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Data report: long-term storage of cuttings for geochemical research[1]

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Chapter contents

Abstract

In this paper, we present the chemical compositions of cuttings samples from Integrated Ocean Drilling Program (IODP) Expedition 319 Site C0009 to assess the influence of long-term storage of cuttings. The cuttings were washed and analyzed just after their recovery, 6 months later, and 33 months later. The analytical elements are Al, Ca, Fe, K, Mg, Na, Ba, Mn, Sr, Zn, Li, and Cr. This report presents the analytical results.

Introduction

At Site C0009 of Integrated Ocean Drilling Program (IODP) Expedition 319 (NanTroSEIZE Stage 2: riser/riserless observatory), riser technology was used for the first time during an IODP drilling operation (see the **"Expedition 319 summary"** chapter [Expedition 319 Scientists, 2010a]). Drilling at Site C0009 provided in situ data for pore pressure, permeability, minimum principal stress magnitude, and real-time mud gas analyses. On the D/V *Chikyu*, cuttings obtained during riser drilling were carried by drilling mud from the seafloor into the mud tank, and cuttings were sampled at 5 m depth intervals. The drilling mud used for riser coring, which is a mixture of seawater, clay minerals (e.g., bentonite), polymers, alkaline solutions (e.g., sodium hydroxide), and organic compounds, can affect the results of subsequent analyses. Cuttings must therefore be carefully cleaned before analysis. Clean-up procedures before shipboard analysis were developed during preexpedition trials and are described in the **"Methods"** chapter (Expedition 319 Scientists, 2010b). Cuttings were recovered throughout the riser-drilled depth range (~700–1600 meters below seafloor [mbsf]) and were washed and analyzed shipboard (e.g., X-ray diffraction, X-ray fluorescence [XRF], and total carbon and nitrogen analysis) as described in the **"Expedition 319 summary"** chapter (Expedition 319 Scientists, 2010a). Aliquots for these samples were stored immersed in drilling mud at 4°C at the Kochi Core Center, an IODP core repository. Interaction of the cuttings with the drilling mud during storage might cause, for example, chemical and physical degradation of cuttings with time.

Here we report the results of our study on temporal variations in the chemical composition of cuttings during 33 months of storage in drilling mud.

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[1] Noguchi, T., and Okamura, K., 2014. Data report: long-term storage of cuttings for geochemical research. *In* Saffer, D., McNeill, L., Byrne, T., Araki, E., Toczko, S., Eguchi, N., Takahashi, K., and the Expedition 319 Scientists, *Proc. IODP,* 319: Tokyo (Integrated Ocean Drilling Program Management International, Inc.).
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Methods and materials

Hole C0009A was spudded on 19 May 2009 at 33°27.4704′N, 136°32.1489′E. We collected three cuttings samples (Fig. **F1**) from lithologic Unit IV (1287.7–1603.7 mbsf), which is composed mainly of silty claystone with minor silt interbeds, as described in the **"Site C0009"** chapter (Expedition 319 Scientists, 2010c). Samples 319-C0009A-130-SMW, 193-SMW, and 213-SMW were collected from 1305.2, 1592.2, and 1595.2 mbsf, respectively. Each of these samples was stored immersed in drilling mud in a polyethylene bottle (~500 cm^3) in a shipboard refrigerator at 4°C and later archived at the Kochi Core Center under the same storage conditions. We removed 45 cm^3 samples from the original bottles on the day of collection and then 6 months and 33 months later. We followed sample treatment procedures described in the **"Methods"** chapter (Expedition 319 Scientists, 2010b). The procedure can be briefly described as follows. Cuttings and mud were gently washed in freshwater and then sieved to obtain three size fractions (>4, 1–4, and 0.25–1 mm). During sieving, a magnet was used to remove iron contaminants from drilling tools and casing. We used only the 1–4 mm fraction for geochemical analysis. The >4 and 0.25–1 mm fractions were excluded to avoid contamination by particles that may have traveled downward through the mud column from shallower in the drilled sequence: coarse particles (>4 mm) may have been fragments of boulders encountered higher in the drilled sequence, and fine particles (0.25–1 mm) may have been transported downward by mud circulation.

