Talanta 89 (2012) 195–200

Contents lists available at SciVerse ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Dissolution of fluoride complexes following microwave-assisted hydrofluoric acid digestion of marine sediments

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ARTICLE INFO

Article history:
Received 20 September 2011
Received in revised form
28 November 2011
Accepted 29 November 2011
Available online 14 December 2011

Keywords:
Microwave digestion
Insoluble fluorides
Hydrofluoric acid
Marine sediments

ABSTRACT

Microwave-assisted, hydrofluoric acid digestion is an increasingly common tool for the preparation of marine sediment samples for analysis by a variety of spectrometric techniques. Here we report that analysis of terrigenous-dominated sediment samples occasionally results in anomalously low values for several elements, including Al, Ba, Ca, Mg, and Sr. Measured concentrations of these elements increased with time between sample preparation and sample analysis, reaching stable values after 8–29 days. This lag is explained by the formation and subsequent dissolution of poorly soluble fluoride phases during digestion. Other elements, such as Fe, Mn, and Ti, showed little or no lag and were quickly measurable at a stable value. Full re-dissolution of the least soluble fluorides, which incorporate Al and Mg, requires up to four weeks at room temperature, and this duration can vary among sedimentary matrices. This waiting time can be reduced to 6 days (or shorter) if the samples are heated to ~60 °C for 24 h.

1. Introduction

Microwave-assisted digestion is an efficient and safe way to prepare solid samples for analysis of a wide range of elements that need to be introduced into an analyzer (e.g. ICP-MS) in the liquid phase. The method can be tailored to digest a variety of materials, including rocks and ores [1,2], soils [3,4], organic materials [5,6], and marine sediments [7]; the resulting solutions can be analyzed for a wide array of major and trace elements [6,8,9] and trace element isotopes [10]. Microwave digestion occurs in a sealed container at high temperature and pressure, and evaporation of acids can also be accomplished utilizing this tool. Isolation of the samples in this device greatly reduces the potential for user contact with dangerous acids.

Different materials and analytes may require different acid matrices for dissolution. For geologic samples it is generally necessary to include hydrofluoric acid (HF) for quantitative digestion, as this acid is one of the few capable of dissolving silicates [4,5,7]. With the use of inorganic acids, and in particular HF, comes the potential for the formation of other acid-insoluble phases. In the case of HF there is the possibility of production of relatively insoluble fluoride complexes with Al, Ca, Mg, and Fe during digestion [11]. X-ray diffraction analysis of these precipitates reveal a number of compounds, including one similar to the mineral ralstonite ($Na_{0.88}Mg_{0.88}Al_{1.12}(F,OH)_6{\cdot}H_2O$ [12]) and a number of Ca–Mg–Al fluorides such as AlF_3, $CaAlF_5$, MgF_2, and $CaMg_2Al_2F_{12}$ [2,13]. These compounds may also incorporate elements that form divalent cations, such as Ba and Sr [13], or trivalent cations such as the rare earth elements (REE) [2]. This behavior of Ca, Mg, and Al has led them to be classified as "insoluble fluoride forming elements," while other "fluorophile elements" (e.g. Ti) easily enter solution in the presence of HF [14].

Accurate measurement of any of the insoluble fluoride forming elements requires the re-dissolution of the fluoride precipitates. A common method to do this has been to repeatedly fume off fluorine in the presence of perchloric acid [12,13]. However, the use of perchloric acid leads to the potential formation of a TiO_2 precipitate [13], is not compatible with microwave digestion, presents a significant safety hazard, and requires the use of a specialized fume hood. Other investigators have used boric acid to complex excess HF and prevent fluoride formation [3]. Like the perchloric acid fuming, the loss of free HF likely leads to progressive redissolution of Ca–Mg–Al fluorides. However, addition of H_3BO_3 increases the total dissolved solids in the solution, potentially leading to higher background measurements during ICP-MS analysis [8]. Addition of Mg to the sample prior to digestion was shown to suppress formation of Al fluorides, allowing accurate measurements of the REEs [2], though these workers used perchloric acid to complete the digestion. For studies interested in measuring Mg contents of samples this may not be an appropriate method.

