

24. ALKALI AND Sr ISOTOPE GEOCHEMISTRY OF WATERS COLLECTED FROM BASALTIC BASEMENT, DEEP SEA DRILLING PROJECT HOLE 504B, COSTA RICA RIFT¹

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ABSTRACT

Basalt formation waters collected from Hole 504B at sub-basement depths of 194, 201, 365, and 440 meters show inverse linear relationships between $^{87}\text{Sr}/^{86}\text{Sr}$ and Ca, $^{87}\text{Sr}/^{86}\text{Sr}$ and Sr, and K and Ca. If the Ca content of a fully reacted formation water end-member is assumed to be 1340 ppm, the K, Sr, and $^{87}\text{Sr}/^{86}\text{Sr}$ values for the end-member are 334 ppm, 7.67 ppm, and 0.70836, respectively. With respect to contemporary seawater at Hole 504B, K is depleted by 13%, Sr is enriched by 2.7%, and $^{87}\text{Sr}/^{86}\text{Sr}$ is depleted by 0.8%. The Sr/Ca ratio of the formation water (0.0057) is much lower than that of seawater (0.018) but is similar to the submarine hot spring waters from the Galapagos Rift and East Pacific Rise and to geothermal brines from Iceland. At the intermediate temperatures represented by the Hole 504B formation waters (70°–105°C), the interaction between seawater and the ocean crust produces large solution enrichments in Ca, the addition of a significant basalt Sr isotope component accompanied by only a minor elemental Sr component, and the removal from solution of seawater K. The Rb, Cs, and Ba contents of the formation waters appear to be affected by contamination, possibly from drilling muds.

INTRODUCTION

The thermally driven convection of seawater through newly formed ocean crust is now a well-recognized phenomenon (Elder, 1965; Anderson et al., 1977; Wolery and Sleep, 1976). This convection process has significant potential for influencing the chemistry of seawater through the interaction of the heated seawater with the basalt of the ocean crust. A complete understanding of the chemical fluxes involved in this process depends on knowing the duration of convection and the chemistry of the fluids and solid alteration phases that result from the seawater/basalt interaction. The chemistry of solid alteration phases has received considerable attention recently (e.g., Andrews, 1977; Böhlke et al., 1980; Honnorez et al., 1979; Humphris and Thompson, 1978a, b; Staudigel, Hart, et al., 1981; Staudigel, Muehlenbachs, et al., 1981; Mevel, 1980; Pritchard, 1980; Robinson et al., 1977). The chemistry of the circulating fluids has been studied only in two areas of the ridge system where hot springs of fluids exit the crust (Edmond, Measures, Mangum, et al., 1979; Edmond, Measures, McDuff, et al., 1979; Edmond, 1981); the fluids were sampled directly during both studies. *In situ* sampling of crustal formation waters during the drilling at Hole 504B, which is in 5.9 m.y. old ocean crust on the Costa Rica Rift, provided another opportunity to study the chemistry of crustal fluids directly. We report here the K, Rb, Cs, Ba, Sr, and Sr isotope chemistry of the Hole 504B formation waters and compare the chemistry of these moderate temperature fluids (less than ~120°C) with the

chemistry of the high temperature hot spring fluids (~350°C) reported by Edmond et al.

SAMPLING AND ANALYTICAL TECHNIQUES

A detailed description of the *in situ* sampling at Hole 504B is given by Mottl et al. (this volume). At first the *in situ* water samples were believed to represent mixtures of formation waters resident in the basaltic crust and the seawater used for drilling. However, the results of tritium analyses of a number of the samples demonstrated that no true formation water had been retrieved (Mottl et al., this volume). Apparently all the samples were in fact surface seawater that had been pumped into the hole some 5 days before the *in situ* sampling. This water, which had reacted with the basalt at temperatures of ~70°C, had a chemical signature that was markedly different from that of surface seawater. The chemistry of the reacted water may also differ from that of true formation water, depending on the extent to which the various elements have approached the true formation water's quasi equilibrium. As discussed by Mottl, Anderson, et al. (this volume), a comparison of Ca and Mg in the calculated end-member for this reacted seawater with the Ca and Mg in pore waters from the sediments immediately overlying the basalt in Hole 504B suggests that at least the concentration of these two elements may closely approximate that expected for a fully reacted true formation water. Additional support for this idea comes from the chemistry of the *in situ* waters collected during the deepening of Hole 504B on Leg 70; the Ca and Mg contents of these waters (M. J. Mottl, Leg 83 shipboard report) lie along the same mixing curve as the shallower samples, despite the fact that they were collected within 24 hours after drilling was stopped at each depth. These deeper waters were also at a higher temper-

¹ Cann, J. R., Langseth, M. G., Honnorez, J., Von Herzen, R. P., White, S. M., et al., *Init. Repts. DSDP*, 69: Washington (U.S. Govt. Printing Office).

ature when retrieved (~110°C), which would presumably lead to more rapid interaction rates than those of the shallower samples. In the following material we will discuss the chemistry of these collected waters as if they in fact have a true formation water component, though the above considerations should be kept firmly in mind throughout.