The 1–4 mm fraction was washed 10 times with deionized water and then soaked in deionized water for 12 h. Washed cuttings were then dried for 24 h in an oven at a constant temperature of 40°C. The dried cuttings were powdered and homogenized with an agate mortar and then stored in clean polyethylene vials. Approximately 50 mg of powdered sample was sequentially digested in nitric acid, perchloric acid, and hydrofluoric acid (Fig. **F2**) using a closed digestion procedure modified from that of Totland et al. (1992). Commercially available high-purity acids (TAMAPURE-AA-100 grade; Tama Chemicals Co. Ltd., Tokyo) and ultrapure water (18.2 MΩ·cm; Millipore) were used for sample preparation. Major and minor element concentrations (Al, Ba, Ca, Cr, Fe, K, Li, Mg, Mn, Na, Sr, and Zn) were determined by inductively coupled plasma–atomic emission spectroscopy (ICP-AES) (Perkin Elmer Optima 4300 at Kochi University; HORIBA Jobin Yvon Ultima 2 aboard the *Chikyu*). ICP-AES conditions are summarized in Table **T1.** Element concentrations were quantified by calibration curve fitting using a standard solution prepared by dilution of ICP multielement standard Solution IV (Merck, Darmstadt, Germany) with 1% nitric acid. Recovery ratios from sample digestion (average of three runs) for each element were obtained by using geological standard materials JA-3 and JMS-1 supplied by the National Institute of Advanced Industrial Science and Technology of Japan (Table **T2**).

Results

Table **T3** shows the results of chemical analyses of Samples 319-C0009A-130-SMW, 193-SMW, and 213-SMW obtained aboard the *Chikyu* by XRF and those obtained by ICP-AES during storage on shore. Analyses of the three samples during storage showed concentrations of 5.7–7.1 wt% for Al, 2.4–4.9 wt% for Ca, 2.3–3.3 wt% for Fe, 1.7–2.3 wt% for K, 0.8–1.2 wt% for Mg, 0.8–1.1 wt% for Na, 320–420 ppm for Ba, 22–37 ppm for Cr, 47–62 ppm for Li, 240–350 ppm for Mn, 140–260 ppm for Sr, and 60–96 ppm for Zn. Because shipboard XRF results took into account loss on ignition during sample preparation, the chemical compositions determined during storage on shore were slightly lower than those obtained shipboard. Figures **F3** and **F4** show the temporal variation of major and minor elements during sample storage. Some element concentrations (e.g., Ca in Sample 193-SMW) changed with increasing storage time (Fig. **F3**), but for most elements these changes were within measurement error. In Sample 130-SMW, the Al content decreased with increasing storage time, whereas in Sample 193-SMW the Al content increased with time. Before our analyses, we were particularly concerned about the possible influence of the large quantities of Na and K in drilling fluids; however, the contents of these elements were reasonably stable during storage.

Acknowledgments

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Figure F1. Photographs of unwashed cuttings Samples (**A**) 319-C0009A-130-SMW, (**B**) 193-SMW, and (**C**) 213-SMW.