Here we document the effect of fluoride formation on the analysis of trace metals in marine sediments. We show that the impact

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doi:10.1016/j.talanta.2011.11.081

of fluoride formation is matrix-dependent, that the fluorides can be easily dissolved, and that the dissolution rate is temperature sensitive.

2. Methods

2.1. Equipment

Sediment samples were digested using a CEM MARS-5 microwave oven (CEM Corp., Matthews, NC) with a 12-position HP-1500 Plus vessel and rotor system. The vessels were composed of PFA plastic. Evaporation of acids after digestion was accomplished with the MicroVap accessory. After evaporation, samples were diluted into preweighed 30 mL HDPE bottles that had been cleaned for at least 24 h in 10% (v/v) reagent-grade HCl. Where diluted samples were heated, an analog block heater was used with anodized aluminum heating blocks pre-drilled with 35-mm drill holes (VWR International, item # 13259-252).

Samples were analyzed for Al, Ba, Ca, Fe, Mg, Mn, Sr, and Ti on a Leeman Labs Prodigy Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES); and for Cd, Mo, Re, U, and V on a VG Elemental Excel ICP-MS.

2.2. Reagents

Nitric acid (HNO_3) and HCl were produced by sub-boiling distillation of reagent grade acids. Hydrofluoric acid (HF, 47–51%) used was Omnitrace Ultra grade (EMD Chemicals). Water used in the digestion process was purified (>16 MΩ cm^{-1}) using a Milli-Q system (Millipore, USA).

Primary stock solutions used for analysis of digested samples were 1000 mg L^{-1} solutions obtained from EMD Chemicals, with the exception of Mo (Ultra Scientific). Most solutions consisted of a single element diluted in nitric acid, although some (e.g. Mo, Ti) were provided in different matrices. All secondary solutions used to create external calibration solutions were diluted from these primary solutions with 2% (v/v) HNO_3.

2.3. Standard materials

Accuracy was assessed by digestion of either MAG-1 (USGS) or PACS-2 (NRC-Canada). Precision was determined by repeatedly digesting a composite Chile Margin sediment (RR9702A-42MC, 2–17 cm, 36°10′S, 73°41′W, 1028 m; obtained from the Oregon State University Marine Geology Repository; corelab-www.coas.oregonstate.edu) that was freeze-dried and homogenized.

2.4. Digestion and evaporation

Each digestion run of twelve vessels included two that contained standard materials. Sediment samples (60 ± 2.5 mg) were weighed into a microwave vessel and bathed overnight in 2 ml concentrated HNO_3 and 1 ml concentrated HCl. The next day 2 ml concentrated HF and 3 ml water were added and the vessels were sealed. The digestion program consisted of a 10 min ramp from room temperature to 180 °C. This temperature was held constant for 40 min, and was followed by a 4 min ramp to 200 °C. This temperature was held constant for 20 min. Pressure was monitored throughout this process for safety.

The evaporation temperatures of the acids used are such that HF and HCl vaporize before HNO_3; therefore, we used three sequential evaporations in the microwave to remove halides from the matrix and retain the dissolved sample in nitric acid. After digestion the vessels were allowed to cool to room temperature, and were then opened. Digestion lids were rinsed with 1 ml concentrated HCl and 1 ml water, which was added to the digestion liquid. The vessels were fitted with evaporation lids, and evaporation of the acid was accomplished using the CEM MicroVap accessory. The liquid was heated with 600 W to a plateau temperature (see below), and the acid fumes were drawn out with a vacuum pump through a series of three bubblers containing (in sequence) 5% boric acid, 5% NaOH, and Milli-Q water before draining into a fume hood cup sink. The plateau temperature was maintained until the microwave software detected a decrease in temperature at the probe site, which indicated the level of the liquid had fallen below the temperature probe and the evaporation was complete. The first evaporation targeted a plateau temperature of 105 °C, and stopped the heating after a decrease of 20 °C. This step was followed by two additional evaporations in which 4 ml 50% (v/v) HNO_3 was added and then heated to a plateau of 110 °C, and stopped after a temperature decrease of 15 °C. Samples were then transferred to acid-cleaned HDPE bottles and diluted to ∼30 ml (∼500-fold dilution) with 12.5% (v/v) HNO_3. Samples in 12.5% (v/v) HNO_3 were stored at room temperature prior to analysis.

