1.5E-06	2.4E-04	6.8E-07	0.016%
33	2.4E-06	1.6E-04	1.1E-06	1.5E-06	2.3E-04	8.6E-07	0.017%
34	3.0E-06	2.4E-04	7.8E-07	5.1E-06	3.5E-04	8.8E-07	0.062%
35	1.7E-06	1.1E-04	7.6E-07	4.0E-06	7.3E-05	5.6E-07	0.032%
36	4.1E-06	3.1E-04	1.7E-06	9.1E-05	3.8E-04	1.2E-06	0.057%
37	3.4E-06	1.7E-04	1.1E-06	4.5E-06	3.4E-04	1.0E-06	0.041%
38	1.5E-06	1.2E-04	6.2E-07	7.3E-06	2.0E-04	5.2E-06	0.015%
39	3.4E-06	2.0E-04	1.2E-06	7.0E-06	3.7E-04	1.1E-06	0.048%
40	3.5E-06	1.2E-03	1.0E-06	5.0E-07	5.0E-04	5.0E-07	0.030%
41	2.6E-06	1.1E-03	8.6E-07	1.7E-06	4.3E-04	4.3E-07	0.044%
42	4.7E-06	1.1E-03	1.3E-06	4.3E-07	4.8E-04	1.3E-06	0.021%
43	1.3E-05	1.1E-03	3.0E-06	5.6E-06	1.0E-03	1.7E-06	0.018%
44	1.4E-05	8.9E-04	3.9E-06	1.1E-05	9.6E-04	1.7E-06	0.023%
45	1.1E-05	7.6E-04	2.6E-06	4.3E-06	1.1E-03	2.1E-06	0.031%
46	6.4E-06	8.2E-04	2.1E-06	3.4E-06	5.6E-04	1.3E-06	0.034%
47	9.2E-06	6.5E-04	3.0E-06	2.1E-05	5.4E-04	1.5E-06	0.067%
48	1.1E-05	1.1E-03	2.1E-06	5.6E-06	1.1E-03	1.7E-06	0.052%
49	1.1E-05	1.0E-03	3.0E-06	6.4E-06	9.6E-04	1.7E-06	0.041%
50	9.4E-06	1.2E-03	3.4E-06	5.6E-06	7.2E-04	2.1E-06	0.026%
51	4.7E-06	7.1E-04	1.3E-06	3.4E-06	3.8E-04	8.6E-07	0.052%
52	3.4E-06	8.0E-04	1.7E-06	6.4E-06	2.4E-04	8.6E-07	0.042%
53	4.3E-06	1.9E-03	3.0E-06	3.9E-06	5.1E-04	8.6E-07	0.050%
54	4.7E-06	1.0E-03	3.0E-06	2.6E-06	4.5E-04	1.3E-06	0.059%
55	1.7E-05	4.2E-04	2.4E-06	1.6E-05	1.6E-03	8.0E-06	0.081%

[a] n.a., not analyzed; b.d., below detection limit

Table A.3. Filter blanks (µg per filter subsection[a]) and SRM recoveries.

	Na	Mg	Al	P	K	Ca
Filter Blank (Coarse)	1.1	0.028	0.47	0.069	0.074	0.31
Filter Blank (Fine)	2.6	0.086	0.47	0.26	0.46	0.85
SRM 2709	98%	98%	85%	111%	98%	108%
SRM 1649a		100%				

	Ti	V	Cr	Mn	Fe	Co
Filter Blank (Coarse)	0.021	0.00047	0.057	0.000033	0.50	b.d.
Filter Blank (Fine)	0.071	0.00012	0.062	0.0015	0.78	0.00023
SRM 2709	110%	103%	95%	85%	98%	93%
SRM 1649a		87%	82%	108%	97%	92%

	Ni	Cu	Zn	Rb	Sr	Zr
Filter Blank (Coarse)	0.0070	0.0014	0.022	b.d.	0.0016	0.0018
Filter Blank (Fine)	0.0078	0.0052	0.052	b.d.	0.0038	0.00098
SRM 2709	102%	96%	114%	118%	110%	100%
SRM 1649a	103%	97%	113%	107%		