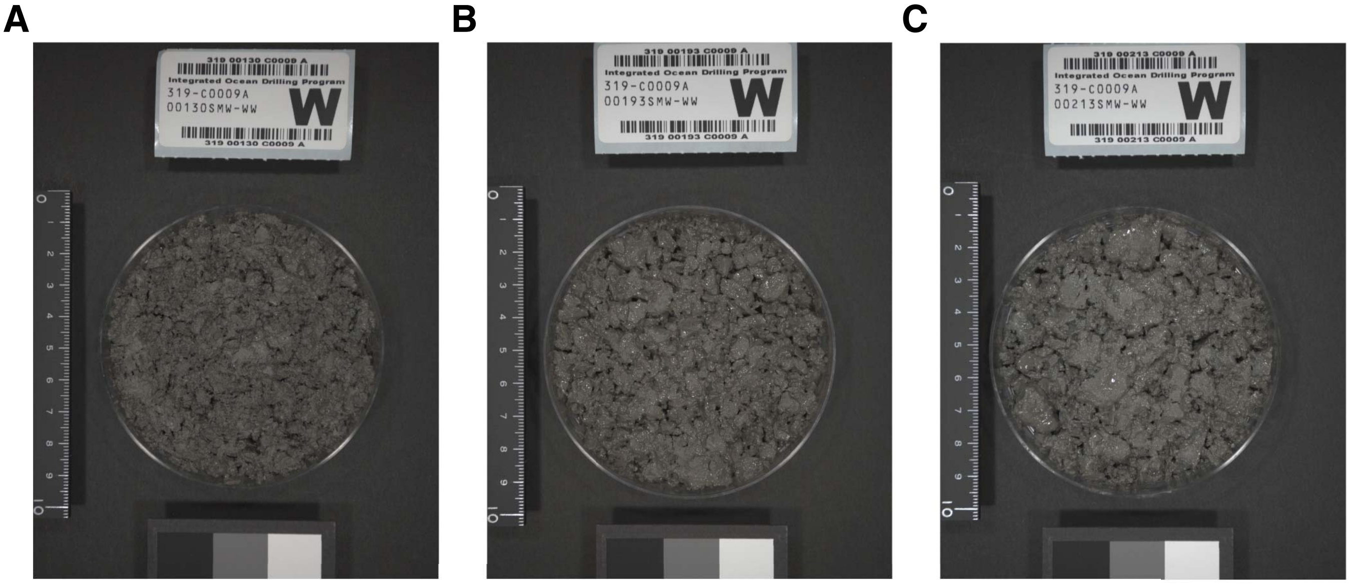

Figure F2. Flow chart of the sample decomposition procedure. PFA = perfluoroalkoxy.

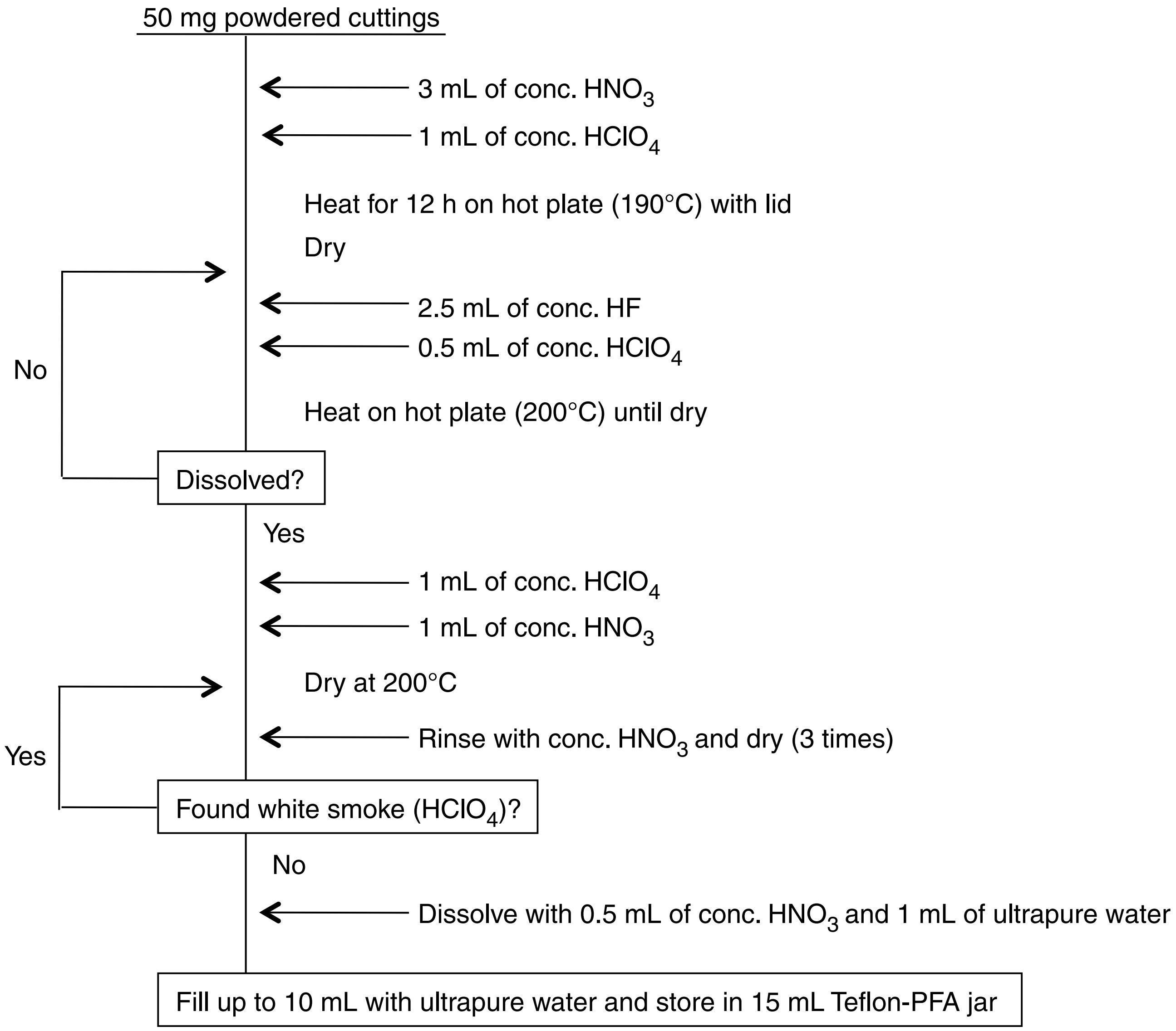

Figure F3. Temporal variation of major element contents for 33 months storage, cuttings Samples (**A**) 319-C0009A-130-SMW, (**B**) 193-SMW, and (**C**) 213-SMW.

