

## Application of high-temperature fusion for analysis of major and trace elements in marine sediment trap samples

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### Abstract

Multielemental information is important for a broad range of ocean biogeochemical studies, yet the quantity of sample material available for analysis is often extremely limited. Here we describe a simple, rapid, and accurate method for multielemental analyses of oceanic sediment trap material. This method involves high-temperature fusion using a lithium metaborate flux for sample digestion and elemental quantification using high-resolution inductively coupled plasma mass spectrometry (HR-ICP-MS). Each analysis consumes only 1 to 2 mg of sample material yet enables simultaneous measurements of 18 elements (Mg, Al, Si, P, Ca, Sc, Ti, V, Mn, Fe, Co, Ni, Cu, Zn, Sr, Cd, Ba, and Pb) with accuracy of > 90% for most elements. The fusion method introduces minimal contamination when appropriate sample handling and procedural precautions are employed. Elemental quantification of samples prepared for ICP-MS analysis using fusion agrees well with those prepared using acid digestion. Additionally, the fusion method has several advantages over acid digestion. No highly toxic reagents like hydrofluoric acid are used. Refractory mineral dissolution is more complete. Si, Ca, and other trace elements can be analyzed without potential losses due to coprecipitation with CaF<sub>2</sub>. The simplicity and reproducibility of the procedure makes it especially suitable for routine, ongoing analyses of oceanic particulate materials.

### Introduction

Many elements play important roles in marine biogeochemical cycles (Elderfield 2003, Morel and Price 2003, Jickells et al. 2005). Phosphorus, along with C, N, and O, is a major component of organic material, whereas Ca, Si, Mg, and Sr are major components of the structural parts of marine organisms. About a dozen elements with atomic masses above 50 have known biological roles as cofactors in enzymes and structural elements in proteins (e.g., V, Mn, Fe, Co, Ni, Cu, Zn, Se, and Cd) and are believed to be essential micronutrients (Morel and Price 2003). Some elements (e.g., Cu, Zn, As, Cd, Hg, and Pb) are toxic to organisms in high concentrations and thus can adversely affect ocean productivity and marine life.

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The formation, flux, and destruction of particulate matter is a key part of the biogeochemical cycling of elements in the ocean (Elderfield 2003). The downward flux of particulate material through the water column carries with it elements incorporated into biogenic materials (e.g., Mg, P, Ca, Sr, and Ba), elements associated with lithogenic particles (e.g., Al, Si, Ti, and Fe), and transition elements and heavy metals (e.g., Cu, Zn, As, Cd, Hg, and Pb) that have been physically and/or chemically scavenged during the particle flux process. This removal of elements from the surface ocean is countered by replenishment via atmospheric deposition, river runoff, and the slow upward advection and diffusion of dissolved elements released during remineralization of organic matter. Even so, concentrations of essential micronutrient elements such as Fe, Co, and Zn in surface waters are strongly depleted in most surface waters. In addition to the intrinsic importance to marine biogeochemical cycles, the elemental composition of marine particles provides important information on phytoplankton productivity in the overlying surface ocean, atmospheric inputs, ocean circulation, and particle regeneration processes within the water column. Delineating the linkages between the composition of the deep-sea particle flux and the overlying ocean environment is also important for development of

chemical proxies for use in marine stratigraphic studies to assess past ocean environments and climate.

Since 1978, the Oceanic Flux Program (OFP) off Bermuda has measured particle flux in the deep Sargasso Sea and the relationship between flux variability and physical and biological processes in the overlying surface ocean (Deuser 1986, Conte et al. 2001, 2003, Jickells et al. 1990). This one-time series alone contains more than 1000 samples of flux material from 3 discrete depths (500, 1500, and 3200 m). This material contains a unique chemical record of temporal variability in upper ocean forcing, marine productivity, atmospheric inputs, and particle flux processes that can be extracted through detailed compositional analysis. Even so, only a small number of samples have been previously analyzed for their elemental composition (Jickells et al. 1984, T. M. Church, unpublished data).

The amount of OFP sample material available for analyses is extremely limited (sometimes less than 5 mg), as much of the sample material needs to be used for core analyses of bulk composition and retained for archival purposes. Hence, the overarching analytical goal of the OFP time series efforts has been to develop simple and routine methods that maximize the information generated from each analysis while minimizing sample consumption. The recent development of high-resolution inductively coupled plasma mass spectrometry (HR-ICP-MS) has enabled highly sensitive quantification of a large suite of elements in a single sample run. The objective of our efforts was to develop a simple, small-sample digestion method for sediment trap material for multielemental analysis by HR-ICP-MS.

Two basic digestion methods have been used for the dissolution of the geological samples that contain silicate minerals: mixed-acid digestion and high-temperature fusion using a flux. The principles and practices behind both types of digestion methods are described in detail by Potts (1995). The reactants in the mixed-acid digestion are strong acids such as  $\text{HNO}_3$ ,  $\text{HCl}_{(\text{aq})}$ , and  $\text{HF}_{(\text{aq})}$ . Oxidants such as  $\text{HClO}_{4(\text{aq})}$  and  $\text{H}_2\text{O}_{2(\text{aq})}$  are sometimes added to remove organic matter. Heat and/or pressure are applied using a microwave oven, a hot water-bath, or a hot plate to break the chemical bonds in the sample materials and to form soluble substances (e.g., Eggemann and Betzer 1976, Anderson et al. 1991). The necessity of using  $\text{HF}_{(\text{aq})}$  to dissolve silicate minerals creates several analytical problems. HF is highly toxic and its use requires great caution. In addition, HF reacts with Si in sample materials to form  $\text{SiF}_4$ , a highly volatile compound. To minimize the loss of Si, sample digestion must be performed in tightly sealed Teflon vials or bombs (Eggemann and Betzer 1976). Additionally, HF reacts with Ca in carbonate-rich samples to form insoluble  $\text{CaF}_2$ . To promote dissolution of fluoride salts as well as to make the residual solution less harmful to both instrument and operator, boric acid is used to bind excess HF to form tetrafluoroborate anion. However, these two positive effects of boric acid are offset by the introduction of a heavy matrix and contamination (Eggemann and Betzer 1976). The formation of  $\text{CaF}_2$

and coprecipitation of other elements is also a potential complication in the analysis of sediment trap and other carbonate-rich materials. Finally, mixed-acid procedures may not completely dissolve some refractory minerals (Anderson et al. 1991). High temperature/pressure systems are needed to attack the most refractory minerals (Potts 1995). A recent work by Pruseth et al. (2005) further pointed out problems of acid digestions for high Si and high Al samples.