2.5. Analysis

Each sample was analyzed using both ICP-OES and ICP-MS. The elements of interest to our study occurred in the samples in a range of concentrations spanning eight orders of magnitude, and neither instrument alone is suitable for measuring all of these elements. Therefore the higher concentration elements (Al, Ba, Ca, Fe, Mg, Mn, Sr, Ti) were measured with ICP-OES, and trace elements (Cd, Mo, Re, U, V) were measured with ICP-MS.

2.6. ICP-OES

Samples were further diluted by a factor of five with 1% (w/v) HNO_3 prior to analysis by ICP-OES, for a total dilution factor of ∼2500. Sample concentrations were calibrated using a standard curve diluted by weight from a secondary solution mixed from 1000 $\mu g\ ml^{-1}$ primary solutions. Aluminum, Ba, Mn, Sr, and Ti were analyzed using axial view, while Ca, Fe, and Mg were analyzed in radial view. Instrumental drift was monitored by repeatedly analyzing the calibration standards over the course of a day's run. Drift was negligible even after 6 h of analysis time and no correction was necessary. We calculated the instrumental detection limit as the value at three standard deviations above the mean of all the day's runs of 1% (w/v) HNO_3. A typical detection limit was 5–10 ng ml^{-1} in solution for Al, Ca, and Fe; ∼1 ng ml^{-1} for Ti; less than 0.5 ng ml^{-1} for Mg and Mn; and less than 0.1 ng ml^{-1} for Ba and Sr.

2.7. ICP-MS

Samples were further diluted by a factor of four with 1% (w/v) HNO_3 just before analysis. All samples, standards, and blanks were spiked with 0.1 ml of an internal standard solution containing Be, In, and Bi (concentrations ∼250 ng ml^{-1} Be and ∼50 ng ml^{-1} In and Bi). These elements were monitored at mass 9 (Be), 115 (In), and 209 (Bi) to account for instrumental drift. The total sample dilution factor was ∼2050. Sample concentrations were calibrated using a standard curve diluted by weight from secondary solutions of 1000 $\mu g\ ml^{-1}$ primary solutions described in Methods. Vanadium, Mo, and Cd (mass 51, 98, and 111 respectively) were corrected for instrumental drift using a weighted average of ^{9}Be and ^{115}In; Rhenium (mass 185) was corrected using a weighted average of ^{115}In and ^{209}Bi; and U (mass 238) was corrected using ^{209}Bi. We calculated the instrumental detection limit in the same way as for ICP-OES analysis. A typical detection limit was 10–50 pg ml^{-1} in solution for V, Mo, and Cd; and less than 1 pg ml^{-1} for Re and U.

Table 1
Time in days before stabilization in the three standard sediments measured in this study.

	Stabilization time (days)[a]		
Element	RR9702A-42MC	MAG-1	PACS-2
Al	29	85	28
Ba	14	85	–
Ca	12	8	–
Fe	15	85	–
Mg	29	85	13
Mn	15	11	–
Sr	12	16	–
U	–	25	–
Cd, Mo, Re, Ti, V	–	–	–

[a] Determined by the *F*-statistic (see text).

