

22. A TECHNIQUE FOR OBTAINING PORE-WATER CHEMICAL COMPOSITION FROM INDURATED AND HYDROTHERMALLY ALTERED SEDIMENT AND BASALT: THE GROUND ROCK INTERSTITIAL NORMATIVE DETERMINATION (GRIND)¹

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ABSTRACT

During Ocean Drilling Program Leg 139 at Middle Valley, Juan de Fuca Ridge, we recovered indurated sediment and hydrothermally altered diabases and gabbros from an active hydrothermal reservoir at Sites 857 and 858. Because few of these samples yielded pore water upon squeezing even at the maximum pressure afforded by the hydraulic presses aboard *JOIDES Resolution*, we developed the GRIND technique (ground rock interstitial normative determination). The GRIND technique consists of fragmenting a freshly collected sample, grinding the sample with distilled water in a ball mill, squeezing the ground mixture, and analyzing the effluent.

Concentrations of Mg, Ca, Na, K, Rb, and, from Site 857 only, Sr, measured in GRIND samples are comparable to measurements of squeezed samples, in contrast to alkalinity, sulfate, dissolved silica, Ba, Mn, Li, and B, which differ substantially between the two methods. GRIND samples with chlorinity greater than about 100 mmol/kg have only minimal artifacts caused by ion exchange. Ion exchange in more diluted pore-water samples causes an increase in Na and a decrease in Mg, Ca, and Sr. The GRIND method could be an invaluable tool for estimating the chemical composition of pore waters in basement.

INTRODUCTION

Knowledge of the composition of pore waters throughout a sediment column is an important tool for understanding the physical, chemical, biological, and geological processes that have currently or recently influenced diagenesis of the sediment and alteration in basement. For example, changes in the pore-water concentrations of dissolved oxygen, nitrate, sulfate, ammonium, manganese, iron, alkalinity, and phosphate provide a measure of biologically mediated reactions. Concentrations of other ions such as dissolved silica, lithium, potassium, rubidium, magnesium, and calcium change from bottom seawater values to values in equilibrium with sediment and basement. These data are useful in assessing rates of inorganic diagenesis. Pore-water profiles of conservative ions such as chlorinity, and in certain circumstances, magnesium, can also be used as a tracer for pore-water flow.

Because the chemical composition of pore waters is so useful for determining present-day processes, much care is taken to recover pore-water samples that are not affected by sampling procedures. Several in-situ and shipboard techniques have been developed to extract pore water from sediment. In-situ techniques rely on positioning an entry port into sediment and then drawing pore water into a reservoir through a filter (e.g., Barnes, 1988). Samples retrieved using in-situ techniques are not affected by artifacts caused by changes in temperature or pressure, but these in-situ tools are expensive and can only be used in soft sediment that will not crack and allow bottom water to flow and contaminate the sample. Shipboard techniques to obtain pore water have relied on squeezing sediment through a filter into a container (e.g., Manheim and Sayles, 1974), or centrifuging a sediment sample. Samples obtained using these methods are subject to artifacts caused by sample handling and changes in temperature, pressure, and oxidation state (de Lange et al., 1992). Squeezing typically produces a

greater volume of pore water than centrifugation; however, little to no water can be extracted from the most lithified sediment or hydrothermally altered basalt or gabbro by either technique.

During Ocean Drilling Program (ODP) Leg 139 in Middle Valley, Juan de Fuca Ridge, we recovered indurated sediment and hydrothermally altered diabases and gabbros from Sites 857 and 858. We tried to recover pore water using a Carver hydraulic press (Manheim and Sayles, 1974) with a maximum pressure of 2.8 MPa. Many of these samples did not yield any pore water even after 12 hr at the maximum safe pressure. These samples comprise over half of the sediment column at Site 857, half of Hole 858F, and all of Hole 858G. Site 857 was positioned to drill into the hydrothermal fluid reservoir that is thought to supply fluids to active hydrothermal vents 1.5 km to the north, where Site 858 is located. Holes 858F and 858G are located within 50 m of active hydrothermal vents where effluent from these vents reaches temperatures of 276°C (Butterfield et al., this volume), about the temperature at 500 mbsf in Site 857 and at 50 mbsf in Holes 858F and 858G (Davis, Mottl, Fisher, et al., 1992). An important focus of Leg 139 was to understand the chemical processes that take place in these holes by examining the pore-water chemical composition, physical properties, mineralogy, and geochemistry of rocks that make up the hydrothermal reservoir.

Because most of the sediment and rock samples did not yield any pore water upon squeezing, we modified a method presented by Cranston (1991), herein referred to as the GRIND technique (ground rock interstitial normative determination), to obtain information on the composition of pore water from indurated sediment and hydrothermally altered basalt and gabbro. In this paper we present a comparison of the chemical composition of pore water obtained by squeezing sediment using a titanium squeezer (Manheim and Sayles, 1974) and by using the GRIND technique on samples from Sites 857 and 858. This comparison provides the data from which we determine probable reactions that occur during the GRIND procedure that result in changes in the chemical composition of the pore waters. Much of the paper focuses on the potential sources for chemical change during sample handling and the inherent problems associated with the GRIND technique, as it is important for future geochemists involved in ODP to understand the limitations of the technique, and of the conclusions one can draw from data obtained using the technique.

¹ Mottl, M.J., Davis, E.E., Fisher, A.T., and Slack, J.F. (Eds.), 1994. *Proc. ODP, Sci. Results*, 139: College Station, TX (Ocean Drilling Program).

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ANALYTICAL METHODS

The general idea of the GRIND technique is to fragment a freshly collected sample, then grind the sample with distilled water in a ball mill. The ground mixture is then squeezed and the effluent is analyzed. No attempt is made to conduct the procedure at in-situ temperature or pressure because of the lack of a ball mill that can be heated to 275°C at 300 bars, and because these elevated temperatures and pressures enhance chemical reactions that occur as a result of dilution of the sample with distilled water. No attempt is made to process the samples at in-situ oxidation state because few of the chemical species of interest are affected by changes in the oxidation state and because samples were exposed to dissolved and atmospheric oxygen during coring and retrieval.

Whole-round samples of indurated sediment and hydrothermally altered basalt were processed as soon as possible after recovery. Typically one subsample was broken off and squeezed while another was subjected to the GRIND technique. Samples subjected to the GRIND technique were first blotted with paper towels to remove seawater that came in contact with the sample during drilling and retrieval. If these samples were not immediately processed, they were wrapped tightly in parafilm and stored in a refrigerator for at most one day.

The GRIND process consists of placing the sample in double plastic bags and fragmenting it using a hammer, until all of the sample is <1 cm in size. About 35 g of the sample is then weighed and placed in a ball mill. A measured volume of deionized distilled water is added to the ball mill, then the mixture is ground and squeezed to extract the pore water/distilled water mixture. The optimal volume of water that must be added to the ball mill is less than the porosity multiplied by the mass of the sample. We generally added 5 mL of deionized distilled water to 35 g of sediment, about a one-to-one ratio between distilled water and pore water. Excess distilled water results in a ground slurry that is difficult to transfer to the squeezer and effectively extract the water. A lesser volume of distilled water may not produce pore water upon squeezing or may produce too small a volume to be of use. The optimal grinding time is 15 min. Shorter periods of time did not adequately crush the sample, and longer periods may enhance reactions between the sample and distilled water.

Pore waters obtained using the GRIND technique are subject to the same analytical procedures as squeezed samples. The analytical methods used to determine the composition of the pore waters are described by the Shipboard Scientific Party (1992) and Wheat and Mottl (this volume) and consist of standard colorimetric, potentiometric, and spectrometric techniques (Tables 1 and 2).