Fusion at high temperature ( $\geq 1000^\circ\text{C}$ ) with lithium metaborate-type fluxes is an alternative preparation procedure for elemental analysis. Fusion has been used for a half-century to dissolve silicate minerals in soils, sediments, minerals, and rocks (Jeffery 1975, Johnson and Maxwell 1981). It produces a melt that cools to form a glass bead that can be nondestructively analyzed using X-ray fluorescence (XRF) analysis or dissolved in dilute acids for analyses using various types of spectrometric methods such as atomic absorption spectrometry (AAS), inductively coupled plasma atomic emission spectrometry (ICP-AES), and ICP-MS (Fleer and Bacon 1991, Murray et al. 2000). The fusion method is rapid and simple; platinum crucibles and a muffle furnace are the two main pieces of equipment required. Fusion completely dissolves refractory minerals such as zircon and titanite and does not suffer from the limitations of the acid digestion method previously described.

However, fusion may have potential drawbacks that need to be evaluated for small-sample analyses. Contamination can be introduced from flux impurities, platinum crucibles, and/or the semi-open reaction environment within the furnace. Finally, the introduction of the flux can create a complex plasma matrix and a solution with a high total solid content, which are undesirable for ICP-MS analyses.

Our objective was to evaluate whether fusion techniques could be adapted for routine, small-sample multielemental analysis of oceanic materials, specifically sediment trap samples. In this article, we show that fusion is a simple, clean, and rapid small-sample preparation procedure that allows simultaneous measurements of both major and trace elements in sediment-trap samples.

## Materials and procedures

*Standard reference material*—A marine sediment reference material having comparable composition to open-ocean particles is not yet commercially available. The one we used, PACS-2 from the National Research Council of Canada (NRCC), is the best available reference material in terms of composition and textural quality. PACS-2 was collected in the harbor of Esquimalt, BC, Canada, and has a particle size  $< 125 \mu\text{m}$  (NRCC). The certified values for PACS-2 were determined using at least two independent analytical methods. However, NRCC does not have certified concentrations for Si, Sc, and Ba. The Si concentration in PACS-2 was reported as an “information value” only, which is less reliable than the certified values due to insufficient measurements and/or suspected inhomogeneity (NRCC). Compositionally, PACS-2 has much

less biogenic carbonates and biogenic silicate than sediment trap material. For example, the Ca content of PACS-2 is roughly 2%; it is 28% in sediment trap material. Hence, in addition to PACS-2, selected sediment trap materials collected during the OFP program have been used for method evaluation and intercomparison.

**Cleaning procedures**—Labware was cleaned in a clean room (unclassified) using Certified A.C.S. Plus acids (Fisher Scientific). Polypropylene and low-density polyethylene bottles were soaked in a 1 M HCl bath for > 12 h. Teflon vials were heated in an acid bath of 8 M HNO<sub>3</sub> on a hot plate at ~50°C for ~4 h and then soaked for an additional 12 h at room temperature. Platinum crucibles and lids were ultrasonicated at 50°C for 1 h in individual Teflon vials containing concentrated HNO<sub>3</sub>. After acid-cleaning, the plastic ware and platinum ware were rinsed 3 times with 18 MΩ cm<sup>-1</sup> Milli-Q water (Millipore, MA, USA) and air-dried in a laminar-flow clean bench.

**Fusion procedure**—All sample preparation except fusion was conducted in a clean room. Sediment reference material or dried sediment trap sample stored in the storage vial (1 to 2 mg) was directly weighed into a 3-mL platinum crucible (95% Pt and 5% Au; Alfa Aesar Johnson Matthey, Ward Hill, MA, USA) using a Mettler AE163 analytical balance and a Teflon-coated spatula. The weighing uncertainty was ± 0.05 mg, approximately 5% of the sample mass. High-purity lithium metaborate flux (LiBO<sub>2</sub>; Johnson Matthey Spectroflux 100A) was added to the crucible to achieve a sample-to-flux mass ratio of approximately 1:2.5 (range 1:2 to 1:3). Sample and flux were hand-mixed using a Teflon-coated spatula to homogenize the material. The platinum crucible was covered and placed inside a 10-mL Coors porcelain crucible with lid. The porcelain outer crucible was then placed on a Coors porcelain desiccator plate. A number of samples (5 in our case) can be fused simultaneously depending on the number of platinum crucibles available.

Because porcelain is prone to shock from abrupt temperature change, we inserted the loaded plate into a 600°C muffle furnace (Fisher Scientific, Model 126) and then ramped the temperature up to 1000°C at a rate of ~4°C min<sup>-1</sup>. The temperature was held at 1000°C for 10 min to flux the sample. The heat was turned off, and the furnace was allowed to cool to < 400°C before the desiccator plate was retrieved and transferred into the clean room.

The clear sample beads formed after fusion were dissolved using dilute nitric acid (1 M, prepared from Optima of Fisher Scientific) and sonication. Briefly, the platinum crucible with sample bead was placed in a 15-mL Teflon vial containing approximately 2 mL Milli-Q water. The platinum crucible was filled with 2 mL of 1 M HNO<sub>3</sub> and ultrasonicated in a Milli-Q water bath at room temperature until the bead was dissolved (approximately 1 h). The 1 M HNO<sub>3</sub> sample solution was then transferred to a 30-mL polypropylene storage vial. This step was repeated twice using 2-mL aliquots of 1 M HNO<sub>3</sub> and a 10-min sonication. The platinum crucible was then rinsed 3

more times with 2 mL of 1 M HNO<sub>3</sub>. The combined sample and rinse solution (~12 mL) was diluted with 1 M HNO<sub>3</sub> to a final volume of 25 mL, yielding an ICP-MS-ready solution with a total (dissolved) solid content of approximately 0.02%. This total solid content is 10 times less than the recommended upper limit (0.1%–0.2%) for ICP-MS analyses.