3. Results and discussion

For this work we are presenting the results from repeated digestions ($n = 23–48$) of the sediment standards as well as repeated analysis of the solutions ($n = 24–103$) over the course of 1 to >1000 days. To compare results across elements and between sediments we normalized the data by dividing the measured value by the stable value. We determined this stable value by calculating the *F*-statistic stepwise, comparing all of the data run before a number of days had passed with all of the data run after that time. Where the *p*-value associated with that *F*-statistic was a minimum, the difference between the variances of these two groups was at its maximum. This procedure located the time of a change in slope from drifting to stable values. To eliminate the possibility that this difference could arise from scatter in the data, we compared the means of the two groups with a *t*-test. Values that pass these two tests ($p < 0.05$ for both cases) are reported in Table 1. The stable values and uncertainty for the elemental analyses are reported in Table 2.

For all three sediments, the elements that took the longest to enter into solution from their fluoride phase were Al and Mg (Fig. 1a–c). This agrees with the observations that these elements occur together as poorly-soluble $MgAlF_5{\cdot}xH_2O$ [11] and in ralstonite [12]. Calcium and Sr re-dissolved more quickly (generally less than two weeks, Fig. 1d–f). Barium (not shown) displayed similar behavior to these two elements, which suggests that Ba and Sr substituted into Ca-fluorides (e.g. [13]). Iron and Mn both re-dissolved after about two weeks, and neither element was particularly low in concentration relative to its stable value from the outset of the measurement (e.g. ∼80–90% for Mn and ∼83–93% for Fe), suggesting limited substitution into fluoride precipitates (Fig. 1g–i). Titanium and V showed no evidence of precipitation as a fluoride in any of the sediments (Fig. 1j–l). Because of their low concentrations, Cd, Mo, Re, and U data were too variable to accurately determine whether these elements are significantly influenced by incorporation into fluoride phases, though the data from MAG-1 suggests that U may have been incorporated into the precipitates (not shown).

3.1. *Differences between sediment matrices*

Our data suggest that formation of insoluble fluorides occurs when sediments are digested using hydrofluoric acid, even in a microwave (Fig. 1). However, there are differences in the behaviors of elements between the three sediment standards investigated. Initial values of most fluoride-forming elements are much lower relative to their stable value in RR9702A-42MC than in MAG-1 and PACS-2. This observation cannot be explained simply by differences in elemental concentrations among the sediments. For example, RR9702A-42MC has ∼2.8 times as much Ca as MAG-1, and initial

Table 2
A comparison of stable values to values after post-dilution heating, and to certified values.

Element	Al		Ba		Ca		Cd		Fe		Mg		Mn		Mo		Re		Sr		Ti		U		V	
	wt%	±	μg g^{-1}	±	wt%	±	μg g^{-1}	±	wt%	±	wt%	±	μg g^{-1}	±	μg g^{-1}	±	ng g^{-1}	±	μg g^{-1}	±	wt%	±	μg g^{-1}	±	μg g^{-1}	±
RR9702A-42MC																										
Stable value [a]	8.50	0.42	439	26	2.82	0.12	0.501	0.142	4.89	0.20	1.54	0.10	545	22	1.82	0.38	14.8	4.4	333	16	0.505	0.022	3.41	0.62	131	12
Value after heating[b]	8.31	0.27	406	13	2.76	0.15	0.500	0.038	4.74	0.15	1.43	0.07	519	15	1.73	0.10	17.0	1.7	318	10	0.484	0.014	4.04	0.55	123	6
MAG-1																										
Stable value[a]	8.74	0.20	523	18	1.07	0.04	0.262	0.096	5.10	0.10	1.90	0.06	794	30	1.18	0.46	5.5	2.0	154	10	0.452	0.018	2.82	0.22	142	14
Certified value[c]	8.68	0.32	480	82	0.98	0.14	0.20	0.06	4.76	0.84	1.81	0.12	760	140	1.17		–		150	30	0.450	0.084	2.7	0.6	140	
PACS-2																										
Stable value[a]	6.51	0.20	942	88	2.07	0.12	2.18	0.34	4.20	0.20	1.48	0.06	461	22	5.26	0.70	6.9	2.6	293	36	0.451	0.018	2.64	0.50	140	12
Value after heating[b]	6.42	0.15	932	37	2.03	0.09	1.90	0.19	4.09	0.12	1.41	0.06	435	12	5.00	1.08	7.1	0.9	280	8	0.432	0.012	2.98	0.40	131	8
Certified value[d]	6.62	0.32	–		1.96	0.18	2.11	0.16	4.09	0.06	1.47	0.14	440	20	5.43	0.56	–		276	30	0.443	0.032	(3)[e]		133	6

[a] The "stable value" is the mean and 95% confidence limit from measurements taken after the number of days had passed as reported in Table 1.