The GRIND method is similar to the one presented by Cranston (1991) in that deionized distilled water is added to a sediment sample. However, we did not degas the distilled water or handle the samples in an oxygen-free environment at in-situ temperatures. The main difference between the two techniques is that Cranston's method is designed for high-resolution sediment sampling using small sample sizes when either sediment availability or manpower for squeezing is limiting, whereas the GRIND method is designed to provide some pore-water chemical data from lithified sediments and hydrothermally altered basalts that do not yield pore water when squeezed at pressures to 2.8 MPa for over 12 hr.

RESULTS AND DISCUSSION

In the following sections we present the data and discuss sources of pore-water contamination during the GRIND technique. Although most of this section focuses on the problems associated with the GRIND technique, the extent of reaction was found to be minimal for some chemical species, indicating that the GRIND technique can provide useful data for the composition of pore water in indurated and hydrothermally altered sediments and rocks.

There are several potential sources for error using the GRIND method. Sample handling occurs at room temperature and pressure,

both of which are much less than in-situ values. Adding distilled water during the grinding stage alters the ionic strength of the pore water. Because of these procedures, ion-exchange or dissolution/precipitation reactions may result. Because the sample is exposed to atmospheric oxygen and dissolved oxygen in the added distilled water, redox reactions may alter the pore-water composition. For example, the oxidation of reduced dissolved iron in the pore water results in an oxidized form that readily precipitates, thus lowering the concentration of dissolved iron. Oxidation reactions are reduced if all of the work is done with deoxygenated water in a nitrogen-filled glove bag.

In the following sections, we compare the chemical composition of pore waters extracted using the GRIND technique with those obtained from squeezing. Profiles of the concentration in pore water vs. depth are presented for the major and minor ions in seawater based on GRIND and squeezed samples in which the GRIND data are adjusted to account for an estimated pore-water chlorinity of 590 mmol/kg at Site 857 and 565 mmol/kg at Site 858. These plots are useful in assessing trends in the data, the range of values obtained using the GRIND and squeezed techniques, and potential sources of contamination during the GRIND technique. We also include plots of the ratio of dissolved elements to chlorinity for GRIND vs. squeezed samples. This allows for a direct comparison of the two methods; however, only 20 of the 60 GRIND samples have corresponding squeezed samples and 3 of these GRIND samples are duplicates or triplicates (Table 3). To examine the effect of dilution on the GRIND samples, we present chemical profiles in which the most diluted GRIND samples are highlighted. We also present plots of the ion concentration divided by chlorinity, to normalize for the extent of dilution, vs. the chlorinity of the sample, which represents the extent of dilution.

Major Ions

Dilution of the pore-water samples during the GRIND method causes a change in the ionic strength and the concentrations of the ions. Assuming the pore water is originally in equilibrium with its surroundings, dilution can result in disequilibrium. If the kinetics of reaction are faster than the time required for grinding and squeezing the sample, the chlorinity-adjusted chemical composition of pore water using the GRIND technique will be different from that obtained by squeezing. Cranston (1991) states that dilution of pore water results in exchange reactions that decrease the concentrations of divalent cations in pore waters while increasing the concentration of monovalent cations.

Depth profiles of dissolved species provide insight into the diffusive, advective, and reactive processes that presently exist, but the effects of sample handling must be understood. Dilution of the sample during the GRIND process generally increases the concentration of dissolved Na (Fig. 1). The most diluted GRIND samples (<100 mmol Cl/kg) are highlighted in depth profiles and the concentration of Na in these samples is systematically greater than that in neighboring squeezed and more concentrated GRIND samples (Figs. 1A and 1B). Likewise, a comparison of GRIND and squeezed samples from the same depth interval reveals that the ratio of Na to chlorinity in the GRIND samples is generally greater than that in the squeezed samples (Fig. 1C), implying that ion exchange increases the concentration of Na in the more diluted pore waters obtained from the GRIND process. Lastly, a plot of the ratio of Na to chlorinity vs. chlorinity shows an increase in Na/Cl with decreasing chlorinity (Fig. 1D).

Note, however, that trends in ion/chlorinity vs. chlorinity plots can result from ion exchange during sample handling as well as from changes in the ion concentration with depth. Clearly, as presented above, ion exchange during sample handling influences the concentration of dissolved Na in GRIND samples (Figs. 1A, 1B, and 1C). Some of the trend in Figure 1D results from a general increase in Na with depth that is real, but which corresponds with a general decrease in chlorinity that is related to a decrease in porosity. In Figure 2 we

Table 1. The composition of water extracted from lithified sediment and hydrothermally altered basalt from Site 857 using the GRIND technique.