**Acid digestion procedure**—Acid digestion of selected OFP sediment trap samples was performed in the lab of T. Church at the University of Delaware, and the samples were analyzed at the ICP-MS facility at Woods Hole Oceanographic Institution (WHOI). The digestion procedure was a modification of established procedures (Sedwick et al. 2005). For the OFP sample subset having large mass as well as particle size (9 to 15 mg, < 1 mm), 7 mL Qz-water (quartz water made by subboiling ultrapure water from Barnstead Nanopure Ultrapure Water System [Model D4741; Dubuque, IA, USA] in a liter-size quartz system manufactured by Quartz-Silice, France), 1.5 mL distilled HNO<sub>3</sub> (16 M), 1 mL distilled HCl (6 M), and 0.5 mL distilled HF (29 M) were added in a 15-mL open Teflon vial. The sample was then heated at 80 to 100°C for 10 to 12 h using a hot plate in a laminar-flow clean bench until the sample was nearly dry. Another aliquot of 5 mL Qz-water, 1 mL HNO<sub>3</sub> (16 M), 0.5 mL HCl (6 M), and 0.3 mL HF (29 M) was added. The sample was heated again on the hot plate for another 6 to 8 h until the sample was completely dry to remove HF. The dried sample was then dissolved in 30 mL of 1 M HNO<sub>3</sub> for ICP-MS analysis.

The SCIFF8/82 replicate sample subset (1 to 4 mg, < 37 μm) was digested in the same manner as above using smaller amounts of acids: 0.5 mL of 16 M HNO<sub>3</sub>, 0.3 mL of 6 M HCl, and 0.2 mL of 29 M HF were added to 5 mL Qz-water for the first digestion step, and 0.2 mL HNO<sub>3</sub>, 0.1 mL HCl, and 0.05 mL HF were added to 2 mL Qz-water for the second digestion step.

**ICP-MS analysis**—Two sets of (9) matrix-matched working standards were prepared for quantification. A stock multielement standard solution was prepared from commercially available standards of the individual elements (Specpure; Johnson Matthey). For samples and reference material prepared using fusion, we diluted the stock standard solution with a 1 M HNO<sub>3</sub> solution containing dissolved LiBO<sub>2</sub> flux. The flux concentration of the final standard solutions approximated the average flux concentration of the samples, i.e., 0.15 mg flux per milliliter solution. For samples prepared using acid digestion, a set of standard solutions was prepared in 1 M HNO<sub>3</sub> without flux.

Samples were analyzed using a Finnigan model Element 2 ICP-MS at WHOI under conditions similar to those recommended by the manufacturer. The Aridus nebulizer and a sapphire injector were used at a gas flow rate of 1.0 L min<sup>-1</sup>. Indium was used as the internal standard to normalize the signal intensity data for samples and standards. (Additional internal standards were not used due to difficulties of selecting suitable internal standards that are not an element of interest.) The sensitivity of In was ~5 × 10<sup>6</sup> counts per second (cps) per ng g<sup>-1</sup> for the low-resolution range (LR, R > 300) and ~2 × 10<sup>5</sup> cps per ng g<sup>-1</sup> for the medium-resolution range (MR, R > 4000).

**Table 1.** Average method detection limit ( $\text{ng g}^{-1}$ ), calculated as 3 standard deviations ( $3\sigma$ ) of low-concentration samples in different ICP-MS run days, and elemental concentrations ( $\mu\text{g g}^{-1}$ ) in the  $\text{LiBO}_2$  flux from the manufacturer ( $\text{LiBO}_2$  blank) and in the flux after undergoing the fusion process (fusion blank).

Element	Detection limit (DL), $\text{ng g}^{-1}$	$\text{LiBO}_2$ blank, $\mu\text{g g}^{-1}$	Fusion blank, $\mu\text{g g}^{-1}$	Sediment trap sample, $\mu\text{g g}^{-1}$	Blank contribution, %
<i>n</i>	15	5	15	314	
Mg	7	< DL	$3.7 \pm 0.6$	6090 (970-14,300)	0.2
Al	7	< DL	$10 \pm 3$	12,600 (440-24,500)	0.2
Si	210	$38 \pm 1$	$52 \pm 5$	97,000 (5000-216,000)	0.1
P	0.3	< DL	< DL	780 (90-9900)	< 0.0001
Ca	18	$86 \pm 3$	$162 \pm 43$	286,000 (44,000-504,000)	0.1
Sc	0.1	< DL	< DL	2.0 (0.1-3.9)	< 0.013
Ti	2	< DL	< DL	483 (17-1221)	< 0.001
V	0.03	$0.144 \pm 0.004$	$0.16 \pm 0.03$	26 (1-230)	2
Mn	0.2	< DL	$1.1 \pm 0.3$	937 (21-1822)	0.3
Fe	9	< DL	$22 \pm 3$	7800 (340-39,500)	0.7
Co	0.05	$0.12 \pm 0.01$	$0.49 \pm 0.09$	13 (1-30)	9
Ni	0.03	$0.05 \pm 0.01$	$0.52 \pm 0.08$	36 (3-425)	4
Cu	0.05	$1.6 \pm 0.1$	$1.6 \pm 0.1$	68 (6-4230)	6
Zn	0.07	$0.54 \pm 0.04$	$10 \pm 2$	110 (20-1660)	23
Sr	1.3	$5.3 \pm 0.3$	$4.8 \pm 0.9$	1760 (250-3720)	0.7
Cd	0.01	$0.027 \pm 0.002$	$0.15 \pm 0.01$	0.94 (0.02-25)	39
Ba	0.7	< DL	$0.9 \pm 0.1$	780 (37-1384)	0.3
Pb	0.04	$0.22 \pm 0.03$	$4.8 \pm 0.4$	79 (10-7043)	15

The uncertainty is 1 standard deviation of the mean ( $1\sigma_m$ ). The average concentration and its range of sediment trap material are listed in column 5. The blank contribution relative to the average concentration of sediment trap material is calculated assuming a sample-to-flux ratio of 1:2.5, i.e., column 4  $\times$  2.5/column 5.