	Mo	Cs	Ba	Hf	W	Pb	U
Filter Blank (Coarse)	0.00048	b.d.	0.028	0.00015	b.d.	0.0075	b.d.
Filter Blank (Fine)	0.0015	b.d.	0.11	0.000057	0.00012	0.016	0.00059
SRM 2709	89%	108%	107%	106%	98%	97%	95%
SRM 1649a	95%	114%	89%	110%	89%	118%	93%

[a] Coarse samples contained 10 subsections strips per filter. Fine samples were analyzed as 25 cm^2 subsections. Each full filter sheet contains 20.6 subsections.

APPENDIX B

BIOGEOCHEMISTRY CONCEPT LIST

The participants in the Delphi process were asked to rate each concept as "unimportant," "somewhat important," "important," or "essential" to understanding biogeochemistry. The following list is ordered by how important each concept was rated by the participants. However, nearly all of the concepts were highly rated. Only #28 had less than half "important" or "essential" ratings.

1. Greenhouse gases in the Earth's atmosphere absorb outgoing infrared radiation, ultimately warming the surface, which allows the presence of liquid water.
2. The Earth's atmosphere and ocean each have an influence over the chemical composition of the other.
3. The amount of CO_2 in the atmosphere is determined by interactions between water, rocks, and the biosphere over short and long time scales.
4. Human activities can significantly alter global biogeochemical cycles.
5. Global, thermally driven atmospheric circulation determines the temperature and amount of precipitation on most of the Earth's surface.
6. The properties of an element dissolved in water are determined by its speciation, which depends on a range of chemical variables including pH.
7. All life extracts chemical resources from its surroundings. The availability of these resources affects what types of life can live in a given environment.
8. Many chemical reactions at the Earth's surface are thermodynamically favorable, but kinetically very slow. Some of these reactions are readily performed by living organisms.
9. Over geologic time, there have been large changes to the conditions of the surface Earth as a result of both physical and biological forcing.
10. Soil is produced in situ by physical, chemical, and biological alteration of rock near the Earth's surface.
11. Many important Earth surface processes, such as weathering, are both biotic and abiotic.
12. The presence of free O_2 in the atmosphere is due to photosynthesis. The amount of O_2 is determined by a balance between respiration and long-term burial of reduced carbon.
13. All life takes advantage of redox chemistry for energy.
14. The ocean varies spatially and temporally as a result of ocean circulation and biological activity.
15. Elements have natural biogeochemical cycles, the specifics of which explain their occurrence and abundance in different environments.
16. The concentrations of dissolved elements in water affect the properties of the solution, e.g., density or buffering capacity.
17. Prokaryotes display a much greater range of metabolisms than multicellular life and can thus survive in a greater variety of geochemical environments.

18. The pH of many natural waters is determined by carbonate buffering.
19. Mineral surfaces can form electrostatic bonds with ions, which can affect ion concentrations in solutions in contact with these surfaces.
20. The surface Earth (that which is in contact with the atmosphere) is oxidizing while the subsurface (that which is not in contact with the atmosphere) is reducing.
21. Soils or sediments that are saturated with water will tend to become anoxic, because biological activity consumes O_2 much faster than it can be replaced by diffusion from the atmosphere.
22. Life on Earth is classified into three domains of life, Bacteria, Archaea, and Eukarya, based on genetic differences.
23. Important aspects of the Earth system are stabilized over long time periods by negative feedback loops.
24. The solubility of a mineral in water depends on the properties of the mineral and the water as well as temperature and pressure.
25. Organisms nearly always have essential chemical connections to other species living in their ecosystem, e.g., “waste” removal.
26. Surface waters and groundwaters can have very low or very high pH values even in non-polluted areas.
27. Most elements have two or more stable isotopes. Processes such as photosynthesis can create isotopic fractionation between different chemical pools.
28. Many organisms produce specialized organic compounds to alter the chemical conditions in their immediate vicinity, e.g., siderophores.