Sample	Core, section, interval (cm)	Depth (mbsf)	Volume (mL)	Squeeze		pH	Alkalinity (meq/kg)	Chlorinity (mmol/kg)	Sulfate (mmol/kg)	Na (mmol/kg)	K (mmol/kg)	Mg (mmol/kg)	Ca (mmol/kg)	Si (μmol/kg)	Mn (μmol/kg)	Sr (μmol/kg)	Ba (μmol/kg)	B (μmol/kg)	Li (μmol/kg)	Rb (μmol/kg)
				pressure (psi)																
139-857C-																				
G-5	37R-1, 140-150	352.25	5.5	25000	7.61	0.590	284.3	2.96	190	15.4	6.11	36.19	167	9.25	179.0	10.3	300	187	4.66	
G-2	46R-2, 0-15	400.58	8.0	5000	7.31	0.478	170.9	0.83	123	6.8	3.31	18.42	133	4.03	64.7	10.5	190	95	2.95	
G-1	46R-2, 0-15	400.58	7.5	2000	7.91	0.581	131.3	0.78	96	5.0	1.33	14.83	133	2.02	47.0	8.2	457	72	2.26	
G-3	46R-2, 0-15	400.58	3.0	10000			273.2	1.48	192	10.1	4.73	32.47	170							
G-7	47R-1, 135-150	405.43	3.9	30000	7.52	0.526	273.2	0.90	187	10.5	3.83	35.16	163	6.29	115.0	21.3	237	151	3.70	
G-4	48R-1, 132-147	410.10	4.2	25000	7.71	0.557	266.0	1.38	183	12.0	4.19	32.61	153	4.62	104.0	11.6	235	126	3.53	
G-6	49R-1, 135-150	415.13	4.2	25000	7.73	0.755	294.5	1.20	204	11.7	4.96	35.86	175	6.62	121.0	15.8	317	149	5.30	
G-21	49R-1, 135-150	415.13	5.5	15000	7.63	1.483	258.7	7.55	179	12.0	6.86	35.11	178	15.3	94.0	2.9	290	63	3.23	
G-8	55R-1, 36-38	442.37	5.2	12000	7.80	0.556	290.6	2.08	207	9.7	8.37	30.54	84	5.10	110.0	8.8	336	130	6.69	
G-9	56R-1, 10-14	446.62	4.5	20000	7.69	0.640	268.4	1.70	191	9.1	5.83	30.29	100	7.48	103.0	10.4	255	96	3.44	
G-10	57R-1, 0-20	451.80	4.2	20000	7.82	0.622	281.9	2.62	204	9.3	8.04	28.80	100	3.50	100.0	8.1	296	115	8.09	
G-11	58R-CC, 0-22	471.00	4.6	30000	7.72	0.786	275.2	2.37	197	9.4	7.68	29.53	112	7.53	97.6	7.5	223	90	4.06	
G-19	62R-1, 142-150	501.46	5.0	25000	7.34	7.988	196.2	2.08	144	6.0	2.61	26.67	178	0.00	72.6	5.8	73	23	4.86	
G-12	66R-1, 4-9	538.87	4.5	30000	7.90	0.952	251.1	2.78	189	6.2	8.06	23.04	123	2.93	82.6	5.3	194	55	5.66	
139-857D-																				
G-1	1R-2, 5-12	583.09	3.0	10000	7.29	0.830	216.1	0.75	158	5.2	7.05	20.69	90	3.43	64.2	6.5				
G-3	3R-2, 0-7	600.84	3.0	30000	7.42	0.607	99.1	0.38	75	2.0	1.60	10.12	83	0.32	21.2	4.0	20	2.00	1.68	
G-2	4R-2, 68-72	611.10	2.5	25000			113.1	0.17	87	2.2	2.34	9.98	72	2.11	27.8	1.7	33	3.47	1.74	
G-4	9R-1, 33-36	657.25	2.5	35000			58.5	0.00	46	1.0	0.75	5.00	76	0.21	9.4	2.1	22	1.17		
G-6	10R-1, 19-21	666.82	4.0	10000	7.33	0.584	238.4	0.74	175	6.2	6.05	23.42	82	2.97	74.0	5.3	116	23.12	5.74	
G-9	11R-1, 20-23	676.42	3.5	30000	7.34	0.649	191.9	0.48	143	4.8	4.73	18.20	83	1.81	59.8	5.9	72		3.63	
G-5	12R-1, 16-20	686.08	4.0	12000	7.26	0.631	160.1	0.52	120	4.3	2.35	16.46	96	1.72	47.0	6.1	58			
G-7	12R-1, 16-20	686.08	4.0	15000	7.20	0.436	157.0	0.20	109	4.6	2.40	19.44	80	2.10	54.3	7.1	65	33.1	3.78	
														0.44	82.4	12.2	62	80.8	1.36	
G-11	15R-1, 10-14	714.92	4.0	35000	7.34	0.679	187.7	0.89	142	5.0	4.70	17.09	98	2.15	44.2	2.8	73	12.3		
G-8	16R-1, 8-11	724.60	3.5	25000			165.0	0.22	124	3.7	3.21	15.62	82	1.67	50.2	3.1	48	7.20	3.12	
G-10	17R-2, 109-111	736.50	3.0	35000			141.5	0.12	111	2.8	2.76	11.28	71	0.94	34.3	1.7	42	2.28	1.78	
G-12	19R-1, 18-19	752.99	3.0	25000			56.6	0.41	47	1.6	0.39	4.18	244	0.09	10.0	0.8	25	6.44	1.28	
G-13	20R-1, 90-92	763.41	2.8	25000			40.3	0.35	34	1.2	0.18	2.90	278	0.09	6.3	0.4				
G-14	21R-2, 30-34	774.02	3.5	15000	7.50	1.154	230.9	1.31	175	5.0	8.70	18.48	59	0.36	12.6	0.8	24	15.2	4.31	
G-15	23R-1, 10-11	791.61	2.5	35000			46.5	0.09	37	1.1	0.30	4.12	98	0.09	5.4	1.2	21	0.72		
G-16	24R-1, 66-69	801.88	3.0	30000	7.26	0.644	146.3	0.16	112	3.3	3.54	12.62	69	0.98	41.5	2.3	37	1.66	2.73	
G-17	25R-1, 41-42	811.22	3.0	35000			44.6	0.15	36	0.9	0.46	3.70	126	0.23	5.6	0.8	15	0.28	0.54	
G-18	27R-1, 28-32	829.90	3.5	15000	7.44	0.920	205.7	1.08	157	2.9	4.91	19.39	98	0.71	62.6	4.8	87	23.4	4.35	
G-20	28R-1, 10-14	839.02	3.0	35000			116.0	0.69	89	3.6	1.71	10.64	190	0.00	28.7	2.1	45	15.4	1.18	
G-22	29R-1, 4-8	848.46	4.0	25000	7.44	0.945	215.6	1.56	167	5.1	8.16	15.52	76	1.88	53.3	3.4	103		3.88	
G-23	31R-1, 5-7	868.56	4.5	30000	7.28	1.171	201.4	0.95	156		5.09	17.45	68	1.65	57.1	3.2	93	10.8	3.97	
G-24	34R-1, 5-7	897.56	3.0	35000			138.8	0.16	111		2.69	10.10	62	0.71	31.7	1.4	30	1.27	1.71	
G-25	35R-1, 5-10	907.28	3.0	35000			64.1	0.05	50		0.67	5.32	76	0.23	9.3	0.3	13	0.47	0.96	
G-26	37R-1, 36-37	926.87	3.2	35000			187.1	0.76	148		3.76	15.10	76	1.19	45.4	1.2	60	5.06	2.24	

Notes: Na values are calculated. In calculating Na, alkalinity is assumed to be 0.5 meq/kg and K is assumed to be 3 mmol/kg if they were not measured. Mg and Ca have been corrected using the equations of Gieskes and Peretsman (1986).

Table 2. The composition of water extracted from lithified sediment and hydrothermally altered basalt from Site 858 using the GRIND technique.

Sample	Core, section, interval (cm)	Depth (mbsf)	Volume (mL)	Squeeze pressure (psi)	pH	Alkalinity (meq/kg)	Chlorinity (mmol/kg)	Sulfate (mmol/kg)	Na (mmol/kg)	K (mmol/kg)	Mg (mmol/kg)	Ca (mmol/kg)	Si ($\mu\text{mol/kg}$)	Mn ($\mu\text{mol/kg}$)	Sr ($\mu\text{mol/kg}$)	Ba ($\mu\text{mol/kg}$)	B ($\mu\text{mol/kg}$)	Li ($\mu\text{mol/kg}$)	Rb ($\mu\text{mol/kg}$)
139-858C-																			
G-10	10X-CC, 30-35	49.63	1.7				278.1	19.070	239.0	7.9	22.10	12.67	72	6.22	149	0.87	84.5		
G-11	11R-1, 0-10	54.55	5.2		7.58	1.180	347.1	10.692	292.3	6.8	27.62	7.45	217	31.08	210	2.29	174.2	34.4	1.2
G-6	12X-1, 131-145	65.38	6.0		7.58	1.302	369.5	8.522	312.4	6.2	25.20	7.60	305	6.78	273	2.83	214.8	106.0	1.3
139-858D-																			
G-5	6X-1, 96-105	29.81	5.0		7.55	1.364	362.7	1.675	244.6	11.6	8.55	46.47	253	12.04	554	19.25		23.1	8.3
139-858F-																			
G-8	7R-CC	75.10	0.5				94.3	0.153											
G-13	9R-CC, 3-5	94.24	2.2				295.6	1.721	211.3	8.0	9.73	30.01	48	2.33	357	2.77	159.7	91.6	6.5
G-9	11R-1, 0-3	113.62	7.0		7.76	2.376	360.8	4.366	263.5	9.2	13.53	35.47	356	14.65	510	6.95	595.6	193.8	8.7
G-4	13R-CC, 0-2	132.91	2.3				172.1	22.456	111.5	3.1	6.12	45.00	75	2.22	309	0.88	113.7	63.5	
G-12	18R-1, 65-72	181.99	4.2		7.78	0.720	295.6	1.169	208.3	8.1	8.48	32.21	72	0.00	399	7.67	240.9	117.6	9.4
G-2	19R-1, 9-12	191.01	4.6				307.3	2.056	212.8	11.6	8.92	34.29	164	3.66	442	13.00	397.1	164.2	
G-15	21R-1, 9-13	210.41	4.0		7.45	0.832	318.9	1.525	217.2	12.1	7.28	38.92	190	1.81	462	15.20	401.6	179.9	5.8
G-7	25R-1, 2-8	248.95	2.0				311.2	1.925	217.8	10.0	7.79	35.48	232	4.26	470	15.84	462.0	198.2	
G-16	27R-1 (middle)	267.80	2.5				65.3	1.350		10.2		8.60	137	1.54	68	0.63	19.1	6.9	1.4
G-17	28R-1, 28-32	277.80	1.5				53.8	0.355		1.3			173		70	8.88			
G-14	29R-1, 85-87	288.06	2.0				68.4	3.594		2.2			158		55	0.69		7.8	
139-858G-																			
G-1	2R-1, 56-58	287.07	2.3	30,000			38.4	0.338	35.5		0.23	2.30	197	0.50	20	0.37	23.5	2.3	0.4
G-2	5R-1, 15-18	315.57	2.5	3,000			83.7	0.195	66.9		1.42	7.82	91	0.53	62	0.92	30.7	4.8	1.4
G-3	7R-1, 55-58	335.37	2.8	3,000			57.3	0.294	48.0		0.70	4.97	152	0.76	34	0.50	28.3	2.9	0.7
G-4	10R-1, 90-91	365.81	2.5	3,000			82.1	0.412	65.1		1.31	8.28	109	0.62	56	0.65	30.8	7.3	1.2
G-5	12R-1, 12-15	384.34	2.8	35,000			61.5	0.305	51.1		1.00	5.22	133	0.00	38	0.42	23.9	4.2	0.8
G-6	15R-1, 20-24	413.52	2.2	35,000			75.6	0.409	61.8		0.79	7.21	145	0.00	52	0.43	25.6	6.0	1.0
G-7	16R-1, 18-22	423.10	2.5	35,000			37.4	0.307	34.5		0.30	2.20	271	0.00	16	0.09	13.6		