$^{111}\text{Cd}$ ,  $^{114}\text{Cd}$ ,  $^{137}\text{Ba}$ ,  $^{206}\text{Pb}$ ,  $^{207}\text{Pb}$ , and  $^{208}\text{Pb}$  were analyzed in the low-resolution range with 20 scans.  $^{25}\text{Mg}$ ,  $^{27}\text{Al}$ ,  $^{28}\text{Si}$ ,  $^{29}\text{Si}$ ,  $^{31}\text{P}$ ,  $^{42}\text{Ca}$ ,  $^{44}\text{Ca}$ ,  $^{45}\text{Sc}$ ,  $^{47}\text{Ti}$ ,  $^{49}\text{Ti}$ ,  $^{51}\text{V}$ ,  $^{55}\text{Mn}$ ,  $^{56}\text{Fe}$ ,  $^{59}\text{Co}$ ,  $^{60}\text{Ni}$ ,  $^{63}\text{Cu}$ ,  $^{66}\text{Zn}$ , and  $^{88}\text{Sr}$  were analyzed in the medium-resolution range with 30 scans. The instrument sensitivities for the isotopes were  $^{25}\text{Mg}$  (6),  $^{27}\text{Al}$  (45),  $^{28}\text{Si}$  (15),  $^{29}\text{Si}$  (0.8),  $^{31}\text{P}$  (8),  $^{42}\text{Ca}$  (0.6),  $^{44}\text{Ca}$  (3),  $^{45}\text{Sc}$  (70),  $^{47}\text{Ti}$  (6),  $^{49}\text{Ti}$  (5),  $^{51}\text{V}$  (100),  $^{55}\text{Mn}$  (80),  $^{56}\text{Fe}$  (60),  $^{59}\text{Co}$  (70),  $^{60}\text{Ni}$  (20),  $^{63}\text{Cu}$  (30),  $^{66}\text{Zn}$  (8),  $^{88}\text{Sr}$  (90),  $^{111}\text{Cd}$  (200),  $^{114}\text{Cd}$  (470),  $^{137}\text{Ba}$  (390),  $^{206}\text{Pb}$  (800),  $^{207}\text{Pb}$  (670), and  $^{208}\text{Pb}$  (2000) in units of thousand cps per  $\text{ng g}^{-1}$ . The analytical uncertainty based on counting statistics of multiple scans was 2% to 10% for the elements.

The working standard curves were linear, with correlation coefficients of standard curves  $> 0.997$  for all isotopes. For Si, Ca, Ti, Cd, and Pb, the concentrations of the individual isotopes were averaged to compute the elemental concentration.

### Assessment

*Cleanliness of the fusion technique*—Because of the use of  $\text{LiBO}_2$  flux and platinum crucibles, and the exposure of the samples in the furnace environment during the fusion step, the procedure could potentially introduce contamination and

make small-sample analyses difficult. To assess potential contamination, we compared results from two sets of  $\text{LiBO}_2$  flux. In the first set (“ $\text{LiBO}_2$  blank”),  $\text{LiBO}_2$  was dissolved directly in 1 M  $\text{HNO}_3$ . Hence, the first set measures impurities in the  $\text{LiBO}_2$  flux only. For the second set (“fusion blank”),  $\text{LiBO}_2$  was treated in the same manner as if it were sediment trap material, i.e., it was subject to each sample preparation step including fusion. Thus, the second set measures additional impurities that were extracted from the platinum crucibles and/or introduced via the semi-open furnace environment. To determine the blanks, we analyzed 2 to 4 times more concentrated flux than the flux used for matrix-matching in the working standards (i.e., 0.015% flux in the final standard solutions).

The results indicate that for most elements, neither the  $\text{LiBO}_2$  flux nor the fusion procedure introduces significant amounts of contamination for quantification of typical elemental concentrations found in sediment trap material. Table 1 compares the mean method detection limits, calculated as 3 standard deviations of low concentration samples in different ICP-MS run days, and elemental concentrations in the 2 blank treatments. Blanks of P, Sc, and Ti in both the  $\text{LiBO}_2$  blank set and fusion blank set were below detection. The  $\text{LiBO}_2$  and fusion blanks of Ca, V, Cu, and Sr were comparable within the

**Table 2.** Ratio of elemental concentrations ( $\mu\text{g g}^{-1}$ ) determined using external standard curves versus standard additions.

	PACS-2	SCIFF8/82	OFF1/01-3
Mg	0.99 (14%)	1.06 (13%)	1.09 (15%)
Al	0.96 (15%)	0.90 (11%)	0.98 (17%)
Si	1.07 (16%)	0.99 (13%)	1.00 (18%)
P	0.81 (12%)*	0.85 (14%)*	0.91 (9%)*
Ca	0.97 (15%)	1.09 (15%)	1.07 (12%)
Sc	0.96 (12%)	0.79 (18%)*	1.16 (15%)*
Ti	1.00 (17%)	0.90 (14%)	0.95 (16%)
V	0.99 (14%)	0.97 (12%)	1.03 (15%)
Mn	1.00 (16%)	1.05 (13%)	1.00 (17%)
Fe	1.10 (17%)	1.07 (18%)	1.03 (17%)
Co	1.03 (14%)	0.98 (18%)	1.03 (20%)
Ni	0.99 (17%)	0.97 (17%)	0.97 (19%)
Cu	0.90 (17%)	0.93 (14%)	1.01 (17%)
Zn	0.94 (19%)	0.97 (13%)	0.94 (18%)
Sr	0.78 (19%)*	1.03 (15%)	1.00 (17%)
Cd	1.15 (8%)*	0.93 (13%)	1.03 (12%)
Ba	0.94 (11%)	1.06 (15%)	1.03 (12%)
Pb	0.95 (9%)	0.99 (12%)	0.89 (11%)