[b] The "value after heating" is the mean and 95% confidence limit from measurements of samples that were heated for ≥24 h in 12.5% HNO_3 after digestion.

[c] MAG-1 certified values with 95% confidence limits are from the USGS (http://minerals.cr.usgs.gov/geo_chem_stand/marine.html) with the exception of Mo, which is from [16].

[d] PACS-2 certified values with 95% confidence limits are from National Research Council Canada (http://www.nrc-cnrc.gc.ca/index.html).

[e] Uranium value for PACS-2 is provided as an information value only.

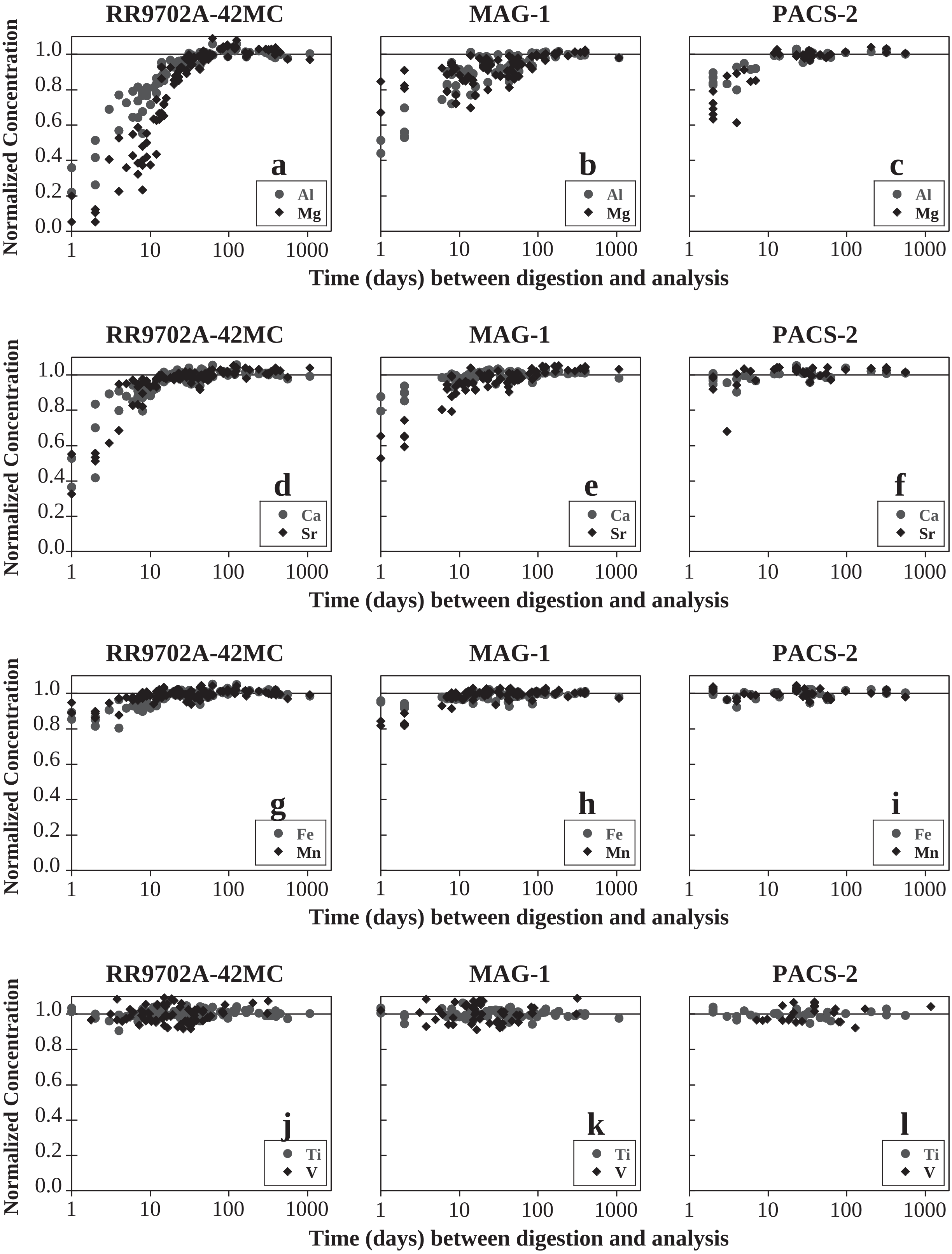

Fig. 1. Normalized elemental concentration vs. time without post-microwave heating.

recovery of Ca is greater for MAG-1. In contrast, MAG-1 contains more Mg than RR9702A-42MC, but recovery of Mg is initially ~80% for MAG-1 and <10% for RR9702A-42MC. The time required for re-dissolution also appears to vary between sediment standards. While stable values for Al and Mg are reached after approximately four weeks in RR9702A-42MC and PACS-2, it may take up to three months for concentrations of these elements to stabilize in MAG-1 digests.

Relative concentrations of Ca, Mg, and Al in a sample may play a role in the fluoride phases that form during digestion [2]. We

