

26. DATA REPORT: MAJOR, TRACE, AND RARE EARTH ELEMENT COMPOSITION OF INTERSTITIAL WATER SQUEEZE CAKES¹

R.W. Murray,² J.M. Gieskes,³ and R.C. Pflaum⁴

INTRODUCTION

On Ocean Drilling Program Leg 152 to the East Greenland Margin, interstitial water samples were taken on a regular basis to elucidate diagenetic chemical reactions occurring both within the sediment column and as a result of basement alteration. Although limited somewhat by poor recovery at Sites 914, 915, and 916 (i.e., the in-shore sites), the shipboard interstitial water program managed to obtain more complete low-resolution profiles at Sites 918 and 919 (i.e., the more offshore sites). These results are detailed in Larson, Saunders, Clift, et al. (1994) and Gieskes et al. (this volume).

An important consideration during interpretation of the interstitial water results is the chemical composition of the solid phase enclosing those interstitial waters. To provide these data, we analyzed the squeeze cakes that resulted from interstitial water extrusion for a large suite of major, trace, and rare earth elements. These results, based on the analysis of 63 squeeze cakes, complement the more detailed sedimentary chemical profiles of Saito (this volume) and provide additional data on some elements not analyzed by Saito (this volume), such as the rare earth elements. Where appropriate, some of the data are used in the interpretations of Gieskes et al. (this volume). The data are provided here to facilitate future chemical studies of the sedimentary sequences sampled by Leg 152 and (as mentioned above) to assist in the interpretation of the interstitial water data.

ANALYTICAL METHODS

Samples were analyzed by inductively coupled plasma-emission spectrometry (ICP-ES) and inductively coupled plasma-mass spectrometry (ICP-MS). Sample preparation broadly followed the procedure described in Murray and Leinen (1993), but the procedure was slightly modified for the particular lithologies encountered during Leg 152, as described below. All acids used during the following sample preparation were double-distilled UltraPure grade from Seastar Chemicals (Seattle, WA, U.S.A.). Bulk sediment samples were freeze dried and subsequently hand powdered with an agate mortar and pestle. Complete digestion of ~0.05 g of sample powder was achieved through a multistep protocol beginning with HNO₃ and HF microwave-assisted dissolution in sealed Teflon vials (15 mL; Savillex Corp., MN, U.S.A.). Powder was poured directly into 0.5 mL of HNO₃, allowed to react for ~1 hr and, following addition of 5 mL of concentrated HF, allowed to soak for at least 24 hr. The HF:silicate ratio was intentionally designed to be relatively high, thus assisting complete attack of terrigenous phases. Sealed Teflon vials were heated as a group in a commercial household microwave oven

for 1.2 hr at 10% power. This heating was followed by three hot-plate drydowns of additions of, in succession, HNO₃, aqua regia, and HNO₃. As a final step, 1.0 mL of H₂O₂ (Ultrex Ultrapure, Baker) was added to the final 1 mL of HNO₃-based sample solution. All solutions were visually clear, with no residue apparent. For ICP-ES analysis, samples were diluted using trace-metal clean water to a 1:500 ratio (by mass) in precleaned, high-density Nalgene polyethylene bottles. Deviations from exact 500× dilution (≤2%) were taken into account during data reduction. An 8-mL aliquot was taken from this 500× dilution and diluted by a factor of 2 (by mass) to arrive at a second solution at 1000× dilution, for eventual use during ICP-MS analysis.

For the analysis of P, Mn, Fe, Al, Ca, Ti, Sr, and Ba, solutions were introduced by conventional nebulization into a Jobin-Yvon JY24 sequential ICP-ES and analyzed in comparison to matrix-matched synthetic standards. Standards were run at the beginning and end of each run. A drift-monitoring solution was run after every second standard and after every third sample. Blanks, internal references, and international Standard Reference Materials (SRM) were run in each batch as unknowns. Every solution, regardless of type, was analyzed in triplicate. Abundances of V (mass 51), Cr (52), Co (59), Ni (60), Cu (63 and 65), Zn (66 and 68), Y (89), Pb (206, 207, and 208), and the rare earth elements La (139), Ce (140), Pr (141), Nd (143, 145, and 146), Sm (147, 149, and 152), Eu (151 and 153), Gd (157 and 160), Tb (159), Dy (162 and 163), Ho (165), Er (166 and 168), Tm (169), Yb (171 and 174), and Lu (175) were determined by ICP-MS at Harvard University, using the isotopes indicated in parentheses. During ICP-MS analysis, an internal standard of 100 ppb ¹¹⁵In was used to correct for ionization suppression, and the data were calibrated against synthetic standards bracketing the observed concentrations within the sample suite. For both ICP-ES and ICP-MS analysis, samples were weighed, dissolved, and run in different random orders at each stage of preparation (i.e., completely mixing site numbers and depths).