Results for the marine-sediment reference material (PACS2) and two OFF sediment trap samples (SCIFF8/82 with size < 37  $\mu\text{m}$  and OFF1/01-3 with size < 1 mm) from 3200 m depth are presented. Shown in parentheses are 2 relative standard deviations (2RSD) of the analytical uncertainties. The certified concentrations of PACS-2 are listed in Table 4. \*Values that deviated from unity within the uncertainty of  $2\sigma$ .

measurement uncertainty of 2 standard deviations. Fusion blanks for Mg, Al, Si, Mn, Fe, and Ba were higher than the  $\text{LiBO}_2$  blank, indicating introduction of some contamination. But even so, they were < 1% of the concentration observed in a typical sample and thus insignificant. However, fusion blanks of Co, Ni, Zn, Cd, and Pb were a factor of 4, 10, 20, 5, and 20, respectively, higher than the  $\text{LiBO}_2$  blanks. As discussed below, a primary source of this contamination is impurities leached from the (new) platinum crucibles during the flux step. The elements with fusion blanks > 1% include V (2%), Co (9%), Ni (4%), Cu (6%), Zn (23%), Cd (39%), and Pb (15%). Even so, the fusion blanks for these elements are rather reproducible and thus can be accurately subtracted.

We have observed that through repeated use, our crucible blanks for Cu, Zn, Cd, and Pb have decreased by 1 to 2 orders of magnitude before leveling off. Therefore, thorough crucible pre-cleaning and a dedicated clean furnace are particularly important for highest accuracy of Cu, Zn, Cd, and Pb measurements.

**Matrix effects**—To assess possible matrix effects arising from compositional difference between the external standard/flux solutions and the sample solutions, we independently quantified the marine sediment reference material PACS-2 and 2 sediment trap samples, SCIFF8/82 (3200 m depth, < 37  $\mu\text{m}$  size fraction) and OFF1/01-3 (3200 m, < 1 mm), using both external standards and standard additions (Table 2). For standard

**Table 3.** Phosphorus concentrations derived from standard additions and the ratios of the slopes of the external standard curves to corresponding standard addition curves for PACS-2 and three trap samples, SCIFF8/82, OFF1/01-3, and OFF5/01-3, on two ICP-MS run days.

Sample ID	P concentration, $\mu\text{g g}^{-1}$	Slope (external standard)/slope (standard addition)
PACS-2	1108	1.15
SCIFF8/82	684	1.10
OFF1/01-3	737	1.05
OFF5/01-3	725	1.14
Average	—	1.11

A universal correction factor (1.11) was derived for correction of matrix suppression.

additions, multielement working standards were prepared to spike the sample solutions. Six-point standard addition curves were constructed to determine the concentration.

The slopes of the standard addition curves were comparable to those of the external standard curves for all elements other than P, which is discussed below. For elements other than P, the concentrations determined using the external standard and standard addition methods overlapped within the uncertainty of 2 standard deviations except for Sc (SCIFF8/82 and OFF1/01-3), Sr (PACS-2), and Cd (PACS-2) (Table 2). The discrepancies for Sc and Cd are likely to be related to analytical uncertainties, as these elements are near the detection limits for our method. For Sr, its concentration in PACS-2 approaches the lower end of the working standards curve, which is optimized for the much higher concentrations present in sediment trap samples.

In summary, the agreement between the two quantification methods indicates that matrix effects due to the addition of the flux are adequately compensated for in the external standard solution. The fact that the two methods agreed for both PACS-2 and the two OFF samples of different particle size fractions further indicates that compositional differences do not induce analytical matrix effects.

In contrast, a suppression of the P signal intensity in the sample was indicated, as the slopes of the standard addition curves for P were consistently lower than those of the external standard curves (Table 3). Thus, P concentrations determined using external standards were systematically lower than those obtained from standard additions by 10% to 20% (Table 2). The matrix suppression effect of P might not have been adequately corrected for using In as the internal standard. P has high first ionization potential (10.486 eV) and thus is only ~30% ionized in the plasma. In contrast, In has low first ionization potential (5.786 eV) and is 100% ionized. Therefore the matrix may suppress P but not In, resulting in inappropriate internal standard for P. Although In has been used universally in many HR-ICP-MS methods due to the stable mass response curve, it may not work well for poor ionizers.

**Table 4.** Mean elemental concentrations for PACS-2, determined using fusion-ICP-MS analyses with external standard curves, versus the certified concentrations.

Element	Certified concentration, $\mu\text{g g}^{-1}$	Measured concentration, $\mu\text{g g}^{-1}$ ( $n = 13$ )	Ratio Measured/certified
Mg	14,700 (9%)	14,100 (6%)	0.96 (11%)
Al	66,200 (5%)	63,900 (5%)	0.97 (7%)
Si	280,000*	362,000 (9%)	1.29 (> 9%)
P	960 (4%)	1003 (8%) <sup>2</sup>	1.04 (9%)
Ca	19,600 (9%)	17,800 (10%)	0.91 (14%)
Sc	not reported	8 (14%)	—
Ti	4430 (7%)	3920 (4%)	0.88 (9%) <sup>‡</sup>
V	133 (4%)	126 (9%)	0.95 (10%)
Mn	440 (4%)	413 (5%)	0.94 (7%)
Fe	40,900 (1%)	39,300 (4%)	0.96 (4%)
Co	11.5 (3%)	9.4 (11%)	0.82 (12%) <sup>‡</sup>
Ni	39.5 (6%)	34.7 (22%)	0.88 (22%)
Cu	310 (4%)	326 (8%)	1.05 (9%)
Zn	364 (6%)	362 (8%)	0.99 (8%)
Sr	276 (11%)	220 (9%)	0.80 (14%) <sup>‡</sup>
Cd	2.11 (7%)	1.93 (3%)	0.91 (8%) <sup>‡</sup>
Ba	not reported	757 (7%)	—
Pb	183 (4%)	185 (15%)	1.01 (16%)

Uncertainties in parentheses are 2 relative standard deviations of the mean ( $2\text{RSD}_m$ ). \*The concentration of Si is reported as an “information value” only, which is less reliable than certified values due to insufficient measurements and/or inhomogeneity. †The concentration of P has been corrected for matrix suppression effects (see text). ‡Values that did not overlap within the uncertainty of  $2\sigma_m$ .