Notes: Na values are calculated. In calculating Na, alkalinity is assumed to be 0.5 meq/kg and K is assumed to be 1 mmol/kg if they were not measured. Mg and Ca have been corrected using the equations of Gieskes and Peretsman (1986).

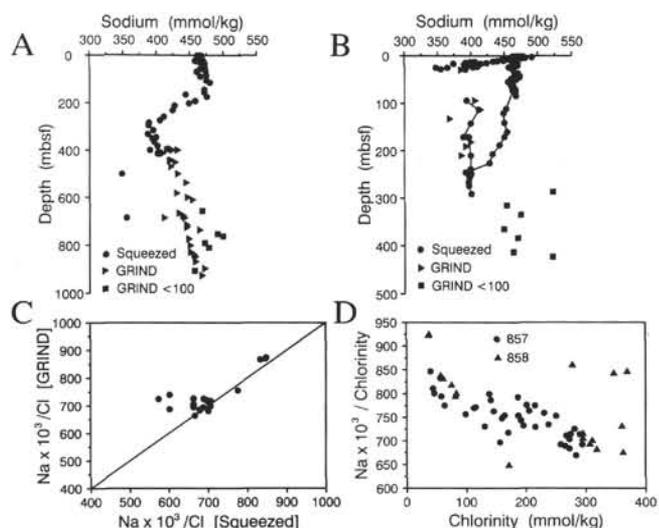


Figure 1. Profiles of Na from squeezed and GRIND samples, including GRIND samples with chlorinity less than 100 mmol/kg. **A.** Site 857. GRIND samples have been corrected to a chlorinity of 590 mmol/kg. **B.** Site 858. GRIND samples have been corrected to a chlorinity of 565 mmol/kg. Lines connect samples from Holes 858A and 858F. **C.** Plot of the ratio of Na to chlorinity in GRIND samples vs. squeezed samples. The slope of the line is 1.0. **D.** The ratio of Na to chlorinity in GRIND samples vs. chlorinity.

present profiles of porosity (Davis, Mottl, Fisher, et al., 1992) at depths where GRIND samples were retrieved along with profiles of chlorinity for all of the GRIND samples. There is an overall decrease in the porosity and chlorinity of the GRIND samples with depth. Superimposed on these decreases are excursions to much lower values, caused by changes in lithology from lithified sediment to hydrothermally altered basalt and gabbro. A good correlation exists between the porosity of the sediment or rock and the resulting chlorinity of the GRIND sample (Fig. 2C), because the volume of distilled water added was generally kept constant at 5 mL. Although the data are consistent with a general increase in Na with depth, ion exchange also must occur. Samples with low porosity are more affected by ion-exchange processes; thus, the lower chlorinity samples have a higher Na/Cl ratio, which results in Na depth profiles that are not smooth. Smoothed profiles are likely because non-smoothed profiles require diffusive fluxes from lithologic units with high concentrations to those with low concentrations. Based on ion diffusion coefficients that are about 30 times greater at 275°C than at 2°C (Nigrini, 1970), calculated chemical fluxes resulting from differences in chemical concentrations between lithologic units that are thin, typically less than 10 m thick, are large enough to impact the concentration in the solid phase. However, the solid phase does not record such fluxes (Goodfellow and Peter, this volume). Therefore, although Na increases with depth, ion exchange caused by dilution during the GRIND process affects the concentration of dissolved Na. Despite the above-mentioned problems, the GRIND technique is useful for obtaining pore-water Na data from samples that yield waters with a chlorinity >100 mmol/kg.

Similar profiles and plots for the other major monovalent (K) and divalent cations (Mg and Ca) are presented in Figures 3, 4, and 5, respectively. As was the case for Na, concentrations of K are generally higher in GRIND samples than squeezed samples (Fig. 3C), but there is no obvious effect of ion exchange in the low-chlorinity (<100 mmol/kg) samples (Fig. 3D). In contrast to the Na and K data, concentrations of Mg and Ca are typically greater in the squeezed samples than in the GRIND samples (Figs. 4C and 5C). Ion exchange in the low-chlorinity GRIND samples is clearly evident in the Mg data but less apparent in the Ca data (Figs. 4D and 5D). Some anomalously high concentrations of Ca, in both the squeezed and GRIND samples,

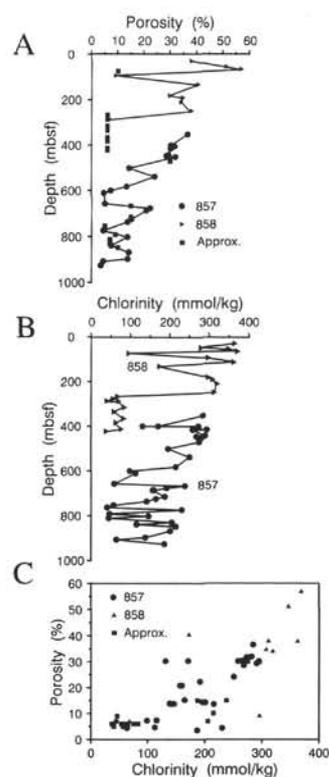


Figure 2. Profiles of porosity and chlorinity of GRIND samples. For GRIND samples that do not have porosity values, we approximated the porosity from neighboring samples (Davis, Mottl, Fisher, et al., 1992). Also shown is a plot of porosity vs. chlorinity.

Table 3. GRIND samples that have a corresponding squeezed aliquot.

