

23. FIRST-ORDER ALTERATION CHEMISTRY OF LEG 49 BASEMENT ROCKS

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INTRODUCTION

There have been many studies of the geochemical effects associated with the low-temperature alteration of oceanic crust by seawater (see for instance, R.A. Hart, 1970, 1976a). Much of this work has been concerned with typical mid-ocean ridge basalts (MORB), low in incompatible elements, such as K, Rb, Ba, Sr, U, and Th, and where the effects of any significant addition of these elements through interaction with seawater is usually obvious. Leg 49, where many of the holes penetrated basaltic basement with "transitional" or moderately large-ion-lithophile (LIL)-enriched characteristics, provided an opportunity to study the effects of seawater interaction on basalts with generally higher primary levels of some incompatible elements.

Our approach was to analyze basalt samples for water, carbon dioxide, and ferrous/ferric ratios, to determine the degree of alteration in terms of hydration, carbonation, and oxidation, respectively. We also looked for any depth- or age-related trends or characteristics that might be significant with respect to these general alteration parameters and the major- and trace-element data of Tarney et al. (this volume) on the same samples.

SAMPLE PREPARATION AND ANALYTICAL METHODS

We selected about 100 basalt samples from Holes 407, 408, 409, 410, 411, and 412 of DSDP Leg 49. Because the samples were initially very damp, owing to absorbed water, they were all dried for two hours at a low temperature; then they were crushed in a Tema swing-mill. Crushing time was kept to a minimum (generally about 1 min) to reduce oxidation that may occur with excessive crushing periods (Fitton and Gill, 1970). Separate powdered samples, previously dried at 110°C, were used for the analysis of H₂O⁺, total Fe as FeO₃, FeO, and CO₂. *The results are presented in Table 1.*

H₂O⁺ was analyzed by a modified Penfield method (Shapiro and Brannock, 1955), using lead chromate as flux. CO₂, released from the sample by dilute orthophosphoric acid, was absorbed in 5 percent monoethandamine solution and titrated with 0.1N tetra *n*-butyl ammonium hydroxide (Read, 1972). Ferrous iron was determined using potassium dichromate as titrant and diphenylamine sulfonate as indicator. Total iron (as Fe₂O₃) was determined by atomic absorption spectrophotometry and calibrated with solutions of international standard rocks. Replicate analysis showed that analytical error was of the order of ±2 per cent of the sample value for all levels of FeO and total Fe, and of the

order of ±5 to 10 per cent for H₂O⁺ and CO₂, although for low values of CO₂ (<0.1 wt.%) this rose to ±20 per cent. Sample preparation and subsequent major and trace element analysis by X-ray fluorescence spectrometry has been described by Tarney et al. (this volume). The major and trace element data are not listed separately here.

GENERAL ALTERATION PARAMETERS

It is now abundantly clear that both submarine weathering and low-grade metamorphism of ocean floor and ridge basalts causes variable element mobility (Cann, 1969; S.R. Hart, 1969; R.A. Hart, 1970, 1976a; Miyashiro et al., 1971; S.R. Hart et al., 1974). Since such alteration markedly affects petrogenetically important elements, the degree of chemical change must be known before meaningful geochemical models can be compared and evaluated. This report is primarily concerned with the overall or first-order chemical changes both between and within the various hole profiles. First-order alteration may be linked to various factors, such as: (1) basement age, (2) depth in basement ("down-hole" profile), (3) sedimentation rate and cover thickness, (4) local temperature gradient, and (5) degree and depth of local fracturing. Within any one profile, second-order alteration factors may relate to the character of individual units or flows, such as the proportion of glass to crystals, degree of vesiculation, character of primary assemblage, etc. There are also important and some fine-scale chemical variations which may be linked to these features, although we will not consider them in detail here. Because chemical effects caused by alteration generally increase with the age of the basaltic basement (R.A. Hart, 1970, 1976b), the samples studied (and plotted on the diagrams) have been divided into "young" crust (1 to 2.5 m.y. — Holes 409, 411, 412A) and "older" crust (10 to 40 m.y. — Holes 407, 408, 410, 410A) to monitor aging effects.