The samples designated PS-A to PS-5 (Table 1) were collected with the Lynes packer and represent a single collection depth (201 m sub-basement). At this depth the water samples contain variable admixtures of the fresh surface seawater used in drilling. (Because of the nature of the collection device, Sample PS-A contains the least, and Sample PS-5 the greatest, component of fresh seawater.) The PS series of samples thus lie on mixing lines between the surface seawater and the reacted formation water. Samples IW 175 and IW 194, which were acquired with the Barnes *in situ* sampler and also represent mixtures of surface seawater and reacted formation water, were acquired at depths of 365 and 440 meters sub-basement. Aliquots of these samples were obtained through the courtesy of Dr. Michael Bender. Sample GO-2, which was collected with the Gearhart-Owen wireline sampler and is also a mixture of surface seawater and formation water, was acquired at a depth of 194 meters sub-basement. During the process of aliquoting, storing, and spiking these water samples, some evaporation took place; the corrections for evaporation are discussed in the following material.

The aliquots (~1 ml) received for analysis were spiked with a mixed spike containing isotopically enriched ^{40}K , ^{87}Rb , ^{135}Cs , ^{136}Ba , and ^{84}Sr . Conventional cation resin exchange techniques (Aldrich et al., 1953) were used to perform chemical separations; mass spectrometry of the isotope dilution mixtures was performed on the 9-in. fully automated instrument at M.I.T. Blanks for the total analytical procedure were 5 ng K, 0.02 ng Rb, 0.5 pg Cs, 2 ng Ba, and 0.1 ng Sr; except for Ba, these blanks were negligible, ranging from 2×10^{-3} to 1×10^{-5} of the sample element carried in the procedure. The Ba blank was 20% of the surface seawater analysis and $\leq 2\%$ of the others; all values were corrected for this blank. Spikes were calibrated against gravimetric solutions of high-purity salts, which had accuracies of $\leq 0.3\%$ for K, Ba, and Sr (elements for which fractiona-

tion corrections were possible), $\leq 0.6\%$ for Rb (for which fractionation was limited), and $\leq 3\%$ for Cs (for which gravimetry was limited). Exclusive of the effects of evaporation (a problem discussed in the material following), the accuracy of the reported values is $\leq 0.5\%$ for K and Sr, $\leq 1\%$ for Rb, and $\pm 3\%$ for Cs and Ba (except for Ba in the surface seawater, which is no better than $\pm 25\%$). Because of the use of a mixed element spike, the precision of the concentrations relative to each other is considerably better than the accuracy of the individual elements. Details of the chemical and mass spectrometric procedures are given in Hart and Brooks (1977).

Sr isotope analyses were performed on NIMA-B, the 9-in. mass spectrometer at M.I.T. Two-hour runs were sufficient to produce precisions of $\leq 0.01\%$; standardization was achieved by using the Eimer and Amend (E & A) Sr standard, which had a mean value, based on multiple runs, of 0.70783 ± 2 . The values reported here have been normalized to an E & A value of 0.70800. The surface seawater sample analyzed has a normalized value of 0.70912, which compares well with the similarly E & A adjusted composite seawater value of 0.70907 reported by Hildreth and Henderson (1971). High precision analyses of seawater reported by Papanastassiou and Wasserburg (1978) resulted in a value of 0.70909; unfortunately, no E & A value is available with these data for normalization.

There remains the question of whether the water retrieved from the sampling devices has been contaminated during the sampling process in any way. The uniformity of the values of K, Sr, and $^{87}\text{Sr}/^{86}\text{Sr}$ from different samples suggests that insofar as these elements are concerned the water is not significantly contaminated. The values of Rb, Cs, and Ba are more problematic, inasmuch as they vary from sample to sample; the potential for the contamination of the measurement of these elements is obviously considerable, because bentonite-barite muds were used during various stages of the drilling operation. See also the discussion by Mottl, Anderson, et al. (this volume).

RESULTS

The concentrations of K, Rb, Cs, Ba, Sr, and the $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios for the various water samples

Table 1. K, Rb, Cs, Ba, and Sr concentrations and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of Hole 504B formation water.

Sample	Sub-basement Depth (m)	K	Rb	Cs	Ba	Sr	$^{87}\text{Sr}/^{86}\text{Sr}$	Ca ^a	K/Rb	K/Cs ($\times 10^6$)	K/Sr	K/Ba ($\times 10^3$)
Surface water		376.9	0.1048	0.301	0.009	7.47	0.70912 \pm 7	409	3597	1.25	50.5	41.3
PS-A	201	363.2	0.1122	0.485	0.143	7.52	0.70889 \pm 6	738	3238	0.75	48.3	2.54
PS-1	201	360.1	0.1123	0.411	0.106	7.52	0.70883 \pm 7	702	3207	0.88	47.9	3.38
PS-2	201	376.2	0.1099	0.329	—	7.54	0.70909 \pm 8	517	3424	1.14	49.9	—
PS-4	201	—	—	—	—	7.46	0.70909 \pm 3	461	—	—	—	—
PS-5	201	372.6	0.1068	0.335	0.095	7.45	0.70906 \pm 7	449	3489	1.11	50.0	3.91
GO-2	194	384.7	0.1206	0.843	0.323	7.70	0.70898 \pm 6	585	3190	0.46	49.9	1.19
IW 175	365	390.1	0.1092	0.553	—	7.66	0.70904 \pm 5	462	3570	0.705	50.9	—
IW 194	440	460.4	0.1549	1.402	0.354	9.33	0.70898 \pm 5	535	2971	0.33	49.3	1.30

Note: All concentrations are in ppm, except Cs, which is in ppb. Concentrations are corrected (+0.67%) for HCl dilution. $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are normalized to 0.70800 for E & A standard; errors are $\pm 2\sigma$.