Sample	Hole	Core, section, interval (cm)
G-5	857C	37R-1, 140-150
G-2	857C	46R-2, 0-15
G-1	857C	46R-2, 0-15
G-3	857C	46R-2, 0-15
G-4	857C	48R-1, 132-147
G-6	857C	49R-1 135-150
G-21	857C	49R-1, 135-150
G-19	857C	62R-1, 142-150
G-5	857D	12R-1, 16-20
G-7	857D	12R-1, 16-20
G-10	858C	10X-CC, 30-35
G-11	858C	11R-1, 0-10
G-6	858C	12X-1, 131-145
G-5	858D	6X-1, 96-105
G-13	858F	9R-CC, 3-5
G-9	858F	11R-1, 0-3
G-12	858F	18R-1, 65-72
G-2	858F	19R-1, 9-12
G-15	858F	21R-1, 9-13
G-7	858F	25R-1, 2-8

result from dissolution of carbonates and/or anhydrite during sample handling, based on corresponding increases in the concentrations of alkalinity and sulfate. As with Na, data for K, Mg, and Ca from samples with chlorinity greater than 100 mmol/kg are useful for estimating in-situ concentrations.

Dilution with distilled water, precipitation reactions, and sample handling at room temperature cause GRIND samples to have generally lower concentrations of alkalinity, sulfate, and dissolved silica than squeezed samples (Fig. 6). The difference in the alkalinity prob-

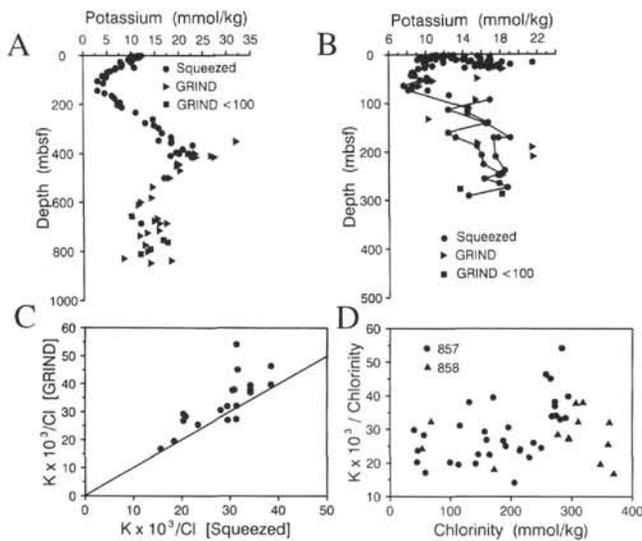


Figure 3. Profiles of K from squeezed and GRIND samples, including GRIND samples with chlorinity less than 100 mmol/kg. **A.** Site 857. GRIND samples have been corrected to a chlorinity of 590 mmol/kg. **B.** Site 858. GRIND samples have been corrected to a chlorinity of 565 mmol/kg. Lines connect samples from Holes 858A and 858F. **C.** Plot of the ratio of K to chlorinity in GRIND samples vs. squeezed samples. The slope of the line is 1.0. **D.** The ratio of K to chlorinity in GRIND samples vs. chlorinity.

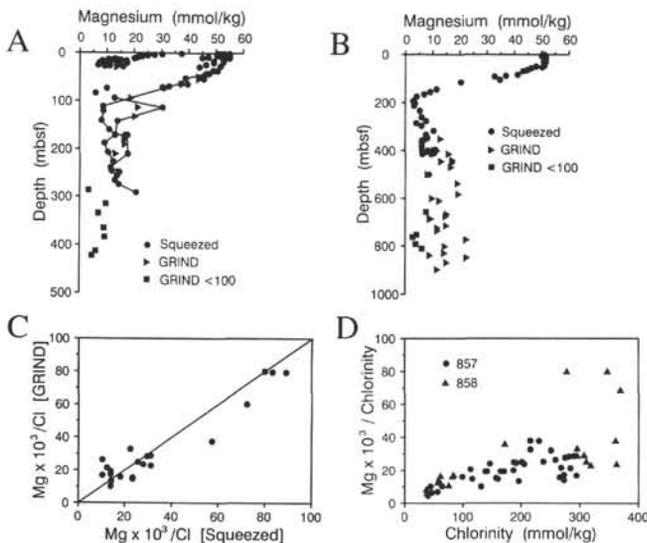


Figure 4. Profiles of Mg from squeezed and GRIND samples, including GRIND samples with chlorinity less than 100 mmol/kg. **A.** Site 857. GRIND samples have been corrected to a chlorinity of 590 mmol/kg. **B.** Site 858. GRIND samples have been corrected to a chlorinity of 565 mmol/kg. Lines connect samples from Holes 858A and 858F. **C.** Plot of the ratio of Mg to chlorinity in GRIND samples vs. squeezed samples. The slope of the line is 1.0. **D.** The ratio of Mg to chlorinity in GRIND samples vs. chlorinity.

ably results from differential rates of carbonate precipitation and dissolution during sample handling. The most dilute GRIND samples (<200 mmol Cl/kg) have higher alkalinities (Fig. 6B), suggesting that these samples are either better preserved or are more affected by dissolution of calcium carbonate. Likewise, the lower concentrations of sulfate probably result from differences in the rate of inorganic precipitation-dissolution reactions. Cranston (1991) found that dilution may lower the concentration of sulfate, but he did not attribute

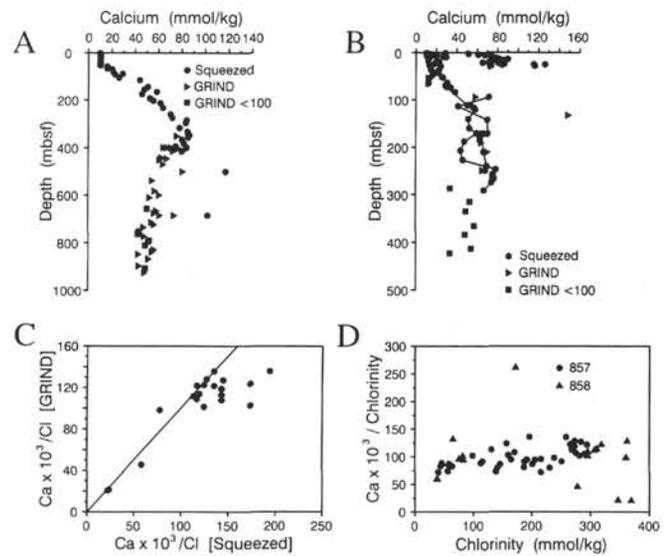


Figure 5. Profiles of Ca from squeezed and GRIND samples, including GRIND samples with chlorinity less than 100 mmol/kg. **A.** Site 857. GRIND samples have been corrected to a chlorinity of 590 mmol/kg. **B.** Site 858. GRIND samples have been corrected to a chlorinity of 565 mmol/kg. Lines connect samples from Holes 858A and 858F. **C.** Plot of the ratio of Ca to chlorinity in GRIND samples vs. squeezed samples. The slope of the line is 1.0. **D.** The ratio of Ca to chlorinity in GRIND samples vs. chlorinity.

this to a specific reaction or exchange process. Anomalously high ratios of sulfate to chlorinity result from dissolution of calcium sulfate during sample handling and processing, as documented by the Shipboard Scientific Party (1992). The presence of sulfate in these samples may reflect contamination with seawater introduced through fractures created during drilling. Based on the discussion above, both the alkalinity and sulfate data obtained using the GRIND technique are suspect. Cranston (1991) found that concentrations of dissolved silica increased in diluted samples, in contrast to our data (Fig. 6E). This difference probably reflects the in-situ and processing temperatures. All of the pore-water GRIND samples from Leg 139 were taken at depths where the temperature exceeds 50°C, about the temperature at which sampling artifacts lower the concentration of dissolved silica below in-situ values (Wheat and Tribble, this volume). Thus, measurements of dissolved silica in pore waters from Leg 139 obtained by both squeezed and GRIND techniques are not representative of in-situ values and will not be discussed further.