APPENDIX C

INTERVIEW PROTOCOL

Introduction

As you have read in the information letter, my name is Chris Mead and I am conducting research investigating what undergraduates think about a range of scientific topics related to the field of biogeochemistry. During this interview I will be asking you a series of questions and follow-up questions including topics you may not have thought about before. The purpose of these questions is to get your own personal understanding of these things, so take as much time as you need to think about them as you answer. In fact, the best thing you can do, from my perspective, is to say out loud what you're thinking if you're unsure about any of the questions. Finally, with your permission, I will be audio taping this interview, but I would like to stress that neither your name nor identifying information will be released at any time.

1. Warm up

a. Tell me what geology classes you've taken (or all science classes, if no geology).
b. What are some of the things you learned about in ______ (class most closely related to biogeochemistry)?

1. Grand Tour

a. The field of biogeochemistry studies how life interacts with, depends on, or changes the Earth in both chemical ways and in physical ways. Can you describe some examples of living things influencing the Earth (the ocean, the atmosphere, rocks, soil)?
b. And can you describe how living things are affected by their surroundings, both local and global?

2. Why is life important?

a. Tell me what Earth might be like if humans had never existed. How would it be different compared to now?
b. Imagine that plants and animals never existed on Earth. What would the planet be like today? How would it be the same and how would it be different? (What has life changed about the planet?)

3. Oxygen

a. Like us, all animals need oxygen, O_2, to breathe. There is clearly plenty of oxygen in this room, but can you think about different places on Earth and tell me where there probably *isn't* any oxygen to breathe?
b. Where does oxygen come from in the places where it is available?
c. Can anything live in places that don't have oxygen?
d. With all of these animals consuming oxygen, why haven't we run out of it?

4. Resources for life

a. Apart from water, your body is made up of carbon, nitrogen, oxygen, phosphorus, calcium, iron, and a dozen other elements. Talk me through where they all came from before they got into your body.
b. Where did the [plant/animal] get them from?
c. Tell me how that might work for a plant.

d. How do those elements get into the soil where plants grow?

5. The ocean
a. What are some specific chemical and physical ways that the oceans and the atmosphere influence each other?
b. What are some chemical and physical ways that the oceans and living things influence each other?
c. How might the Earth be different if we didn't have oceans at all? Assume that there is still some water, but much less so there aren't oceans.
d. Tell me what things about the ocean change over time (days, months, years, thousands of years) and what things are always the same.
e. What things about the ocean are different in different places and what things are the same?

6. Global temperatures
a. What things make the Earth the temperature it is, on a global level?
b. What makes a particular place on Earth the temperature it is?
c. What could make those change?

7. Demographic questions
a. What year in school are you?
b. What is your major?
c. Approximately how many college science classes have you taken?

APPENDIX D

BIOGEOCHEMISTRY CONCEPT INVENTORY

Complete Biogeochemistry Concept Inventory (correct answers in **bold**).

1. Which of the following is true about oxygen (O_2) and living things?
a. All living things need O_2 to survive.
b. Not all living things need O_2 to survive.
c. All living things can use O_2, but not all need to do so to survive.

2. Humans need oxygen, carbon, and nitrogen to live. Which of these are obtained directly from air?
a. Oxygen only.
b. Oxygen and carbon only.
c. Oxygen and nitrogen only.
d. Oxygen, carbon, and nitrogen.

3. The human body uses many different elements, such as sodium and iron. Which of the following is true about these elements?
a. Each of them is necessary to survive.
b. Some of them can be replaced by other elements.

4. All plants produce oxygen gas (O_2) through photosynthesis. Do plants use any of the oxygen that is produced?
a. No, plants do not require O_2.
b. Yes, plants require O_2.

5. Where do humans get the chemical energy they need to survive?
a. From chemical reactions between certain molecules in food, such as carbohydrates, and O_2.
b. From chemical reactions between vitamins in food, such as C or B_{12}, and O_2.
c. From chemical reactions between certain molecules in food, such as carbohydrates, and stomach acid.
d. From chemical reactions between vitamins in food, such as C or B_{12}, and stomach acid.

6. Which of the following is true about the way living things obtain energy to live?
a. All living things use chemical energy from redox (reduction/oxidation) reactions.
b. Not all living things use chemical energy to live.
c. All living things use chemical energy, but not all use energy from redox reactions.