^a Ca concentrations are from Mottl, Anderson, et al. (this volume and Leg 83 shipboard report).

are given in Table 1. Also listed are Ca concentrations, which can be used to determine the relative proportions of surface seawater and reacted formation water in the samples. The best estimate of the Ca content of the reacted formation water is ~1340 ppm (Mottl et al., this volume), as opposed to 409 ppm in the surface seawater. The proportion of formation water in the samples in Table 1 thus ranges from 4% (in Sample PS-5) to 35% (in Sample PS-A). The Sr isotope ratios and the ratios K/Rb, K/Cs, K/Sr, and K/Ba are plotted versus Ca content in Figures 1 to 3. With the exception discussed hereafter, the PS series samples all fall along a single curve (or mixing line), as they should, since they are points along a curve with the same end-members (mixtures of the same two substances)—formation water and surface seawater. The samples from other sub-basement depths (GO-2, IW 175, and IW 194) fall on the same mixing line as the PS series samples in the K/Sr and $^{87}\text{Sr}/^{86}\text{Sr}$ plots but fall significantly below the mixing lines in the K/Rb, K/Cs, and K/Ba plots. Taken at face value, this means that the end-member formation waters at all four depths are probably similar in K, Sr, $^{87}\text{Sr}/^{86}\text{Sr}$, and Ca content but different in Rb, Cs, and Ba. This interpretation seems unlikely, however, since Sample GO-2 is from nearly the same depth as the samples in the PS series. In view of the drilling procedures mentioned previously, it seems more likely that the different levels of Rb, Cs, and Ba at the different sampling depths simply reflect contamination.

In the PS series samples, the contamination of the water with excess amounts of Ba is indisputable, since Sample PS-5 does not lie on the mixing line between seawater and sample PS-A (Fig. 3), as it would if one end-member were uncontaminated seawater. The mixing line

actually defined by Samples PS-A, PS-1, and PS-5 suggests a Ba content of ~0.08 ppm for the seawater end-member; this is higher than the Ba content measured in the surface seawater (0.009 ppm), and in fact is higher than the Ba content in any other seawater by a factor of 4 to 16 (Bernat et al., 1972).

The content of Rb and Cs in the PS series does fall on a mixing line through surface seawater and is thus consistent with the assumption of uncontaminated seawater as one end-member. This is to be expected, inasmuch as surface seawater was pumped through the drill hole for 1 hour shortly before the packer sample was taken. It is difficult to prove, however, that the other end-member (formation water) was not mixed with contaminated seawater at some stage prior to sampling, this contaminated end-member then being mixed with pure seawater during the sampling. Samples GO-2 and IW 194 define a negative trend in Rb-Ca and Cs-Ca plots (not shown), suggesting a mixture between a formation water end-member and a seawater end-member contaminated by Rb and Cs. This is consistent with the fact that the pumping of surface seawater through the hole was stopped for 3 days before taking Sample GO-2 and 1 day before taking Samples IW 175 and IW 194. Finally, although the K/Rb trends in Figure 2 would extrapolate to a reasonable end-member (relative to the hot spring data of Edmond, Measures, McDuff, et al., 1979), it is noteworthy that K decreases with Ca, whereas Rb and Cs increase with Ca. Although it is not impossible that the three alkalis would behave in opposite directions like this, it is more likely that the increased Rb and Cs contents reflect contamination.

If we assume that the Cs contents are a result of contamination and that the contaminant is derived from

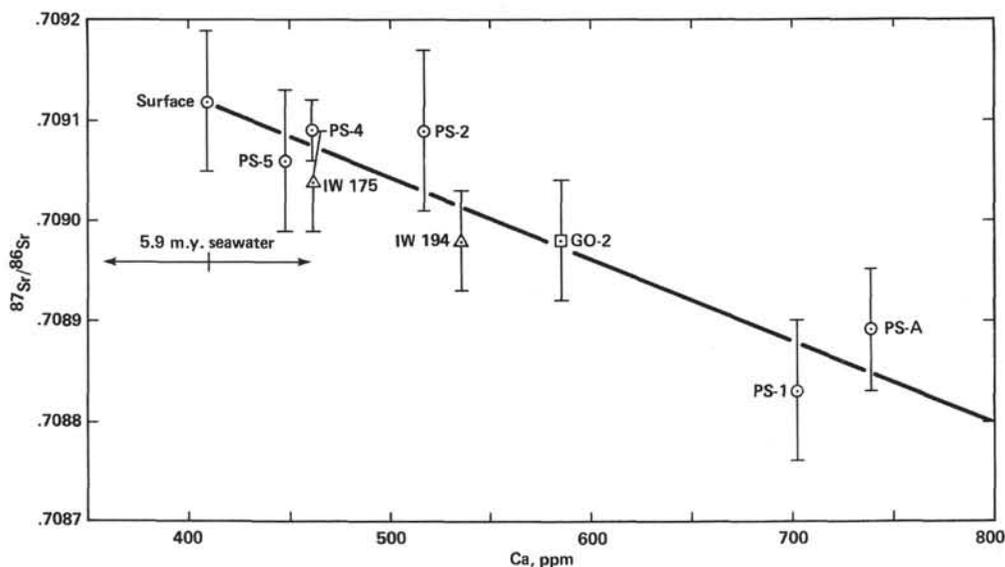


Figure 1. $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of formation water mixtures versus Ca content. Formation waters sampled at four depths in basement all fall on a single mixing line between modern seawater and a hypothetical fully reacted formation water end-member (at Ca \approx 1340 ppm). Open circles, 201-meter depth; open square, 194-meter depth; open triangles, 365- and 440-meter depth. The Sr isotope composition of 5.9 m.y. old seawater is shown for comparison. The equation of the mixing line is $^{87}\text{Sr}/^{86}\text{Sr} = 0.70945 - 8.125 \times 10^{-7}\text{Ca}^{\text{pfw}}$ where pfw is pure formation water.