Minor and Trace Ions

At Site 857 the general trend between GRIND and squeezed concentrations of Sr is similar to that for Mg (Figs. 3C and 7C). Dilution during the GRIND technique causes ion exchange which removes Sr from pore waters at Site 857 (Fig. 7D). The greatest effect is observed in GRIND samples from Site 857 with chlorinity less than about 100 mmol/kg (Fig. 7D). Concentrations of Sr in GRIND samples from Site 858 are much greater than those in squeezed samples (Fig. 7C). The ratio of Sr from GRIND samples to Sr in squeezed samples is about 3.8 for Site 858 compared to less than 1 for Site 857. These high GRIND values must be caused by dissolution reactions during the GRIND technique. Although the dissolution reactions are unknown, differences between Sites 857 and 858 could be a result of the Sr-bearing minerals at each site. Even though sediment or rock from Site 857 contains about twice as much Sr than sediment or rock from Site 858 (Goodfellow and Peter, this volume), the Sr at Site 858 is probably in secondary minerals that readily dissolve during dilution, whereas Sr at Site 857 is probably in primary minerals that are more resistant to dissolution. Ion exchange in samples from Site 858

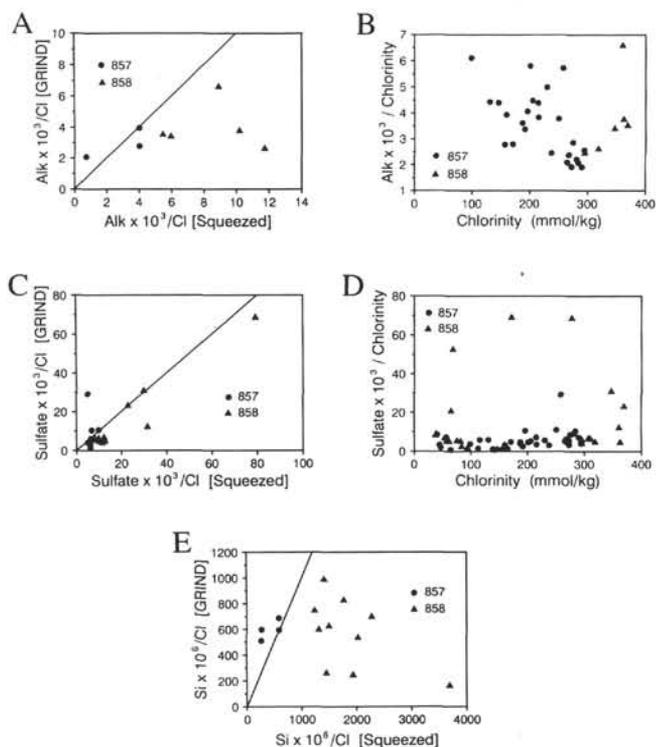


Figure 6. Plots of the alkalinity (A), sulfate (C), and dissolved silica (E) to chlorinity ratio of GRIND samples vs. squeezed samples. The slopes of the lines are 1.0. The ratio of alkalinity (B) and sulfate (D) to chlorinity in GRIND samples vs. chlorinity.

with chlorinity less than 100 mmol/kg may lower Sr concentration in the GRIND sample (Fig. 7E).

Concentrations of dissolved Ba in GRIND samples are at least 2.4 times greater than those in squeezed samples (Fig. 8). The high and scattered concentrations of Ba in the GRIND samples from Site 857 probably reflect desorption from surfaces during the dilution phase of the GRIND technique (Fig. 8C). Ba concentrations measured in GRIND samples from Hole 858G approach the limits of detection in these low-chlorinity samples, implying that contamination is minimal. Dilution does not appear to remove Ba systematically from samples with chlorinity less than about 100 mmol/kg (Fig. 8D), in contrast to the Mg and Sr data. Based on the large difference between the GRIND and squeezed samples and the observed scatter, the concentrations of Ba in pore waters obtained using the GRIND technique are suspect.

Most concentrations of dissolved Mn in GRIND samples are less than the values measured in squeezed samples (Fig. 9). This decrease is probably caused by oxidation during grinding and squeezing as oxygen is introduced by exchange with the atmosphere and in the deionized distilled water. Oxidized Mn is very insoluble relative to reduced Mn; thus, oxidation of dissolved Mn lowers the concentration in the GRIND pore-water samples. The most diluted GRIND samples (<100 mmol Cl/kg) from Site 857 have lower Mn concentrations than neighboring samples (Fig. 9D), implying that ion-exchange processes may influence the concentration of Mn, or that oxidation reactions are accelerated in the more dilute pore-water samples which have greater concentrations of dissolved oxygen than samples that are less diluted. In either case the Mn data are suspect.

Concentrations of dissolved Rb in GRIND samples are generally higher than values measured in squeezed samples, as was the case for Na (Figs. 1 and 10). Unlike the Na data, concentrations of the monovalent cation Rb do not increase in samples with chlorinity less than about 100 mmol/kg, and yet concentrations of Rb may actually be less

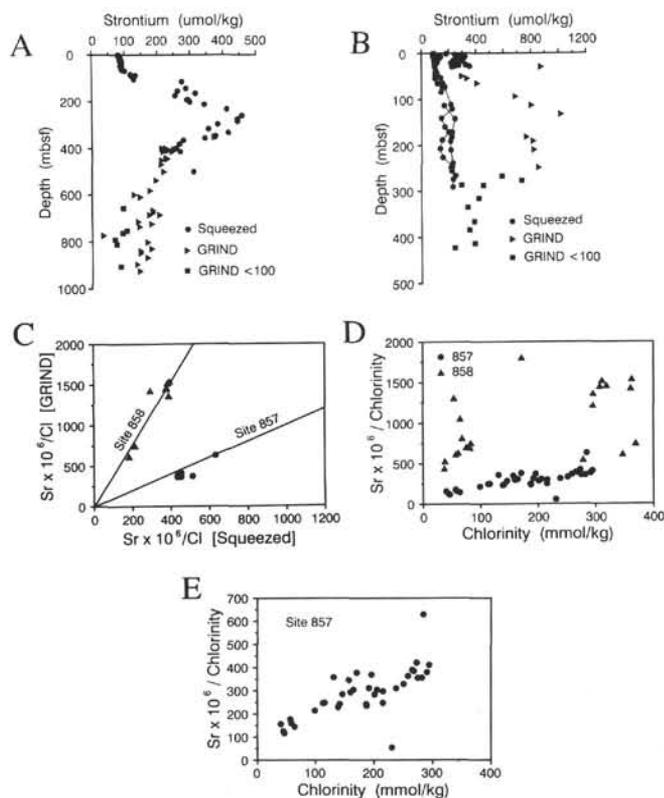


Figure 7. Profiles of Sr from squeezed and GRIND samples, including GRIND samples with chlorinity less than 100 mmol/kg. A. Site 857. GRIND samples have been corrected to a chlorinity of 590 mmol/kg. B. Site 858. GRIND samples have been corrected to a chlorinity of 565 mmol/kg. Lines connect samples from Holes 858A and 858F. C. Plot of the ratio of Sr to chlorinity in GRIND samples vs. squeezed samples. The slopes of the lines are 1.0 and 3.8. D. The ratio of Sr to chlorinity in GRIND samples vs. chlorinity. E. The ratio of Sr to chlorinity in GRIND samples vs. chlorinity.