7. What role do enzymes play in helping living things obtain energy?
a. Enzymes make certain chemical reactions thermodynamically favorable that would not be favorable otherwise.
b. Enzymes make certain chemical reactions occur faster than they would otherwise.
c. Enzymes do not play a role in the process of obtaining energy for living things.

8. Which of the following explains why the Earth has an atmosphere with 21% oxygen gas?

a. When the Earth's atmosphere was first formed it contained 21% oxygen gas.
b. The Earth's atmosphere originally contained about 1% oxygen gas. The rest of the oxygen was produced over time through photosynthesis.
c. The Earth's atmosphere did not originally contain any oxygen gas. All of the oxygen gas in the atmosphere today was produced over time through photosynthesis.
d. The Earth's atmosphere originally contained about 1% oxygen gas. The rest of the oxygen was released from rocks over time.
e. The Earth's atmosphere did not originally contain any oxygen gas. All of the oxygen gas in the atmosphere today was released from rocks over time.

9. How much oxygen gas was in the Earth's atmosphere when life first evolved?
a. About the same amount as we see today.
b. About twenty times less oxygen gas than we see today.
c. There was no oxygen gas in the atmosphere when life first evolved.

10. If all life on Earth suddenly went extinct, what would happen to the amount of oxygen in the atmosphere?
a. It would remain the same.
b. It would decrease slowly over time.
c. It would increase slowly over time.

11. How are deep sea organisms able to obtain the oxygen they need to survive?
a. Oxygen gas (O_2) is formed naturally by seawater, so there is oxygen even very deep in the ocean.
b. The oxygen they use comes directly from the H_2O molecule, so they do not require O_2.
c. Deep sea organisms use other elements instead of oxygen, such as sulfur.
d. They cannot live near the bottom of the ocean because there is no O_2.
e. There is O_2 even at the bottom of the ocean, because the seawater is mixed over time.

12. The Earth has a protective layer known as the ozone later that keeps out ultraviolet radiation. Which of the following is also true about that layer?
a. Pollution has made it thicker, and that is making the planet hotter.
b. Pollution has made it thinner, and that is making the planet hotter.
c. Pollution has made it thicker, but there is no connection with the Earth's temperature.
d. Pollution has made it thinner, but there is no connection with the Earth's temperature.

13. Which of the following is true about the greenhouse effect on Earth?
a. The greenhouse effect has always occurred on Earth, even during ice ages.
b. The greenhouse effect has not always occurred on Earth. It first started about 500 million years ago.
c. The greenhouse effect has not always occurred on Earth. It first started about 150 years ago.

d. The greenhouse effect has never occurred on Earth.

14. In which ways can rocks be weathered?
a. Rocks can only be weathered by physical processes, such as abrasion by wind or water.
b. In addition to physical weathering, certain types of rock, such as limestone, can be dissolved by water over time.
c. In addition to physical weathering, all types of rock can be dissolved by water over time.

15. How do plants affect the weathering of rocks?
a. Plants stabilize rocks, thus reducing weathering.
b. Over time, plant growth can break up rocks through physical weathering, but plants do not affect chemical weathering.
c. Plants release chemicals that cause chemical weathering of rocks (e.g., dissolution), but plants do not contribute to physical weathering.
d. Plants cause both physical and chemical weathering.
e. Plants do not affect the weathering of rocks.

16. Where did the majority of the salt in the ocean come from originally?
a. The oceans were salty from the time they first formed.
b. Weathering and erosion of salt deposits on land.
c. Weathering and erosion of all types of rock on land.
d. Weathering of the ocean floor.
e. Hydrothermal vents in the deep ocean.

17. Under what circumstances can carbon be found in rocks?
a. Carbon can only be found in rocks with fossils in them.
b. Carbon can be found in rocks even when fossils are not present.
c. Carbon is never found in rocks.

18. Is ocean water acidic, neutral, or basic?
a. Ocean water is moderately acidic.
b. Ocean water is slightly acidic.
c. Ocean water has a neutral pH.
d. Ocean water is slightly basic.