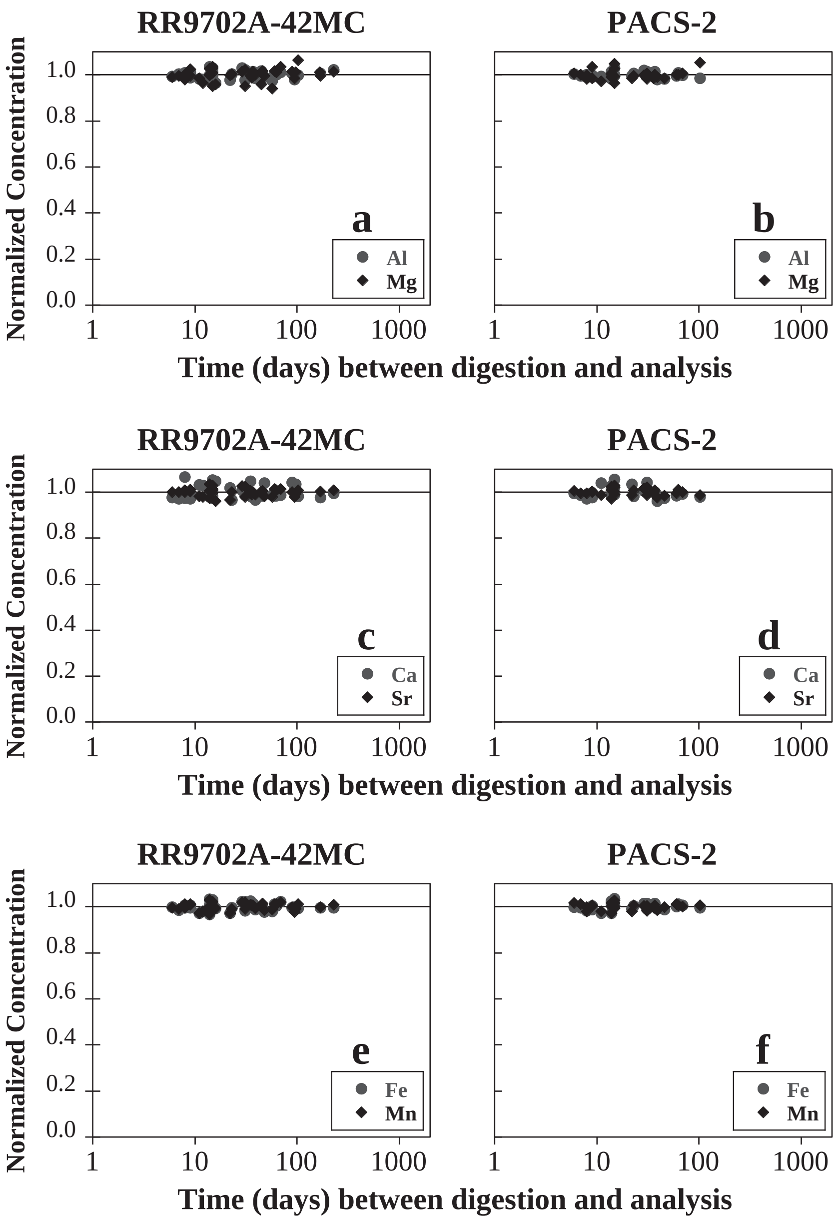

Fig. 2. Normalized elemental concentration vs. time with post-microwave heating (≥24 h at ∼60 °C in 12.5% HNO_3).

find that MAG-1, with the greatest amount of Al relative to Ca and Mg out of the three sediments in this study, seems to form digests with the most refractory Al fluorides. However, we do not have enough information to quantitatively assess the influence of this factor in this study. Other workers have studied the relationship between material properties and elemental recoveries in soils after microwave digestion [3], but again such an analysis is outside the scope of this report. Although the cause of differential recoveries is unknown to us, we have identified a straightforward and matrix-independent solution to the problem of formation of a precipitate.

3.2. *Redissolution of fluorides*

The insoluble fluorides formed during microwave-assisted hydrofluoric acid sediment digestions dissolve slowly over time at room temperature in 12.5% (v/v) HNO_3 (Fig. 1a–i). The time to reach complete dissolution differs between elements (Table 1). We previously [15] settled on a waiting period of four weeks, because the composition of our sediments was essentially the same as that of RR9702A-42MC, and accurate Al data was important to our study.

In samples digested for a separate study, we experimented with heating the digestions after dilution in HDPE bottles. The samples were digested using the same method described in Methods. Once diluted to 30 mL with 12.5% (v/v) HNO_3 in bottles, we added heat using an anodized aluminum heating block with 35 mm drill holes. In addition to the unknown samples processed in this way we also included RR9702A-42MC ($n = 31$), PACS-2 ($n = 27$), and MAG-1 ($n = 2$).