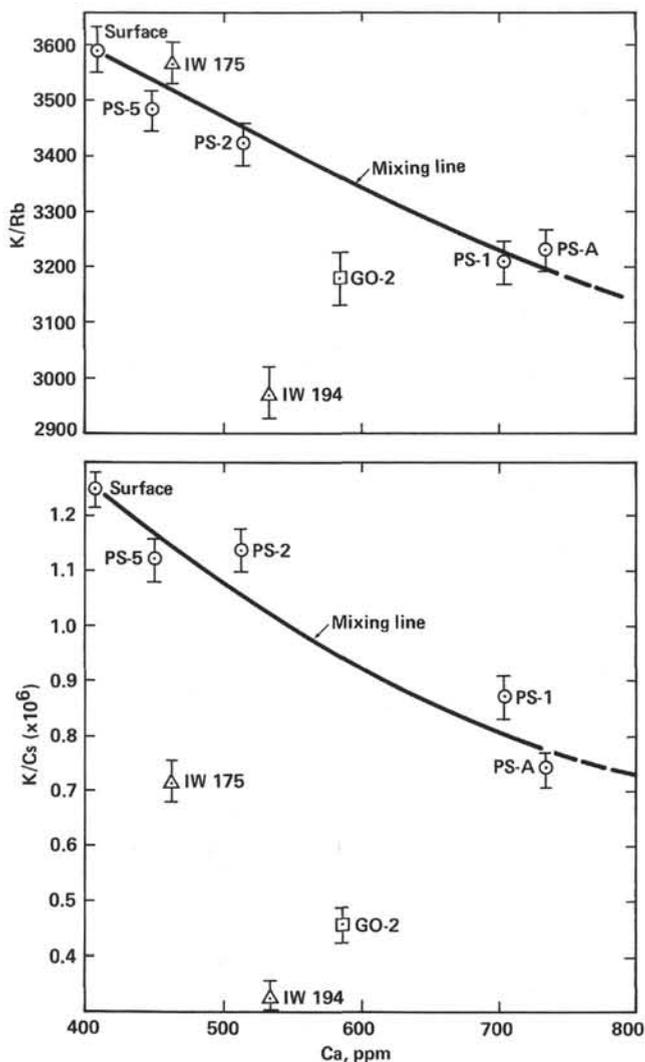


Figure 2. K/Rb and K/Cs ratios of formation water mixtures versus Ca content. Errors in K/Rb and K/Cs are taken to be $\pm 1\%$ and $\pm 3\%$, respectively. The error in Ca is negligible on the scale of this diagram. The curve is a best-fit mixing line to the PS series samples (open circles). Note that the samples from other depths do not fit the PS series mixing line, showing that the end-member alkali ratios for these samples must be different from those for the PS series samples.

clays with typical K/Rb and K/Cs ratios of 250 and 4000 respectively, we can use the Cs contents to estimate the extent to which Rb and K are contaminated. This calculation suggests that K is affected by less than $\sim 0.7\%$ and Rb by less than 10% ; thus, the K data are relatively insensitive to possible contamination relative to the range observed (5%), whereas the Rb effect could be a large part of the range observed ($\sim 20\%$). We conclude that the Rb, Cs, and Ba data must be treated as suspect. The K and Sr data, on the other hand, are unlikely to be seriously affected by contamination, principally because of their high concentrations relative to Cs and Ba. (The K/Cs and Sr/Ba ratios of the waters are several orders of magnitude larger than these ratios in clays, sediments, basalts, and so forth.)