19. Is unpolluted rainwater acidic, neutral, or basic?
a. Rainwater is slightly acidic.
b. Rainwater has a neutral pH.
c. Rainwater is slightly basic.

20. What effect does carbon dioxide have on the pH of water?
a. Carbon dioxide makes water more acidic.
b. Carbon dioxide makes water more basic.
c. Carbon dioxide does not have an effect on the pH of water.

21. How much would the pH of the ocean have to change to harm ocean life?
a. It would have to change at least two pH units (e.g., from pH 7 to pH 5).
b. It would have to change at least one pH unit (e.g., from pH 7 to pH 8).
c. It would have to change only a few tenths of a pH unit (e.g., from pH 7 to pH 6.7).

22. In what way have human activities altered the way the surface Earth works?
a. Human activities have changed the way the Earth looks, but are not large enough to have changed how biological, chemical, or geological systems work.
b. Human activities are large enough to have changed how biological, chemical, or geological systems work.

23. What effect have human activities had on life in the ocean near land?
a. Human activities have caused some of the ocean near land to be uninhabited.
b. Human activities have caused most of the ocean near land to be uninhabited.
c. Human activities have had no effect on ocean life near land.

24. How would the Earth's average temperature be different if humans did not exist?
a. It would be warmer.
b. It would be the same.
c. It would be colder.

25. Which of the following is true about the effects human activities are having on the pH of the ocean and the health of ocean life?
a. Human activities are causing the ocean to become more acidic. This change is likely to harm some ocean life.
b. Human activities are causing the ocean to become more acidic. This change is unlikely to affect the health of ocean life.
c. The ocean is too large to be affected by human activities.

26. What could cause a lake or river to be strongly acidic (low pH)?
a. Only industrial/agricultural activities could be responsible.
b. Industrial/agricultural activities or natural causes could be responsible.
c. Only natural causes could be responsible.

27. Which areas of the ocean are the most densely inhabited by ocean life?
a. The areas far from continents.
b. The areas close to continents.
c. The warmer areas.
d. Life is evenly distributed throughout the ocean.

28. How much is ocean water mixed over time?
a. The surface water is mixed, but the deep water is not.
b. None of the ocean water is mixed.
c. All of the ocean water is mixed.

d. Water within each ocean (Atlantic, Pacific, etc.) is mixed, but not between oceans.

29. What chemical interactions occur between the ocean and the atmosphere?
a. The ocean influences the chemistry of the atmosphere, but the atmosphere does not influence the chemistry of the ocean.
b. The ocean and the atmosphere do not have any chemical interactions.
c. The atmosphere influences the chemistry of the ocean, but the ocean does not influence the chemistry of the atmosphere.
d. The ocean and the atmosphere both influence the chemistry of the other.

30. What effect do fungi and bacteria have on the decomposition organic matter (for example, dead trees)?
a. Organic matter cannot decompose without fungi or bacteria.
b. Organic matter decomposes very slowly without fungi or bacteria.
c. Organic matter decomposes at the same rate regardless of whether fungi or bacteria are present.

31. What elements have natural global cycles on Earth?
a. Only carbon has such a cycle.
b. Only carbon, nitrogen, and oxygen have such a cycle.
c. Only carbon, nitrogen, oxygen, sulfur, phosphorous, and hydrogen have such a cycle.
d. All elements have some kind of natural global cycle on Earth.

32. To what extent do living things depend on other species to survive?
a. Nearly all living things rely on other species to survive.
b. Plants and animals rely on each other, but microorganisms such as bacteria are self-sufficient.
c. Animals depend on plants for survival, but plants and microorganisms are self-sufficient.
d. Almost no living things rely on other species to survive.

APPENDIX E

COMPLETE LIST OF STUDENT MISCONCEPTIONS

Table E.1. Student Misconceptions and the Frequencies of their Observation.