Further observation of four samples (PACS-2, SCIFF8/82, OFP1/01-3, and OFP5/01-3) undergoing standard additions revealed that the offsets of the four standard addition curves (from the external standard curves) are very similar, indicating that the signal suppression is not affected by differences in sample composition (Table 3). This allows a universal correction factor to be applied to the slope of the external standard curve. We used a correction factor of 1.11 (the average ratio of the slope of the external standard curves to the standard addition curves) to correct the P data. After applying this correction, the concentrations of P in PACS-2, SCIFF8/82, OFP1/01-3, and OFP5/01-3 were within 10% of those determined using the standard addition method.

**Accuracy and reproducibility of the fusion method**—To assess the accuracy and reproducibility of the fusion method, we analyzed 13 replicate aliquots of PACS-2. The samples, with a mass range of 1 to 5 mg, were prepared by fusion on different days and analyzed by HR-ICP-MS on 6 run days. The resulting concentration data compared to the published certified concentrations are presented in Table 4.

For Mg, Al, P, Ca, V, Mn, Fe, Ni, Cu, Zn, and Pb, the measured and certified concentrations were within 10% uncer-

tainty range; they were not significantly different within the uncertainty of 2 standard deviations of the mean (Table 4). For Ti, Co, Sr, and Cd, the fusion values were 10% to 20% lower than the certified values. As mentioned earlier, Sr and Cd measurements in PACS-2 are subject to large uncertainties. However, the slightly lower concentrations obtained using fusion for Ti and Co (88% and 82% of certified values, respectively) are not as easily explained.

Reproducibility of the fusion/ICP-MS methods was comparable to or better than that reported for PACS-2 for Mg, Al, Ca, Ti, Mn, Sr, and Cd (Table 4). For P, V, Fe, Co, Ni, Cu, Zn, and Pb, measurement variability was approximately 2 to 4 times higher than that reported for PACS-2. The higher variability of our data may possibly be attributed to the small sample mass we analyzed, which may have caused a higher-than-average level of material inhomogeneity. The uncertainties of the elemental concentrations in PACS-2 represent 95% confidence limits for measurements using 250 mg or more of sample material, whereas the fusion measurements are conducted using 1 to 5 mg of samples.

**Comparison of fusion with acid digestion**—Because acid digestion methods are most commonly used to prepare samples for ICP-MS, we next assessed how fusion results compare with those obtained using acid digestion for analyses of sediment trap materials.

In the first assessment, two sets of replicate subsamples from a single sediment trap sample (SCIFF 8/82, < 37  $\mu\text{m}$  size fraction) were processed independently using both fusion and acid digestion. The digestions were then analyzed at the ICP-MS facility at WHOI on the same run day. Eight aliquots (1 to 4 mg each) were processed using acid digestion, and 12 aliquots (1 to 2 mg each) were processed using fusion.

The results from both types of digestions are comparable for some elements but different for others (Table 5). For the acid digestion set, Si was below detection because it was volatilized in the form of  $\text{SiF}_4$  during the processes. Concentrations from the two methods are equivalent for Al, P, Sc, and Mn. For Mg, Sr, and Ba, the average concentrations from fusion are approximately 10% to 15% lower than those from the acid digestion, although this difference is statistically significant at the 1% significance level only for Mg and Sr. Conversely, for Ca, V, Fe, Co, Ni, Cu, Zn, Cd, and Pb, the means of the fusion data are 20% to 50% higher than those for the acid digestion data. This difference is significant at the 1% level for V, Fe, Co, and Cu. The concentration of Ti from fusion is 2 times higher than that from the acid digestion. One explanation for the elements with high “fusion” concentrations is that refractory minerals (e.g., titanite) are completely dissolved during fusion whereas they were only partially dissolved using the acid digestion. Coprecipitation of these elements with  $\text{CaF}_2$  during the acid digestion may result in similar effects. The lower “fusion” concentrations of Mg, Sr, and Ba, a group of elements that are associated with carbonates, need further investigation, as Ca behaved in the opposite way.

**Table 5.** Concentrations ( $\mu\text{g g}^{-1}$ ) from acid digestion and fusion for SCIFF8/82 with uncertainties of  $2\text{RSD}_m$  in parentheses.

Element	Acid digestion, $\mu\text{g g}^{-1}$ $n=8$	Fusion, $\mu\text{g g}^{-1}$ $n=12$	Ratio fusion/acid	<i>P</i> value	Jickells et al. (1984)
Mg	8780 (8%)	7700 (10%)	0.88 (13%)*	< 0.01	—
Al	18,400 (6%)	18,400 (13%)	1.00 (14%)	0.98	16200
Si	—	244,531 (7%)	—	—	—
P	649 (7%)	625 (11%)	0.96 (13%)	0.39	621
Ca	166,000 (7%) (7%)	187,000 (18%)	1.13 (19%)	0.12	—
Sc	3.4 (6%)	3.2 (11%)	0.94 (13%)	0.15	—
Ti	420 (8%)	905 (8%)	2.15 (11%)*	< 0.01	—
V	29 (6%)	37 (9%)	1.28 (11%)*	< 0.01	40
Mn	962 (9%)	964 (5%)	1.00 (10%)	0.95	1045
Fe	8190 (4%)	10,660 (5%)	1.30 (6%)*	< 0.01	8800
Co	7.83 (9%)	10.2 (15%)	1.30 (17%)*	< 0.01	—
Ni	50 (6%)	60 (17%)	1.20 (18%)*	0.02	47
Cu	60 (5%)	73 (6%)	1.22 (8%)*	< 0.01	88
Zn	80 (8%)	120 (32%)	1.50 (33%)*	0.01	141
Sr	1710 (9%)	1460 (10%)	0.85 (14%)*	< 0.01	—
Cd	0.58 (6%)	0.81 (33%)	1.40 (34%)*	0.03	—
Ba	820 (20%)	750 (6%)	0.91 (21%)	0.18	—
Pb	69 (9%)	91 (20%)	1.32 (22%)*	0.01	72

The ratios of the mean concentrations of the two methods are listed in column 4. The *P* values from the Student *t* tests for means are listed in column 5. Concentration data from previous analyses by Jickells et al. (1984) using various methods are listed in column 6. Note that Si was below detection in the acid-digested samples. Phosphorus has been corrected for signal suppression matrix effects (see text). \*Values that deviated from unity within the range of  $2\sigma_m$ .