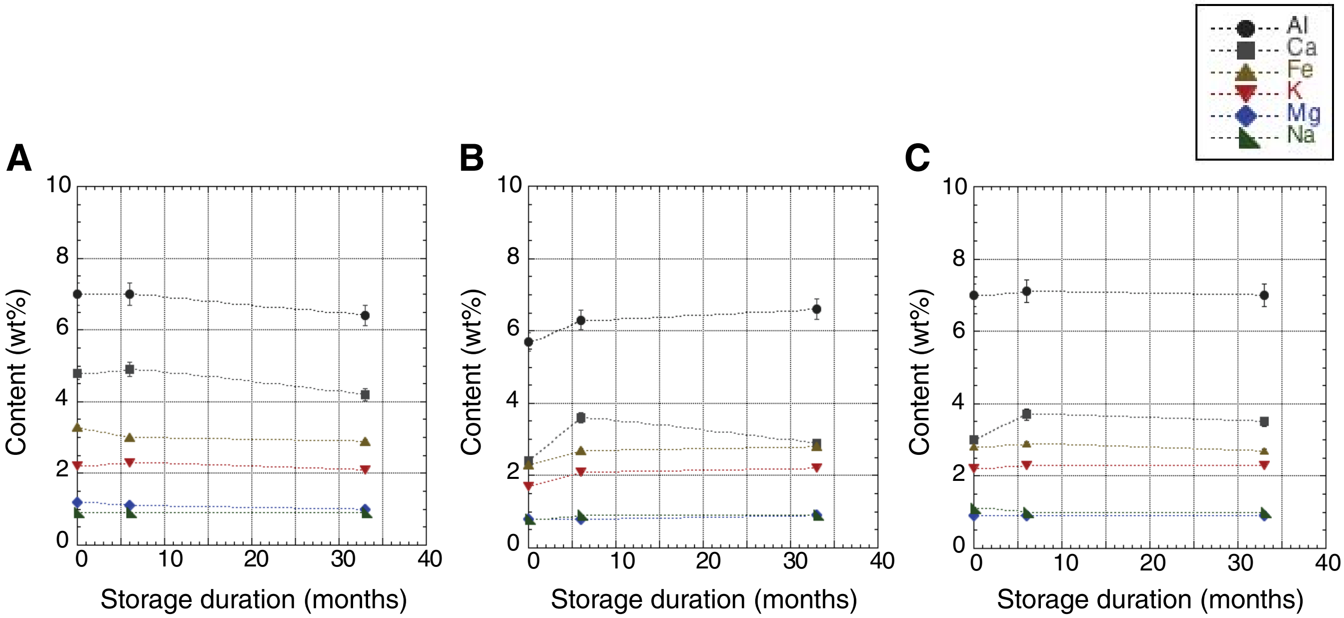

Figure F4. Temporal variation of minor element contents for 33 months storage, cuttings Samples (**A**) 319-C0009A-130-SMW, (**B**) 193-SMW, and (**C**) 213-SMW.