Misconception	**Instances**
The atmosphere is letting more sunrays in, causing warming	1
The ozone hole is causing climate change	6
Climate change is caused by the Earth moving closer to the sun	1
Earth temperatures only change as a result of catastrophic events	1
Earth surface temperature is determined by heat escaping from the Earth's interior	11
Hot spots and other volcanism are important sources of heat to the ocean	1
Humans' primary greenhouse gas emissions are from breathing	1
Milankovitch cycles are the only way to change climate	1
Plants are a major source of greenhouse gases	1
Geologic processes do not affect CO_2	2
Ocean absorbing CO_2 causes warming	2
Glaciers melting is a cause (not an effect) of climate change	3
The atmosphere itself (not greenhouse gases) warms the planet	1
The greenhouse effect is caused by chemical reactions that trap heat	1
The greenhouse effect is a literal greenhouse	1
The greenhouse effect is caused by gas pressure rather than properties of specific gases	1
Greenhouse gases trap heat because of their density	1
O_2 is a greenhouse gas	1
CO_2 absorbs reflected light	1
The greenhouse effect is a local phenomenon	3
Current atmospheric CO_2 levels are the highest ever in Earth history	2
Global average ocean temperature has never been below 50°F in Earth history	1
Rises in atmospheric CO_2 have not happened in Earth history	3
The temperature of Earth has not changed through time	1
The temperature of the ocean has not changed through time	1
Sea level has not changed through time	1
O_2 in the ocean is primarily transported by diffusion	1
There is no O_2 in deep water because the pressure is too high	1
There is no O_2 in the deep ocean (or at deep-sea hydrothermal vents)	19
There is no O_2 in any water	2
There is continual decrease in O_2 concentration with depth in the ocean	2
O_2 settles out or dissipates from water over time	1
Fish get O_2 from the H_2O molecule itself (not dissolved O_2)	5
Ocean life does not need O_2	2
Deep-sea vents are a source of O_2	2
Abiotic O_2 production has sustained significant (> ~1%) O_2 at times in Earth history	1
O2 is present in upper crust/mantle	3
O2 was trapped under the Earth prior to its release by biology	1
Oxygen is stable as liquid oxygen at the ocean floor	1
Anaerobes are a globally important source of O_2 to the oceans	1
There would be a significant amount (> ~1%) of O_2 in the atmosphere without life	16
Cannot have life without O_2	6
Ocean pH is acidic	5
Acidic rainwater only occurs as a result of human activities	3
Rain water is "pure"	1
CO_2 does not react with ocean water	4
The ocean does not absorb CO_2	1

Ocean pH is not being impacted by atmospheric CO_2	1
Soil formation is an inevitable consequence of the rock cycle	3
Soil formation usually takes millions of years	2
Soil can only form from organic rich rocks	1
Soil is entirely inorganic	1
There is a layer of soil underneath the bedrock layer	1
Ocean life is substantially limited by trash	1
Ocean pH is affected by trash	1
The middle of the ocean is most densely populated because it's the furthest away from humans	1
Humans have dramatically decreased the O_2 in the atmosphere	2
Industrial emissions (non CO_2) cause heat waves	1
Humans can affect plate tectonics	1
Humans are making the ocean saltier	1
Earth would be completely stable without humans	4
Ocean temperature would not change through time without humans	1
The oceans would not change through time without humans	2
Ocean life is unchanging over time	1

Table E.2. Student Misconceptions Not Included in the Main Text and the Frequencies of their Observation.

Misconception[a]	**Instances**
Some fish use SO_2 for respiration	1
Tube worms are anaerobic	1
SO_3 can be oxidized for energy	1
Water evaporates into H_2 and O_2	1
The Earth would be warmer without an atmosphere	3
Earth cycles are all negative feedback loops	1
Humans have been on earth about 3000 years	1
Arsenic based life replaces O_2 with As	1
There could be fires on Earth without life	1
Organisms produce new species (short term)	1
There would be no atmosphere without life	1
Temperatures are always warmer in deserts than more humid environments	1
Land near the ocean is always cooler and more humid	2
Temperatures are always lower near the ocean	1
The ocean does not influence the atmosphere	1
Seasons are caused by the moon	1
Seasons are caused by the distance from the sun (not angle)	6
Seasons are related to interaction between the ocean and the atmosphere	1
CO_2 changes as a result of extinctions (driven by life)	1
Humans are altering the carbon composition of the earth by holding carbon in their bodies	1
Life has increased the amount of carbon on earth	1
Plants are creating carbon (creating matter)	1
There would be less CO_2 in atmosphere without life	1
CO_2 displaces O_2 in ocean water	1
O_2, CO_2, and N_2 bubble up from the ocean to supply the atmosphere	1
Respiration (from fish) is the primary source of CO_2 to the ocean	1
There is more organic carbon in the ocean than inorganic carbon	1