Also shown in Table 5 are archived elemental concentration data from the analyses of Jickells et al. (1984) and Deuser et al. (1983). Jickells et al. (1984) used a one-acid (boiled concentrated  $\text{HNO}_3$ ) digestion method. Fe, Mn, and Zn were analyzed using flame AAS. V, Ni, Cu, Cd, and Pb were analyzed using graphite furnace AAS. Phosphorus was measured using UV-visible spectroscopy and the molybdenum blue method. Another undigested sample aliquot was analyzed for Al using instrumental neutron activation analysis (Deuser et al. 1983). The archived data are comparable to the new data here, indicating that results obtained using earlier analytical methods are in good agreement with the newer ICP-MS results.

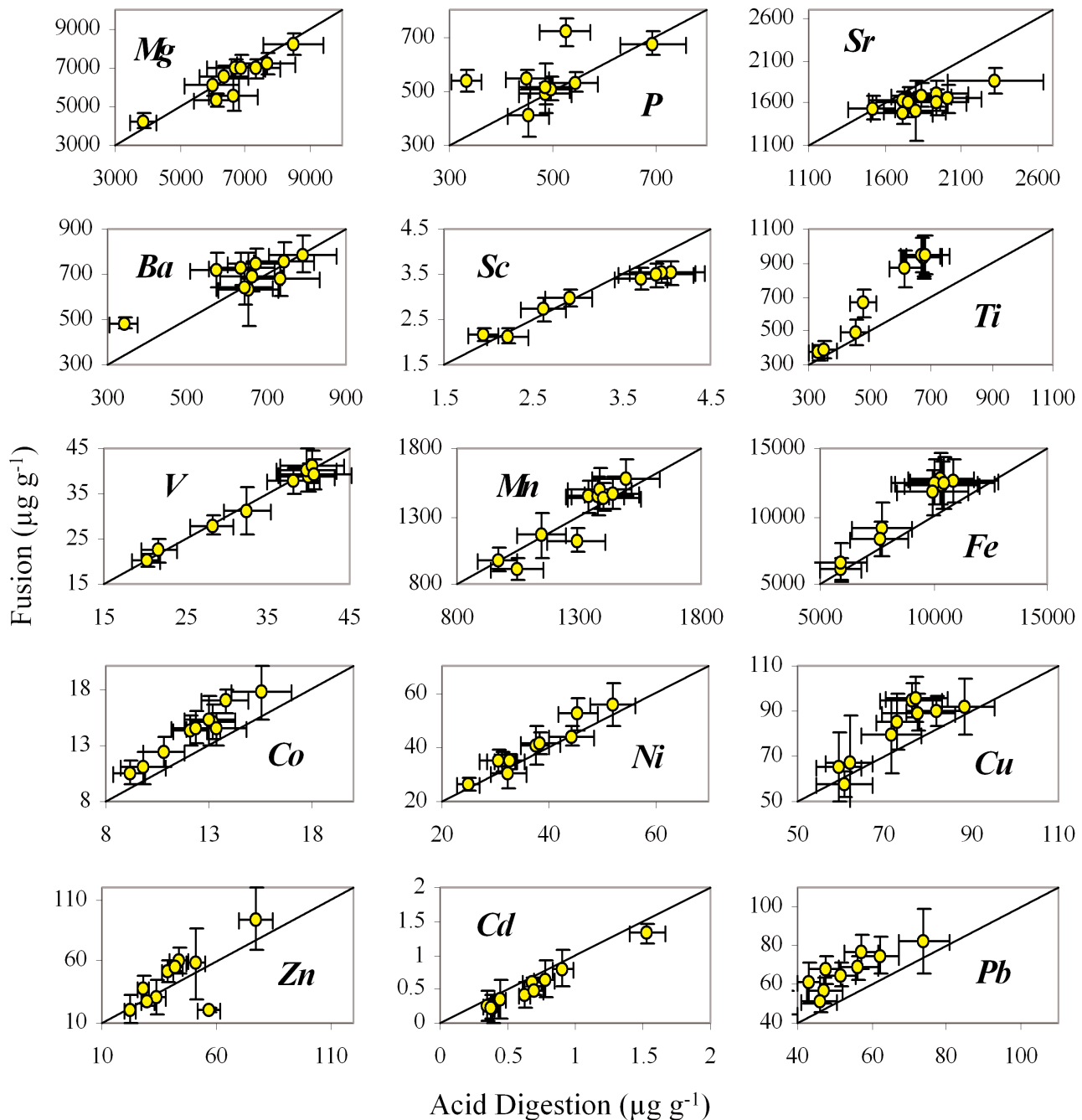
As a further method of intercomparison, we also analyzed 10 OFP samples (3200 m depth, < 1 mm particle size fraction) that were collected from 2000–01 and processed using trace metal clean methods (Conte et al. 2001). For this set, a 1/10 sample aliquot was shaken and divided coarsely into two fractions. The entire acid digestion fraction (9 to 15 mg dry weight) was processed after the supernatant was removed by rinsing and centrifuging. For the fusion aliquot, the sample was rinsed, centrifuged, and freeze-dried. Two 1- to 2-mg subsamples of the freeze-dried material were analyzed.

Initial inspection of the results indicated that the acid-digested portion contained significantly more carbonate, presumably because the larger carbonate particles had settled out before the fusion aliquot was poured out. Hence, it was neces-

sary to normalize the concentration data. For elements in the carbonate group (Mg, P, Sr, and Ba), we normalized the concentration data to Ca. For crustal elements, transition elements, and heavy metals (Sc, Ti, V, Mn, Fe, Co, Ni, Cu, Zn, Cd, and Pb), we normalized the data to Al. This normalization procedure has inherent errors because it depends on the accuracy of analyses of Ca and Al, it makes assumptions about what elements are associated with specific major phases, and it assumes that the phases containing these elements have comparable size and sinking velocities, and thus would be subject to similar biases when the samples were divided.