Precision was estimated by complete quadruplicate analysis (i.e., from the powder weighing step onward) of Sample 152-918A-10H-4, 145–150 cm. For the elements determined by ICP-ES, precision is always better than 3% (conservative), except for Ba, which is within 10%. For the elements determined by ICP-MS, precision is ~5% for V, Ni, Cu, Y, and Ce; ~10% for Zn, La, Pr, Gd, Tb, and Ho; ~15% for Cr, Co, Nd, Sm, Eu, Dy, Er, and Pb; and between 15% and 20% for Tm, Yb, and Lu. Unfortunately, not all samples were analyzed for Ni and Cu because of machine difficulties. Accuracy was more difficult to assess. Standard Reference Material BCSS-1 (an estuarine sediment from the Gulf of St. Lawrence, available from the National Research Council of Canada) was analyzed with the samples. Results of this analysis were consistently 5%–10% lower than the accepted (yet poorly constrained) values for many of the more refractory elements, although elemental ratios show good agreement. We noted, however, that our preparation scheme did not completely digest BCSS-1, as evidenced by the presence of several (~10) dark grains at the end of the dissolution protocol. Such incomplete dissolution was not observed in the preparation of the Leg 152 samples themselves. We therefore estimate that accuracy is within precision. In fact, these contrasts in dissolution are consistent with the different lithology of the Gulf of St. Lawrence SRM and the open ocean Leg 152 samples.

¹Saunders, A.D., Larsen, H.C., and Wise, S.W., Jr. (Eds.), 1998. *Proc. ODP, Sci. Results*, 152: College Station, TX (Ocean Drilling Program).

²Department of Earth Sciences, Boston University, Boston, MA 02215, U.S.A. rickm@bu.edu

³Scripps Institution of Oceanography, University of California, La Jolla, CA 92093, U.S.A.

⁴Earth and Planetary Science, Harvard University, Cambridge, MA 02138, U.S.A. (Present address: Department of Geology and Geophysics, University of Hawaii, 2525 Correa Road, Honolulu, HI 96822, U.S.A.)

RESULTS

Analytical results for ICP-ES analysis are given in Table 1, and the results for ICP-MS analysis are given in Table 2.

ACKNOWLEDGMENTS

We thank the extremely helpful technical staff of the Leg 152 ODP shipboard personnel. John Brader helped in sample preparation at Boston University. Reviews provided by S.M. McLennan and R.M. Owen are appreciated. Research was funded by JOI/USSAC Cruise Science Support grants to R.W. Murray and J. Gieskes.

REFERENCES

- Larsen, H.C., Saunders, A.D., Clift, P.D., et al., 1994. *Proc. ODP, Init. Repts.*, 152: College Station, TX (Ocean Drilling Program).
- Murray, R.W., and Leinen, M., 1993. Chemical transport to the seafloor of the equatorial Pacific Ocean across a latitudinal transect at 135°W: tracking sedimentary major, trace, and rare earth element fluxes at the Equator and the Intertropical Convergence Zone. *Geochim. Cosmochim. Acta.*, 57:4141–4163.

Date of initial receipt: 1 November 1995

Date of acceptance: 22 May 1996

Ms 152SR-229

Table 1. ICP-ES results, bulk sedimentary chemistry of interstitial water squeeze cakes, Leg 152.