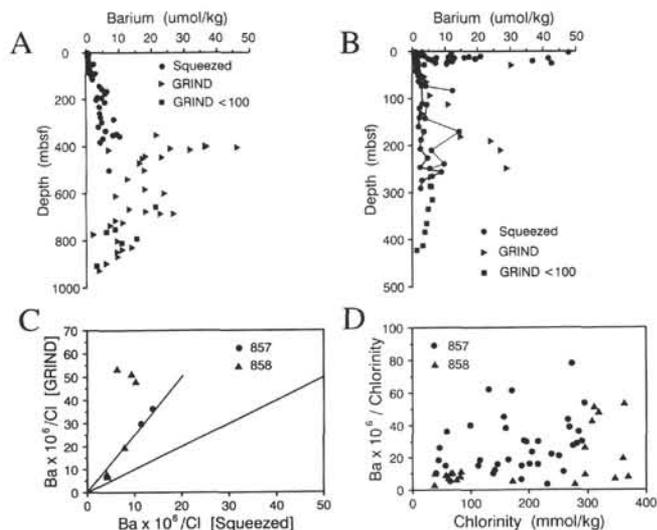


Figure 8. Profiles of Ba from squeezed and GRIND samples, including GRIND samples with chlorinity less than 100 mmol/kg. A. Site 857. GRIND samples have been corrected to a chlorinity of 590 mmol/kg. B. Site 858. GRIND samples have been corrected to a chlorinity of 565 mmol/kg. Lines connect samples from Holes 858A and 858F. C. Plot of the ratio of Ba to chlorinity in GRIND samples vs. squeezed samples. The slopes of the lines are 1.0 and 2.4. D. The ratio of Ba to chlorinity in GRIND samples vs. chlorinity.

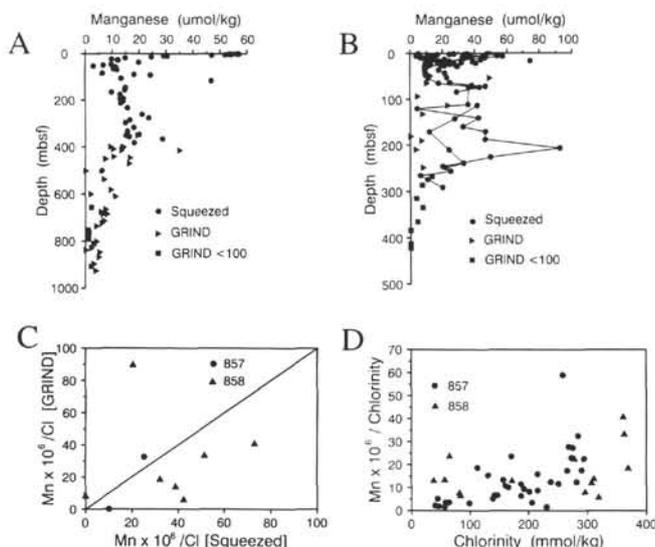


Figure 9. Profiles of Mn from squeezed and GRIND samples, including GRIND samples with chlorinity less than 100 mmol/kg. **A.** Site 857. GRIND samples have been corrected to a chlorinity of 590 mmol/kg. **B.** Site 858. GRIND samples have been corrected to a chlorinity of 565 mmol/kg. Lines connect samples from Holes 858A and 858F. **C.** The ratio of Mn to chlorinity in GRIND samples vs. squeezed samples. The slope of the line is 1.0. **D.** The ratio of Mn to chlorinity in GRIND samples vs. chlorinity.

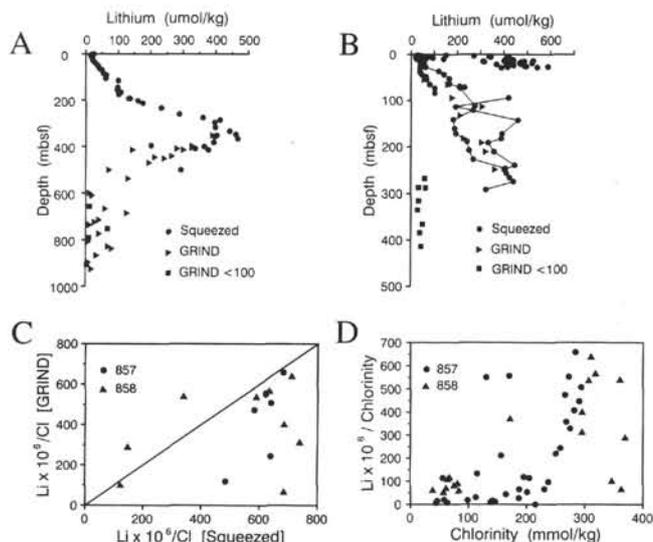


Figure 11. Profiles of Li from squeezed and GRIND samples, including GRIND samples with chlorinity less than 100 mmol/kg. **A.** Site 857. GRIND samples have been corrected to a chlorinity of 590 mmol/kg. **B.** Site 858. GRIND samples have been corrected to a chlorinity of 565 mmol/kg. Lines connect samples from Holes 858A and 858F. **C.** The ratio of Li to chlorinity in GRIND samples vs. squeezed samples. The slope of the line is 1.0. **D.** The ratio of Li to chlorinity in GRIND samples vs. chlorinity.

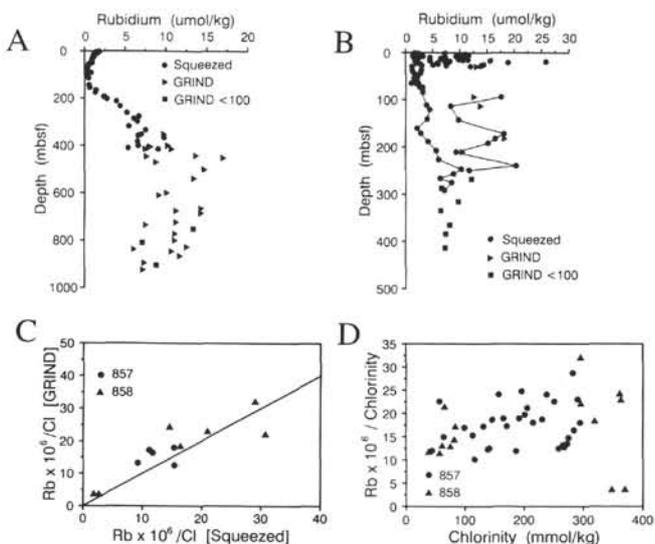


Figure 10. Profiles of Rb from squeezed and GRIND samples, including GRIND samples with chlorinity less than 100 mmol/kg. **A.** Site 857. GRIND samples have been corrected to a chlorinity of 590 mmol/kg. **B.** Site 858. GRIND samples have been corrected to a chlorinity of 565 mmol/kg. Lines connect samples from Holes 858A and 858F. **C.** The ratio of Rb to chlorinity in GRIND samples vs. squeezed samples. The slope of the line is 1.0. **D.** The ratio of Rb to chlorinity in GRIND samples vs. chlorinity.

than expected in samples with chlorinity less than about 100 mmol/kg (Fig. 10D). Variation in the concentration of Rb in GRIND samples from Site 857 compared with the tight trend observed in the squeezed data illustrates the composite of artifacts that affect concentrations of Rb in GRIND samples (Figs. 10A and 10B). Although some scatter exists in the profiles (Figs. 10A and 10B), concentrations of Rb in pore waters from the GRIND technique appear to be representative of the in-situ concentrations.