The scatterplots of the normalized concentration data from the two digestion methods suggest that the concentrations from both methods are generally similar (Figure 1). For individual samples, Mg, Sc, Ti, V, Mn, Fe, Co, Ni, Cu, Sr, Cd, and Pb in all 10 samples overlapped within the range of 2 standard deviations. For other elements, Zn and Ba were different, respectively, in one sample. P was different in two samples. Results of paired Student *t* tests for means show that the concentrations of Mg, P, Ba, Sc, V, Mn, and Zn are comparable at the 5% significance level (with *P* values of 0.26, 0.10, 0.08, 0.06, 0.65, 0.53, and 0.52, respectively). Ni has a *P* value of 0.01.

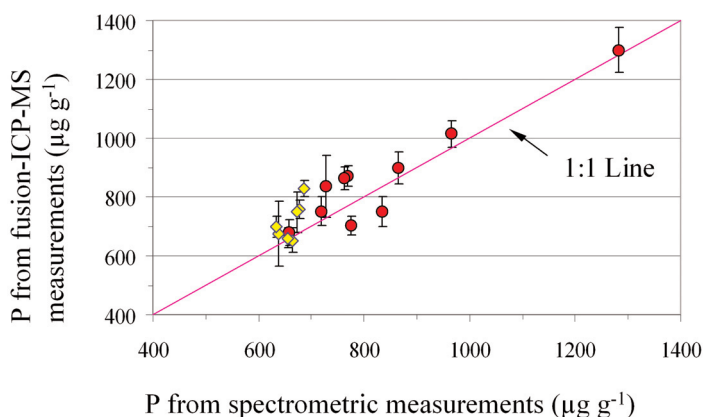
For elements that have concentrations different at the 1% significance level, Ti, Fe, Co, Cu, and Pb tended to have higher concentrations for fusion than for the acid digestion whereas Sr and Cd tended to be lower. Interestingly, the magnitudes of



**Fig. 1.** Concentrations from the acid digestion ( $x$ -axis) compared to those from fusion ( $y$ -axis) for 10 OFP samples from 3200 m depth. Data from the acid digestion have been normalized to correct for differences in carbonate content (see text). The error bars are  $1\sigma$  based on the counting statistics. P has been corrected for matrix effects (see text).

the concentration elevation of Ti, Fe, Co, Ni, Cu, and Pb are similar, to a certain extent, to those observed in the replicate analyses of SCIFF8/82 (Table 5). Therefore, it is likely that at least some of these offsets are due to incomplete (acid) digestion of certain refractory mineral phases (e.g., titanite) and/or coprecipitation with  $\text{CaF}_2$ . Additional concentration offsets may be attributed to our normalization procedure.

*Comparison of fusion with spectrophotometric analysis of phosphorus*—To intercompare the P concentration data with archived P concentrations, we analyzed 18 archived OFP samples from 500, 1500, and 3200 m depths ( $< 37 \mu\text{m}$  size fraction) that had been previously analyzed for soluble reactive phosphorus (SRP) using the spectrophotometric method of Solorzano and Sharp (1980). The archived data were analyzed



**Fig. 2.** P concentrations (corrected for matrix effects) in OFP samples quantified using fusion-ICP-MS analyses versus archived concentration data obtained using the Solorzano and Sharp (1980) spectrophotometric method. The diamonds are samples collected from 1980–84, and the circles are samples collected from 1985–89. The error bars are  $1\sigma$  of the fusion data.

at different times by different analysts. The samples we analyzed for this comparison were selected to roughly encompass the maximum P concentration range of the OFP sample set. A correction factor of 1.11 was applied to the raw fusion data to correct for the signal suppression (see above).

Figure 2 compares the P concentrations obtained using fusion/ICP-MS with the archived data. The fusion data agree well with the archived data. Assuming a 5% relative standard deviation for the SRP measurements, data from the fusion-ICP-MS measurements overlapped those from the spectrophotometric measurements within the uncertainty of 2 standard deviations except for one sample. Using paired Student *t* tests, no statistical difference is observed for the two datasets at the 1% significance level. This comparison indicates that P, when suitably corrected for ICP-MS signal suppression, can be accurately quantified using the fusion/ICP-MS method.

### Conclusions and recommendations

High-temperature fusion is a simple, rapid, accurate, precise, and clean method for small-sample preparation of multi-elemental analysis of oceanic materials by ICP-MS. Fusion completely dissolves resistant minerals (e.g., barite, titanite) that can be problematic using acid digestion. Fusion also allows quantification of Si and Ca without volatilization loss or precipitation, and minimizes losses of other elements due to coprecipitation.

Fusion can be used to process milligram quantities of sample material without introducing significant amounts of contaminants when appropriate precautions are taken. The main pieces of equipment required for the fusion procedure are platinum crucibles and a clean, dedicated furnace. Cleanliness of the furnace is equally important, as the samples are not sealed during the fusion process. Because platinum crucibles contain impurities—Pb and Cu are present in Au and

Ag ores—vigorous precleaning of crucibles (i.e., repeated fusion of flux followed by warm concentrated nitric acid soaking) is recommended before platinumware is used for small-sample processing.

The HR-ICP-MS analysis is relatively insensitive to matrix effects from the flux and to moderate variations in sample composition. Therefore, external standard curves can be used to accurately quantify elemental concentrations. An exception is P, which shows a consistent signal suppression matrix effect. However, the signal suppression effect can be accurately corrected for, allowing good quantification of P as well.

In conclusion, we recommend fusion for multi-elemental analysis of sediment trap and similar oceanic materials containing high biogenic Si and Ca content. The process is rapid, simple, and accurate yet allows both major and trace elements to be simultaneously quantified using only a few milligrams of sample material. This makes the method especially amenable for routine analyses.

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