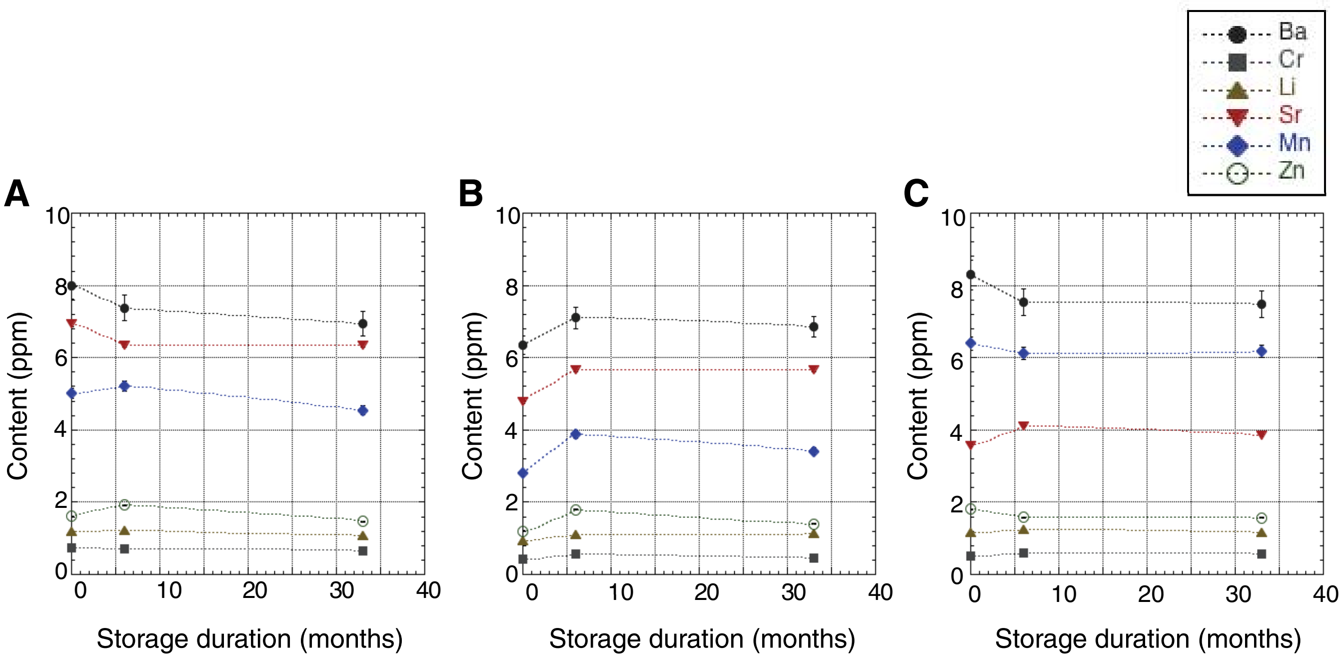

Table T1. Operation parameters for ICP-AES.

Parameter	Operation level
Power (W)	1300
Plasma gas flow (L/min)	15
Auxiliary gas flow (L/min)	0.2
Nebulizer gas flow (L/min)	0.7
Sample uptake (mL/min)	1.0
Spectrometer integration period (s)	10

Table T2. Recovery ratio of acid digestion procedure using two reference materials (JA-3 and JMS-1).

	JA-3		JMS-1	
	Recovery (%)	Measurement error (%)	Recovery (%)	Measurement error (%)
Major elements:				
Al	100	3.4	86	4.4
Ca	94	1.0	92	3.9
Fe	95	2.1	90	1.3
K	94	2.8	87	0.9
Mg	98	0.5	93	2.0
Na	90	2.4	88	2.4
Minor elements:				
Ba	97	1.4	95	4.9
Mn	98	2.3	92	0.9
Sr	96	0.9	91	2.9
Zn	100	1.0	90	0.9
Cr	98	1.3	95	1.7
Li	90	2.5	90	2.3

Measurement errors: relative standard deviation = 1σ, *n* = 3.

Table T3. Chemical composition of Hole C0009A cutting samples in this study and onboard X-ray fluorescence (XRF) analysis.

Methods:	ICP-AES result									Shipboard XRF result		
Cutting samples:	130-SMW			193-SMW			213-SMW			130-SMW	193-SMW	213-SMW
Storage duration (months):	0	6	33	0	6	33	0	6	33	NA	NA	NA
Major elements (wt%):												
Al	7.0	7.0	6.4	5.7	6.3	6.6	7.0	7.1	7.0	8.2	8.0	7.9
Ca	4.8	4.9	4.2	2.4	3.6	2.9	3.0	3.7	3.5	5.6	3.7	3.4
Fe	3.3	3.0	2.9	2.3	2.7	2.8	2.8	2.9	2.7	3.8	3.2	3.2
K	2.2	2.3	2.1	1.7	2.1	2.2	2.2	2.3	2.3	2.7	2.7	2.6
Mg	1.2	1.1	1.0	0.8	0.8	0.9	0.9	0.9	0.9	1.3	1.1	1.1
Na	0.9	0.9	0.9	0.8	0.9	0.9	1.1	1.0	1.0	1.2	1.5	1.4
Minor elements (ppm):												
Ba	400	370	350	320	350	340	410	380	370	ND	ND	ND
Mn	350	320	320	240	280	280	320	310	310	410	390	410
Sr	250	260	230	140	190	170	180	210	190	ND	ND	ND
Zn	80	96	74	60	90	70	90	80	79	ND	ND	ND
Li	60	61	54	47	56	57	58	62	58	ND	ND	ND
Cr	37	35	33	22	28	23	26	30	29	ND	ND	ND

ICP-AES = inductively coupled plasma–atomic emission spectroscopy. NA = not applicable, ND = not determined.