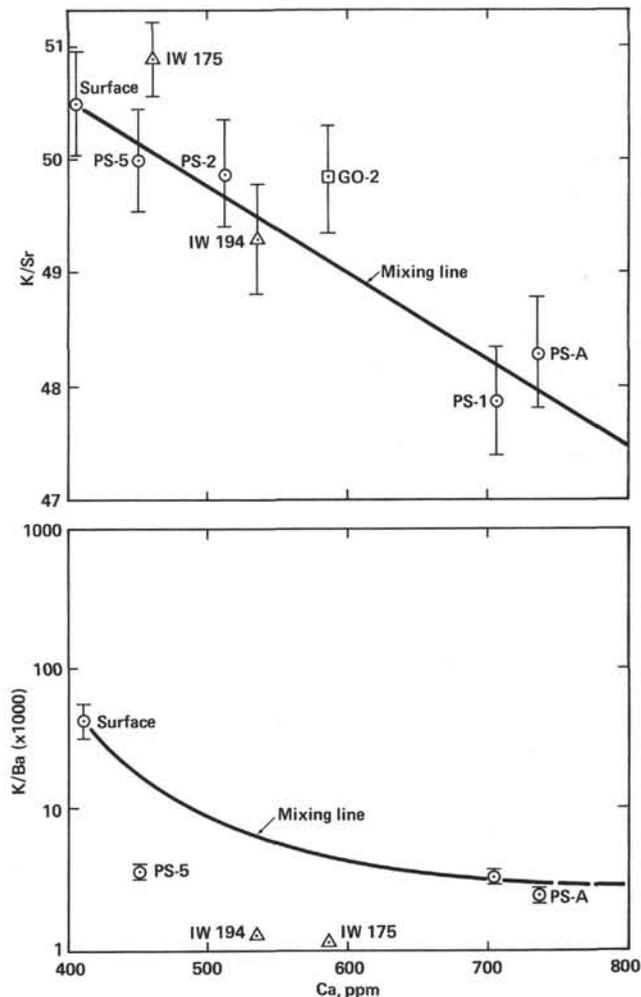


Figure 3. K/Sr and K/Ba ratios of formation water mixture versus Ca content. Errors in K/Sr and K/Ba are taken to be $\pm 1\%$ and $\pm 3\%$, respectively (except for K/Ba for surface water, which is $\pm 25\%$). The various samples approximate a single mixing line for K/Sr versus Ca but not for K/Ba.

Thus far, we have considered the data principally in the form of element ratios to avoid the analytical complications necessary to account for the evaporation that occurred during the handling of the samples. Samples IW 175 and IW 194, which were stored in screw caps before being spiked, are known to have undergone evaporation (note the high Sr concentration of IW 194 relative to the other waters). We made a first-order correction for the effects of evaporation by noting that the K/Sr and $^{87}\text{Sr}/^{86}\text{Sr}$ versus Ca plots suggest a similar formation water end-member for all samples. A plot of Sr versus Ca (Fig. 4) shows that the PS series of samples fit a single mixing line within errors, except for Sample PS-2, which is 0.9% above the line; the other samples, which were subject to evaporation, lie well above the line. The concentrations in Samples PS-2, GO-2, IW 175, and IW 194 were normalized so that all samples fell on the mixing line defined by the other samples in the PS series, which were assumed to be unaffected by evapora-

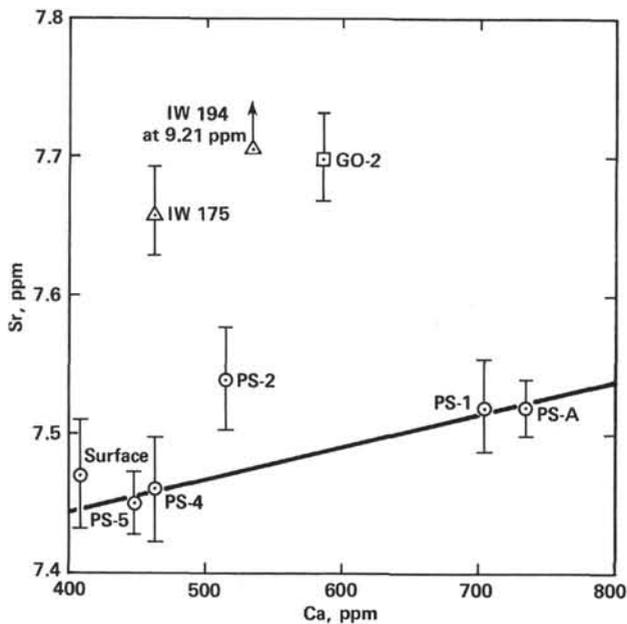


Figure 4. Sr versus Ca content of formation water mixtures. Four samples lie above a simple mixing curve due to evaporation effects during sample handling; otherwise, Sr concentrations are determined with a precision of 0.3% to 0.5%.

tion. The atomic absorption data of Mottl, Anderson, et al. (this volume) confirmed the correctness of this procedure for Samples PS-2 and GO-2. The K contents of the samples normalized in this way are plotted against Ca in Figure 5; the data now fit a single mixing curve within error, except for the data for Samples GO-2 and IW 175, which are slightly (1.6–1.8%) above the line. A plot of $^{87}\text{Sr}/^{86}\text{Sr}$ versus Sr content (Fig. 6) also shows that this simple normalization procedure produces a fit of all samples to a single mixing line. Note also that the mixing lines in Figures 4 to 6 all pass through the surface seawater data, showing that the data are consistent with the expectation, based on the water sampling technique used, that the recovered samples are mixtures of the surface seawater used as drilling fluid and a basalt-reacted formation water.

DISCUSSION

If the Ca concentration in the presumed formation water end-member can be established, the mixing lines in Figures 1 and 4 to 6 can be used to deduce the values of K, Sr, and $^{87}\text{Sr}/^{86}\text{Sr}$ values for the formation water end-member. By using pore water data from the overlying sediments, Mottl et al. (this volume) derived a Ca content of ~1340 ppm for the end-member formation water. The resulting values of K, Sr, and $^{87}\text{Sr}/^{86}\text{Sr}$ for the formation water end-member are as given in Table 2.