Core, section, interval (cm)	Depth (mbsf)	P (ppm)	Mn (ppm)	Fe (%)	Al (%)	Ca (%)	Ti (%)	Sr (ppm)	Ba (ppm)
152-914A-1H-2, 140-150	2.90	580	770	4.68	6.98	3.26	0.487	260	500
152-914B-15R-1, 69-77	216.79	520	720	6.94	6.67	2.41	1.19	330	450
17R-4, 140-150	241.40	470	580	6.97	6.36	1.90	10.1	200	340
152-915A-1R-1, 145-150	1.45	520	730	4.70	6.78	2.90	0.453	140	440
15R-1, 0-5	121.20	2450	1950	8.13	3.93	8.18	0.362	260	300
18R-2, 140-150	151.50	1900	6450	7.06	6.19	19.4	1.01	20	90
19R-2, 140-150	161.00	870	630	14.7	12.6	0.095	2.12	bdl	130
21R-5, 46-56	173.30	480	600	9.15	8.51	1.07	1.26	250	370
22R-2, 145-150	180.45	460	650	9.23	8.67	0.709	1.27	75	280
152-916A-13R-2, 140-150	81.50	1910	1450	10.6	9.39	1.05	1.08	80	160
152-918B-1H-3, 145-150	4.45	720	810	5.09	6.54	3.73	0.722	250	410
152-918A-2H-4, 150-155	7.75	810	820	5.44	7.48	3.28	0.717	275	520
152-918B-2H-4, 145-150	12.75	770	690	3.93	6.99	3.86	0.465	380	570
3H-5, 145-150	23.75	770	790	5.40	7.08	3.31	0.644	280	490
152-918A-4H-4, 145-150	26.75	790	730	5.32	7.73	2.66	0.556	300	750
152-918C-1H-4, 145-150	31.75	660	950	5.83	5.74	6.22	0.915	300	290
152-918A-7H-4, 145-150	55.25	780	650	4.63	6.88	3.10	0.534	290	620
10H-4, 145-150	83.75	850	1430	7.66	6.35	6.22	1.22	290	230
13H-4, 145-150	112.25	760	650	6.03	7.56	2.47	0.619	240	650
16H-4, 140-150	139.20	1010	1190	8.37	6.80	5.68	1.25	310	250
19H-4, 140-150	167.70	850	1190	7.76	6.98	5.32	1.13	170	210
23X-4, 140-150	205.70	750	910	6.19	6.09	3.91	0.990	170	350
26X-4, 140-150	232.40	920	1110	8.24	6.87	4.57	1.20	150	210
31X-4, 0-10	275.10	880	630	5.31	7.67	2.51	0.574	280	650
37X-5, 90-100	322.00	840	1000	6.99	6.62	4.36	1.10	320	330
152-918D-13R-1, 0-5	403.90	700	630	4.67	7.11	2.96	0.550	300	590
22R-2, 140-150	486.70	560	890	6.51	6.66	3.74	1.05	200	340
25R-3, 149-157	515.86	560	750	4.52	5.78	5.06	0.686	180	410
28R-3, 140-150	546.20	650	750	6.45	7.82	2.43	1.19	180	360
31R-CC, 5-8	571.75	420	600	7.26	6.91	1.75	1.04	120	360
34R-1, 2-10	599.62	400	550	4.92	5.38	1.73	0.866	120	400
37R-1, 140-150	630.00	480	480	6.27	7.08	4.83	0.847	340	360
40R-1, 140-150	658.90	470	380	5.34	5.88	6.02	0.708	340	450
44R-2, 139-150	698.99	480	440	5.00	5.39	9.75	0.699	470	450
47R-1, 50-60	725.10	470	460	6.75	6.19	3.71	0.983	190	630
51R-2, 140-150	766.10	470	400	5.15	5.84	8.50	0.800	480	710
55R-4, 112-122	807.42	400	310	5.65	5.79	5.15	0.770	370	630
62R-1, 121-129	870.51	360	450	4.94	4.82	5.16	0.724	290	360
68R-1, 91-100	925.91	960	440	7.59	5.42	1.61	0.976	120	450
74R-1, 3-14	982.73								
80R-1, 0-11	1040.60	1040	860	4.38	5.10	4.16	0.693	140	420
83R-1, 136-141	1070.96	400	950	4.10	4.82	3.84	0.555	130	470
88R-1, 93-100	1118.73	540	1990	6.87	3.87	16.9	0.844	560	320
91R-1, 119-129	1147.69	1110	350	6.18	6.40	5.04	0.812	400	2700
95R-2, 140-150	1182.20	100	310	10.7	4.30	0.385	0.480	40	190
152-919A-1H-2, 145-150	2.95	840	1160	7.02	6.64	5.97	1.07	390	330
1H-4, 145-150	5.95	850	840	6.11	7.62	3.07	0.644	260	620
2H-2, 145-150	10.95	730	990	6.48	6.03	4.67	0.925	190	300
2H-4, 145-150	13.95	780	980	6.44	5.99	6.00	0.950	220	260
3H-2, 145-150	20.45	800	960	5.96	7.12	4.72	0.840	270	440
3H-4, 145-150	23.45	800	1120	6.83	6.16	5.58	1.04	200	240
4H-2, 145-150	29.95	900	1100	7.57	6.75	4.84	0.991	180	250
4H-4, 145-150	32.95	750	830	6.20	6.76	2.98	0.800	140	380
5H-2, 145-150	39.45	830	1260	7.13	6.73	6.46	1.07	240	210
5H-4, 145-150	42.45	790	1220	8.00	6.57	5.98	1.19	190	200
6H-3, 145-150	50.45	710	1140	7.15	6.05	6.53	1.08	240	220
7H-3, 145-150	59.95	580	540	4.33	7.11	2.27	0.458	120	440
8H-3, 145-150	69.45	1200	1110	6.74	6.56	5.18	1.10	350	360
9H-3, 145-150	78.95	850	740	5.82	6.61	3.38	0.813	160	310
10H-3, 145-150	88.45	730	1150	6.81	6.61	6.17	1.08	210	260
152-919B-3H-3, 145-150	94.45	700	890	6.90	6.45	3.74	0.927	160	320
4H-3, 145-150	103.95	780	900	6.47	6.99	4.16	0.890	170	290
7H-3, 145-150	132.45	900	720	6.06	7.69	2.62	0.623	260	700