Twenty-four hours at ∼60 °C in these blocks produces precise data for each of the insoluble-fluoride-forming elements within six days after digestion in RR9702A-42MC (Fig. 2a–c) and PACS-2 (Fig. 2d–f), and for PACS-2 the measured values closely match certified values (Table 2). The small number of MAG-1 replicates prevents us from assessing the effect of heating after the digestion process on this standard. However, we note that our two replicates of MAG-1 suggest this procedure works for this sediment as well. The diluted samples were weighed before they were put in the heating block and again after they had cooled to room temperature post-heating, and mass lost was <1% in almost all cases. Because the loss of mass is small, it cannot account for the higher concentrations of elements in heated samples compared to unheated ones as a result of evaporation of solution. Reprecipitation of fluorides after heating is not evident in our data (Fig. 2). Therefore we conclude that this treatment is sufficient to redissolve fluorides and stabilize elemental concentrations in 12.5% (v/v) HNO_3.

This procedure allows for full recoveries of fluoride-forming elements while avoiding both the hazards associated with the use of perchloric acid and the high analytical background measurements caused by boric acid addition. The waiting time between digestion and analysis is reduced by at least 80% for the most refractory elements, restoring the efficiency provided by microwave-assisted digestion.

Acknowledgements

This research was financially supported by the National Science Foundation (OCE-0526278 and OCE-0753487). Additional support was provided by the Gordon & Betty Moore Foundation. We thank our anonymous reviewers, whose comments improved the quality of the paper. Any opinion, finding, and conclusions or recommendations expressed in this material are those of the authors and do not necessarily reflect the views of the National Science Foundation.

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