The formation waters collected at Hole 504B were at basement temperatures (as measured *in situ*) from 70°C (PS series samples, 201 m) to ~105°C (Sample IW 194, 440 m). They thus represent interaction with the crust at temperatures intermediate between those normally observed at other sites in the upper 500 meters of crust (15–80°C, from smectite oxygen thermometry, Staud-

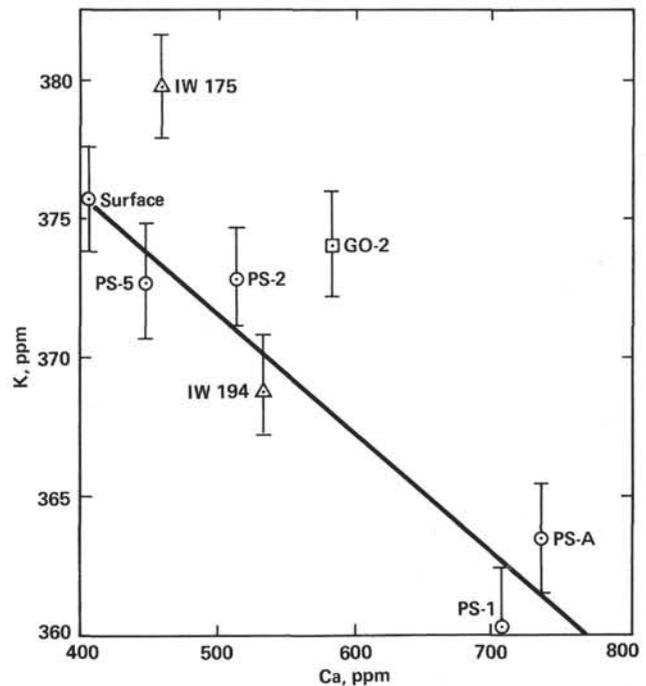


Figure 5. K versus Ca content of formation water mixtures. Analytical error in K is $\pm 0.5\%$. The data for surface water, PS-2, GO-2, IW 175, and IW 194 have been corrected down by 0.997%, 0.991%, 0.972%, 0.974%, and 0.801%, respectively, to account for evaporation (as determined by forcing all data from Fig. 4 to fit a single mixing curve).

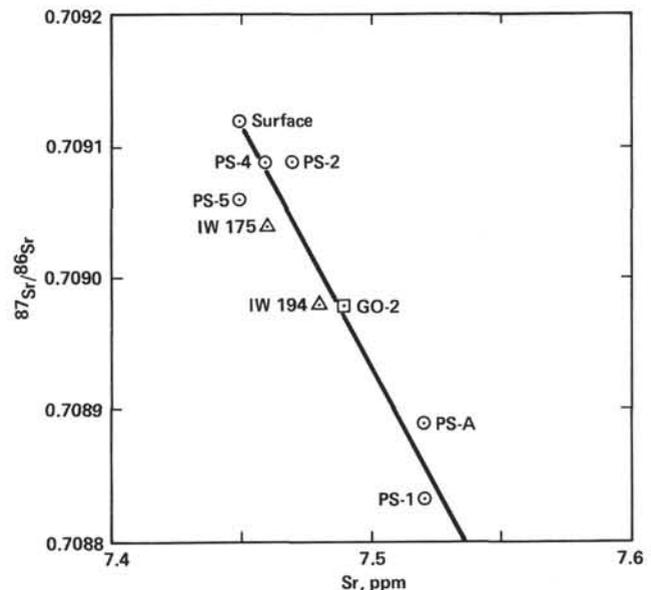


Figure 6. $^{87}\text{Sr}/^{86}\text{Sr}$ versus Sr content of formation water mixtures. Sr contents of some samples have been corrected for evaporation by the factors given in the Figure 5 legend. Analytical uncertainties (not shown) are $\pm 0.5\%$ for Sr concentrations and from ± 3 to $\pm 8 \times 10^{-5}$ for $^{87}\text{Sr}/^{86}\text{Sr}$ (Table 1). The data fit a single mixing line within these analytical uncertainties. Note that this mixing line is not completely independent, because the evaporation corrections were derived by forcing Sr in Figure 4 to fit a single line.

Table 2. Calculated K, Sr, and $^{87}\text{Sr}/^{86}\text{Sr}$ of formation water.

K, ppm	334
Sr, ppm	7.67
$^{87}\text{Sr}/^{86}\text{Sr}$	0.70836
Ca, ppm	1340
K/Sr	43.5
Sr/Ca	0.0057

igel, Muehlenbachs, et al., 1981) and those at the hot springs at the Galapagos Rift and East Pacific Rise (350°C); Edmond, Measures, McDuff, et al., 1979; Edmond, 1981). Study of the low temperature alteration of the crust (Staudigel, Hart, et al., 1981) shows that K will be depleted in circulating fluids by interaction with the crust, Sr will not change significantly, and Ca will be enhanced (with Sr/Ca ratios in the range from 0.001 to 0.008). In addition, the $^{87}\text{Sr}/^{86}\text{Sr}$ component of the solutions will increase as result of the interaction with basalt, leading to $^{87}\text{Sr}/^{86}\text{Sr}$ ratios intermediate between those of seawater (0.7091 today) and basalt (0.7030). Study of the high temperature hot spring solutions shows that K and Ca are enriched in these solutions, Sr is little changed, and a strong Sr isotopic component from the basalt is added to the fluids (Edmond, Measures, Mangum, et al., 1979; Edmond, Measures, McDuff, et al., 1979; Albarede et al., 1980).