Notes: For Site 918, data are arranged in order of depth (mbsf), not according to hole. For Section 152-918D-74R-1, no ICP-ES data were gathered. bdl = below detection limit.

Table 2 (continued).

Core, section, interval (cm)	Depth (mbsf)	V (ppm)	Cr (ppm)	Co (ppm)	Ni (ppm)	Cu (ppm)	Zn (ppm)	Y (ppm)	La (ppm)	Ce (ppm)	Pr (ppm)	Nd (ppm)	Sm (ppm)	Eu (ppm)	Gd (ppm)	Tb (ppm)	Dy (ppm)	Ho (ppm)	Er (ppm)	Tm (ppm)	Yb (ppm)	Lu (ppm)	Pb (ppm)
2H-4, 145-150	13.95	217	87	30			108	22.5	22.1	42.4	5.90	25.0	5.38	1.48	5.06	0.80	5.04	0.90	2.52	0.32	2.75	0.36	7.43
3H-2, 145-150	20.45	158	88	27			101	19.3	32.7	61.6	8.15	32.5	6.14	1.71	5.38	0.86	5.36	0.81	2.64	0.44	2.41	0.37	11.38
3H-4, 145-150	23.45	196	76	30			104	23.1	22.8	45.7	6.62	29.3	5.99	1.83	5.98	0.99	6.41	1.09	3.13	0.43	3.16	0.41	8.88
4H-2, 145-150	29.95	188	80	31			109	24.7	24.1	47.5	6.87	28.6	6.69	1.97	6.42	0.99	6.55	1.12	3.15	0.40	3.10	0.50	7.62
4H-4, 145-150	32.95	205	97	30			115	22.0	23.2	43.6	6.05	24.8	5.08	1.38	4.98	0.72	4.66	0.69	2.35	0.32	2.43	0.36	9.32
5H-2, 145-150	39.45	219	100	33			102	22.2	18.1	36.4	5.23	23.6	5.37	1.65	5.83	0.83	6.07	0.97	2.98	0.43	2.95	0.49	5.59
5H-4, 145-150	42.45	244	103	37			119	24.6	18.1	36.5	5.61	24.6	5.59	1.72	5.60	0.90	5.99	1.06	3.14	0.42	2.82	0.47	5.39
6H-3, 145-150	50.45	251	117	37			102	21.6	17.7	33.8	4.94	21.8	4.89	1.50	5.10	0.69	5.24	0.77	2.46	0.37	2.46	0.35	5.19
7H-3, 145-150	59.95	132	76	16			101	19.9	35.4	66.6	8.80	33.9	6.27	1.39	5.10	0.72	4.78	0.76	2.31	0.39	2.25	0.35	19.45
8H-3, 145-150	69.45	271	96	41	58	142	135	27.7	20.7	43.5	5.51	22.3	4.88	1.42	5.22	0.75	4.48	0.67	2.07	0.28	1.83	0.31	5.19
9H-3, 145-150	78.95	197	83	28			112	22.2	26.8	52.3	6.58	28.8	5.73	1.48	5.22	0.78	5.06	0.89	2.45	0.38	2.38	0.39	10.08
10H-3, 145-150	88.45	268	124	39			113	22.9	18.6	36.4	5.08	22.6	5.05	1.57	4.87	0.83	5.25	0.88	2.53	0.42	2.61	0.41	6.01
152-919B-																							
3H-3, 145-150	94.45	192	79	31			110	21.7	22.7	45.6	5.97	27.2	5.61	1.58	5.60	0.80	5.55	0.88	2.90	0.45	2.72	0.46	9.17
4H-3, 145-150	103.95	217	91	32			116	25.0	26.3	51.7	7.12	30.0	6.15	1.67	5.97	0.87	5.99	0.94	3.05	0.44	2.73	0.41	10.27
7H-3, 145-150	132.45	143	107	24			127	17.9	43.3	77.3	10.10	39.5	6.47	1.59	5.31	0.76	4.50	0.72	2.35	0.32	2.29	0.35	12.08

Note: For Site 918, data are arranged in order of depth (mbsf), not according to hole.