In contrast to Na, K, and Rb, concentrations of dissolved Li in GRIND samples are generally less than the values measured in squeezed samples (Fig. 11). Either (1) dilution of GRIND samples to a final sample chlorinity that is below about 250 mmol/kg results in reactions that remove about 75% of the dissolved Li from the sample, or (2) concentrations of Li in samples retrieved below the first sill in Site 857 (471 mbsf) and below the start of lithologic Unit V (mafic extrusive rock) in Holes 858F and 858G (267 mbsf) are generally lower than concentrations in the cooler overlying sediment. Because the Li data are unlike the Na, K, and Rb data and because concentrations of Li generally increase downhole in sediments with intruded sills (Gieskes et al., 1982), we suggest that dilution of pore waters during the GRIND technique greatly impacts the concentration of dissolved Li. This implies the GRIND data for Li are suspect.

Concentrations of dissolved B are generally lower in GRIND samples than in squeezed samples (Fig. 12). Similar to the Li data, dilution of samples with chlorinity less than about 250 mmol/kg probably causes the removal of about half of the dissolved B from the sample (Fig. 12D); however, most of the low-chlorinity and B concentrations are in samples retrieved from below the first sill in Site 857 and below the start of lithologic Unit V in Holes 858F and 858G. These are generally lower than concentrations in the cooler overlying sediment. Thus, as for Li, the observed B/chlorinity vs. chlorinity trend may reflect changes in the in-situ concentration with depth and not artifacts incurred during sample handling. Until one of the two possibilities can be validated, B data should remain suspect.

CONCLUSIONS

Concentrations of Mg, Ca, Na, K, and Rb in GRIND samples from Sites 857 and 858 and Sr in GRIND samples from Site 857 are comparable to values from squeezed samples. These good correlations imply that the GRIND technique is a useful tool for obtaining reliable information on the chemical composition of pore water from indurated and hydrothermally altered sediment and basalt. We have made no attempt to statistically treat these correlations because much of the data are centered about a small concentration range and because at present this technique should only be used to estimate pore-water-

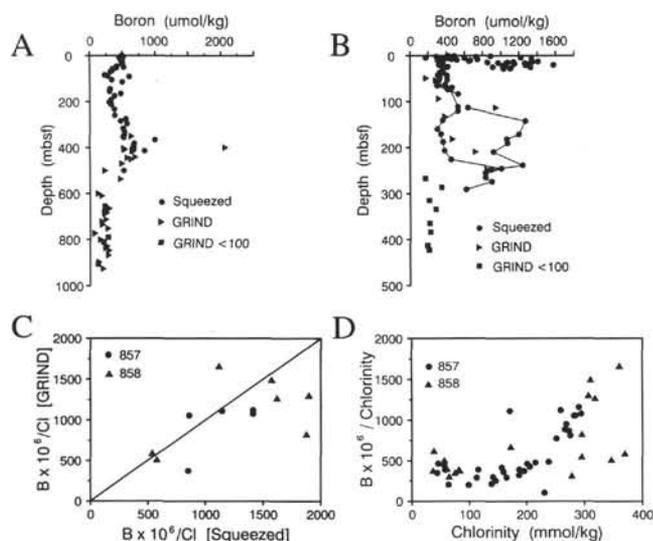


Figure 12. Profiles of B from squeezed and GRIND samples, including GRIND samples with chlorinity less than 100 mmol/kg. **A.** Site 857. GRIND samples have been corrected to a chlorinity of 590 mmol/kg. **B.** Site 858. GRIND samples have been corrected to a chlorinity of 565 mmol/kg. Lines connect samples from Holes 858A and 858F. **C.** The ratio of B to chlorinity in GRIND samples vs. squeezed samples. The slope of the line is 1.0. **D.** The ratio of B to chlorinity in GRIND samples vs. chlorinity.

concentration, until more is known about the effects of different sediment types and in-situ conditions on the chemical reactions that occur during the GRIND procedure. The reproducibility of the GRIND method has been assessed by determining the average standard deviation of the concentration to chlorinity ratio for the one sample that was analyzed in triplicate and the two samples that were analyzed in duplicate. The average standard deviations for Ca, Na, K, and Sr are below 6%. The average standard deviations for Mg and Rb are 17% and 9%, respectively.

In contrast to Mg, Ca, Na, K, Sr, and Rb, concentrations of alkalinity, sulfate, dissolved silica, Ba, Mn, Li, and B in most GRIND samples do not correlate well with concentrations measured in pore waters from squeezed samples, because of precipitation, dissolution, and ion-exchange reactions that occur during sample processing. The average standard deviations of these analyses on GRIND samples are between 11% and 26% for alkalinity, Si, Ba, Mn, B, and Li, and 43% for sulfate.

The GRIND technique produces the most reliable results when the sample chlorinity is greater than about 100 mmol/kg. Ion exchange in

samples with chlorinity lower than 100 mmol/kg may provide Na to the pore waters while removing Mg, Ca, and Sr. Further study is required to confirm this result.

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REFERENCES*

- Barnes, R.O., 1988. ODP in-situ fluid sampling and measurement: a new wireline tool. In Masche, A., Moore, J.C., et al., *Proc. ODP, Init. Repts.*, 110: College Station, TX (Ocean Drilling Program), 55–63.
- Cranston, R.E., 1991. Testing a higher resolution interstitial-water method for the Ocean Drilling Program. In Barron, J., Larsen, B., et al., *Proc. ODP, Sci. Results*, 119: College Station, TX (Ocean Drilling Program), 393–400.
- Davis, E.E., Mottl, M.J., Fisher, A.T., et al., 1992. *Proc. ODP, Init. Repts.*, 139: College Station, TX (Ocean Drilling Program).
- de Lange, G.J., Cranston, R.E., Hydes, D.H., and Boust, D., 1992. Extraction of pore water from marine sediments: a review of possible artifacts with pertinent examples from the North Atlantic. *Mar. Geol.*, 109:53–76.
- Gieskes, J.M., Elderfield, H., Lawrence, J.R., Johnson, J., Meyers, B., and Campbell, A., 1982. Geochemistry of interstitial waters and sediments, Leg 64, Gulf of California. In Curay, J.R., Moore, D.G., et al., *Init. Repts. DSDP*, 64 (Pt. 2): Washington (U.S. Govt. Printing Office), 675–694.
- Gieskes, J.M., and Peretsman, G., 1986. Water chemistry procedures aboard *JOIDES Resolution*—some comments. *ODP Tech. Note*, 5.
- Manheim, F.T., and Sayles, F.L., 1974. Composition and origin of interstitial waters of marine sediments based on deep sea drill cores. In Goldberg, E.D. (Ed.), *The Sea* (Vol. 5): New York (Wiley Interscience), 527–568.
- Nigrini, A., 1970. Diffusion in rock alteration systems: I. Prediction of limiting equivalent ionic conductances at elevated temperatures. *Am. J. Sci.*, 269:65–91.
- Shipboard Scientific Party, 1992. Explanatory notes. In Davis, E.E., Mottl, M.J., Fisher, A.T., et al., *Proc. ODP, Init. Repts.*, 139: College Station, TX (Ocean Drilling Program), 55–97.

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