The data on the intermediate temperature Hole 504B formation waters are similar to the data from the lower and higher temperature regimes in that Ca is enhanced (by a factor of 3), Sr is little changed (is only 3% higher than seawater), and the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio contains a significant component due to the basalt. The formation water Sr isotope ratio of 0.7084 is lower than that of either modern seawater (0.7091) or seawater 5.9 m.y. old (0.70896; Hart and Staudigel, 1978). However, the K content of the formation water is lower (13%) than seawater, and so these waters are more akin to the low temperature crustal regimes than the high temperature hot spring regimes. This simply reflects the nature of alteration minerals formed in the crust at high versus low temperatures; smectites are predominant at low temperatures (up to ~150°C) and are sinks for alkalis (Staudigel, Hart, et al., 1981), whereas the greenschist facies mineralogy encountered at higher temperatures (chlorite, epidote, etc.) does not provide favorable hosts for the alkalis. Neither a high nor a low temperature mineralogy exerts a significant fractionation effect on Sr (relative to the original basalt; Humphris and Thompson, 1978a, b); thus, the circulating solutions are little changed in Sr concentration compared with seawater. It is obvious, however, that some form of Sr exchange occurs between the seawater and the basalt during the alteration processes, inasmuch as both the low and the high temperature solutions are lower in $^{87}\text{Sr}/^{86}\text{Sr}$ (are more basaltic) than contemporaneous seawater. Only during the latest stages of circulation, some 10 m.y. after crust formation, during which carbonates are the main reaction product of the circulation, do the solu-

tions once again approach pure seawater in Sr isotope composition (Richardson et al., 1980).

The enrichment of Ca in circulating hydrothermal fluids is marked throughout the temperature range, apparently as a result of the low Ca tolerance of most alteration phases other than carbonates. The Sr/Ca ratio of seawater is ~0.018; that of the formation water (Table 2), ~0.0057; that of the Galapagos hot springs, ~0.005 (Edmond, Measures, Mangum, et al., 1979); and that of low temperature (15–50°C) crustal solutions (as recorded by vein calcites, Staudigel, Hart, et al., 1981), 0.001 to 0.008. Thus, hydrothermal solutions over a wide temperature range (15–350°C) have surprisingly uniform Sr/Ca ratios (~0.005), which are lower than seawater by a factor of 3 to 4. Even the 100 to 270°C geothermal brines from Iceland have Sr/Ca ratios similar to the ocean crust solutions discussed above (~0.006; Holland, 1978).

The direct measurement of the Sr isotope ratios in two Hole 504B alteration minerals (a smectite and a calcite/aragonite mixture from ~5 m sub-basement) gave initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of 0.70848 and 0.70866, respectively. Both of these values are lower than that expected for 5.9 m.y. old seawater (0.70896), showing the presence of a basalt-Sr component in the fluids from which these alteration minerals were deposited. However, both of these minerals have $^{87}\text{Sr}/^{86}\text{Sr}$ slightly higher than the value calculated for the formation water end-member (0.7084).

ORIGIN OF FORMATION WATERS

From the tritium data of Mottl et al. (this volume), the formation waters appear to represent present seawater that has reacted with the basaltic rocks of the ocean crust during relatively short-term residence. The chemistry of the formation waters may thus bear the imprint of a complex combination of processes, such as (1) the addition of basaltic components by the direct (congruent) solution of basalt in seawater; (2) the preferential leaching (incongruent solution) of basalt; and (3) the removal of basaltic and seawater components during the precipitation of alteration phases, such as smectite and carbonate. These three processes may not be serial and distinct; they may proceed more or less simultaneously.

The effects of simple congruent solution may be tested by simple mixing calculations. Figure 7 shows the $^{87}\text{Sr}/^{86}\text{Sr}$ versus Ca plot for the formation waters (Fig. 1 data); also shown are congruent solution (mixing) lines for the addition of basalt to both modern and 5.9 m.y. old seawater. The calculated formation water end-member (Table 2) is also plotted, and it is obviously inconsistent with the congruent solution of basalt in present-day seawater. Since the tritium data show that the reacted solution is present-day surface seawater, Figure 7 shows that the reaction has not been one of simple congruent solution, but that Processes 2 and 3 must also have operated to some extent. Although the calculated formation water end-member plots almost precisely on a congruent solution curve for basalt and 5.9 m.y. old seawater, this must be viewed as coincidental in light of the tritium data.