Climate change means milder winters and hotter summers everywhere	1
Climate change means we're running out of O_2	1
Deserts are necessarily getting drier (not at an equilibrium)	1
The ocean has progressively grown in volume over earth history	1
The oceans will eventually fill up with sediments	1
Tectonic plates float on the ocean	1
California is going to break off from North America	1
Colorado plateau rocks are all ocean sediments	1
Mountain ranges are where they are because of wind patterns	1
Humans can completely control / manage ecosystems	1
Non-human life intentionally manages (sustains) its local environment	1
There would be no resource competition without humans	1
Acid rain substantially lowers ocean pH	3
Life has not changed the atmosphere	1
The early Earth's atmosphere was toxic to all life	1
Life has significantly changed the N_2 concentration of the atmosphere	1
Humans gets the nitrogen they need from breathing	2
N is the most common element in a forest	1
Plants get appreciable fixed N from lightning and volcanoes	1
There is no O_2 in hot springs	1
Plants do not need trace metals	1
Sunlight is a "food source" for plants	2
Water is "food" chemically	1
Ocean plants get nutrients from ocean floor	2
The ocean would be unchanged without life	2
The deep ocean is sparsely inhabited due to pressure	1
The ocean would have less salt without life	1
The ocean would have more salt and organics without life	1
The shallow ocean has lots of nutrients because of life [reversed cause & effect]	1
The density of life in the ocean is determined by chlorophyll abundance [reversed cause & effect]	1
Ocean life more abundant in tropics than poles regardless of proximity to land	1
The most important organisms in the ocean are sharks, whales, and dolphins	1
Nothing can survive in ocean "dead zones"	1
Eutrophication is a non biological process where something is added to the water that consumes O_2 or impedes its use	1
Ocean plants do not produce O_2	1
The atmosphere is ~10% water	1
There could not be an atmosphere without water	1
Longitude in and of itself is a factor in local climate	1
The Earth's core is on fire	1
Cities influence the Earth's rotation	1
The biosphere is the same as the atmosphere [wrong word use?]	1
Calcium in the ocean comes from the atmosphere	1
Most or nearly all O_2 is produced on land	1
There is no O_2 underground because of pressure	1
Eutrophication primarily affects pH	2
Oxygen directly affects ocean pH	2

Ocean pH is unstable (ignores buffering)	1
The ocean bottom has a separate layer that acts like lakes and rivers	1
Ocean circulation is random	1
The oceans do not circulate	1
Ocean water rapidly loses heat, like at night	1
The oceans are connected to each other through ground water	1
The Pacific Ocean is a lot warmer than Atlantic	2
The Pacific Ocean is much calmer than Atlantic	1
Sea level rise is caused by rainfall	1
The atmosphere warms/cools the ocean, not the other way around	2
The ocean does not influence the atmosphere (temperature)	1
Ocean currents are influenced (short time scales) by plate movements	1
Scientists do not know the difference between global warming and global cooling	1
It is impossible to know what the early Earth would have been like	1
We don't know what's at the bottom of the ocean	1
Natural disasters more likely without life (life has a stabilizing effect)	3
The atmosphere has changed to allow life to occur	1
Evolution is goal directed	2

[a] Misconceptions are organized loosely by subject

APPENDIX F

STATEMENT OF PERMISSION FROM CO-AUTHORS

Co-authors on the previously published articles “Source Apportionment of Aerosol Iron in the Marine Environment Using Iron Isotope Analysis” and “Unique Hg Stable Isotope Signatures of Compact Fluorescent Lamp-Sourced Hg” have granted their permission for use of the articles in this dissertation. This list of co-authors includes: A. Anbar, B. Majestic, P. Herckes, J. Lyons, and T. Johnson.