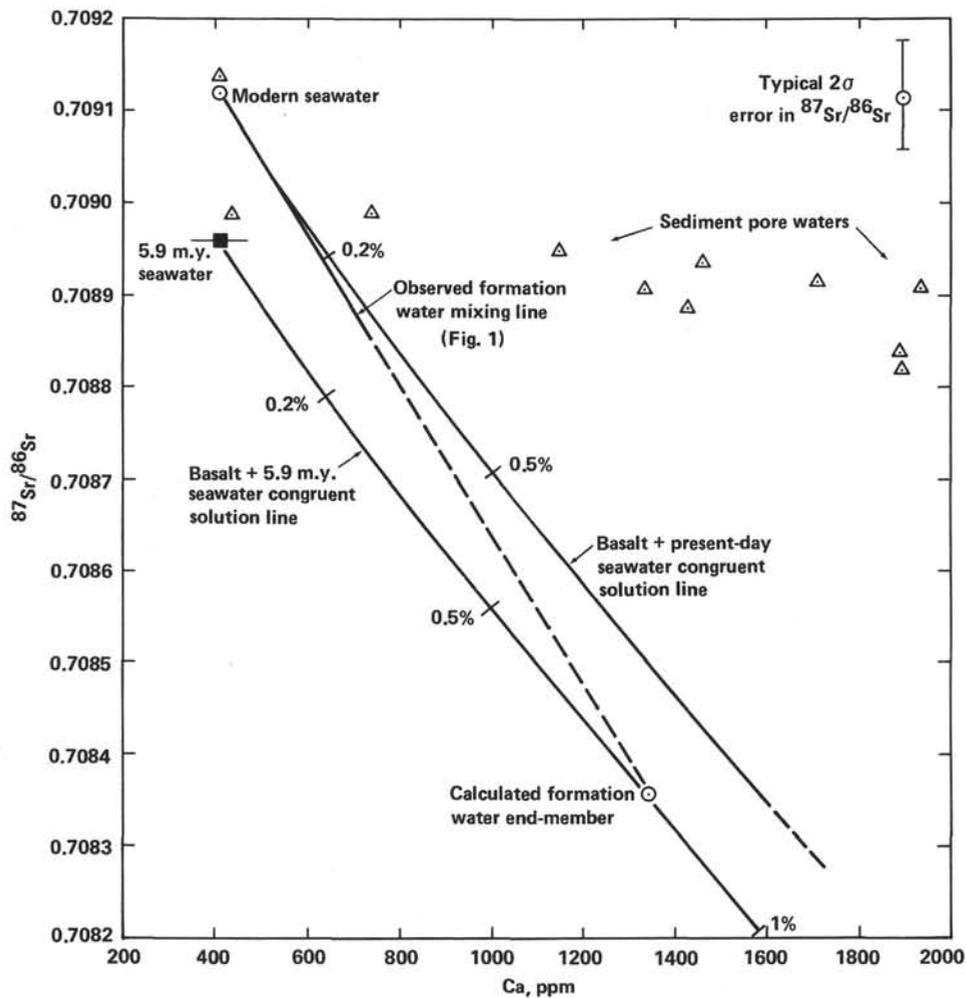


Figure 7. $^{87}\text{Sr}/^{86}\text{Sr}$ versus Ca mixing diagram. The observed formation water mixing line from Figure 1 is shown, with its extrapolation to the assumed fully reacted formation water end-member at $\text{Ca} \approx 1340$ ppm. Also shown are seawater/basalt congruent-solution or mixing lines, using either present-day or 5.9 m.y. old seawater as one end-member and basalt with $^{87}\text{Sr}/^{86}\text{Sr} = 0.7027$, $\text{Sr} = 100$ ppm, and $\text{Ca} = 12$ wt. % as the other end-member. Tick marks are shown on this curve for 0.2%, 0.5%, and 1% basalt by weight in the mixture. Also shown (open triangles) are data for $^{87}\text{Sr}/^{86}\text{Sr}$ and Ca in sediment pore waters from Holes 501 and 504.

The other components, such as K and Sr, can be treated similarly. The K content is obviously incompatible with the simple congruent solution of basalt (see above), inasmuch as the K concentration of the formation water is lower than that of modern seawater. On a plot of $^{87}\text{Sr}/^{86}\text{Sr}$ versus Sr concentration (not shown), this simple mechanism also fails, inasmuch as the formation water plots far below a seawater/basalt mixing line. Furthermore, no reasonable choice of values for the seawater or the basalt end-member will accommodate the formation water data point. Thus, some combination of Processes 2 and 3 must have been involved in addition to or instead of the simple congruent solution. Isotopic exchange between basalt and seawater without accompanying Sr elemental exchange (Process 2) would lower the Sr isotope ratio without affecting the Sr concentration and produce a formation water value that lies below a simple mixing curve on a plot of $^{87}\text{Sr}/^{86}\text{Sr}$ ver-

sus Sr. The removal of Sr from solution by the deposition of Sr-containing alteration minerals (Process 3) would have the same result. The latter process would not necessarily show up in a plot of $^{87}\text{Sr}/^{86}\text{Sr}$ versus Ca (Fig. 7) if the Sr were being removed in smectites, which typically have Sr/Ca ratios much higher than basalt.

One final insight may be derived from Figure 7, which also includes Sr isotope data for the pore waters from sediments from Holes 501 and 504. The trends of the Sr isotope ratio with respect to Ca are completely different for the pore waters and the formation waters. Although the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio for the low-Ca pore waters is consistent with derivation from 5.9 m.y. old seawater, the Sr isotope ratio decreases measurably more slowly than the 5.9 m.y. old seawater with increasing Ca content. This implies the existence of a minor basaltic component in the sediment pore waters, a component derived either from reaction with volcanogenic detritus

within the sediments themselves or from a slight admixture of basalt-containing formation water from the basement beneath the sediments.

In either event, the disparity between the trends in the pore water and the formation water (Fig. 7) may warrant the reconsideration of the estimated Ca content of the formation water end-member (Table 2), which was derived by analogy with the Ca content of the pore water from the sediment closest to the basement surface. This pore water cannot be an unreacted sample of formation water, at least with respect to $^{87}\text{Sr}/^{86}\text{Sr}$ and Sr content. It is possible that significant Sr isotope equilibration took place between the sediment pore waters and the carbonate of the sediment during diagenesis. If so, the difference between pore water Sr and formation water $^{87}\text{Sr}/^{86}\text{Sr}$ is consistent with the determination of the formation water Ca content by analogy with the pore water Ca contents.

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