Oxidation and Hydration Relationships

There is considerable variation in the alteration parameters of H₂O⁺, oxidation ratio (Fe₂O₃/FeO in wt. %), and CO₂ within the samples analyzed (Table 1), many values of which are clearly higher than those of fresh anhydrous basalts. Figure 1 shows the systematic variation between H₂O⁺ and oxidation ratio, and in general follows the alteration trend of MAR basalts near 24° and 30°N (Miyashiro et al., 1969). This type of variation is more indicative of very low grade submarine weathering than of hydrothermal alteration in the greenschist facies ("spilitization" trend in Figure 1). The spread of water and oxidation values overlaps typical MORB variation as illustrated by R.A. Hart (1976b, fig. 12),

TABLE 1
Distribution of Common Alteration Parameters in Leg 49 Basalts
(wt. %) (blank indicates insufficient sample for determination)

Sample (Interval in cm)	Total Fe as Fe ₂ O ₃	FeO	Fe ₂ O ₃	Fe ₂ O ₃ /FeO	H ₂ O ⁺	CO ₂
407-35-1, 37-39	14.55	7.17	6.58	0.92	1.06	0.01
407-36-2, 46-48	11.80	6.08	5.05	0.83	1.51	0.16
407-36-3, 73-75	12.22	7.93	3.41	0.43	0.84	0.07
407-36-3, 74-76	12.05	6.73	4.57	0.68	1.58	0.13
407-37-2, 74-76	14.55	9.38	4.13	0.44	0.97	0.06
407-38-2, 140-142	14.20	8.43	4.83	0.57	1.30	0.11
407-38-3, 57-59	14.15	8.48	4.73	0.56	1.19	0.09
407-39-2, 59-61	13.82	8.13	4.79	0.59	1.06	0.11
407-39-3, 61-64	14.39	9.47	3.87	0.41	1.00	0.06
407-40-1, 57-61	14.96	7.17	6.99	0.97	1.51	0.01
407-42-1, 48-50	15.30	9.11	5.18	0.57	0.91	0.04
407-44-1, 75-76	13.32	6.69	5.89	0.88	1.30	0.37
407-46-2, 65-67	10.97	5.94	4.37	0.74	1.81	0.16
407-47-3, 30-32	11.86	6.70	4.42	0.66	1.56	0.08
407-47-4, 41-47		4.97			2.26	0.09
408-36-2, 15-18	11.50	4.64	6.34	1.37	0.85	2.71
408-36-3, 46-49		4.70			1.88	0.67
408-36-5, 44-47	11.27	3.86	6.98	1.81	2.42	0.88
408-36-5, 45-49	10.88	4.08	6.35	1.56	1.14	0.96
408-37-1, 30-35	10.72	5.67	4.42	0.78	2.37	0.11
408-37-2, 130-133	12.94	7.86	4.21	0.54	1.01	0.22
408-38-2, 20-22	12.56	7.94	3.74	0.47	1.57	0.19
408-38-4, 32-33	12.23	7.21	4.22	0.59	1.60	0.22
409-7-6, 71-75	11.55	7.45	3.27	0.44	1.04	0.01
409-7-7, 3-4	11.78	8.48	2.36	0.28	0.59	0.05
409-8-1, 104-107	11.77	7.31	3.65	0.50	0.82	0.04
409-9-1, 135-140	12.40	8.06	3.45	0.43	0.83	0.07
409-10-1, 10-12	11.64	7.66	3.13	0.41	1.08	0.03
409-10-2, 16-20	11.42	7.34	3.27	0.45	0.91	0.08
409-10-3, 69-72					1.15	
409-10-3, 69-76	11.94	7.41	3.71	0.50	0.50	0.16
409-10-4, 91-94	11.25	7.53	2.88	0.38	1.21	0.04
409-10-5, 41-44	11.35	8.00	2.46	0.31	0.78	0.06
409-10-6, 130-132	11.27	7.86	2.54	0.32	0.52	0.06
409-10-7, 4-6	11.36	8.09	2.37	0.29	0.79	0.04
409-11-1, 61-63	12.20	7.45	3.92	0.53	0.79	0.02
409-11-2, 80-82	11.13	7.74	2.53	0.33	0.78	0.04
409-11-3, 80-82	11.50	8.14	2.46	0.30	0.69	0.15
409-12-1, 141-143	10.77	7.31	2.65	0.36	0.50	0.22
409-13-1, 39-41	11.37	7.03	3.56	0.51	0.87	0.37
409-13-3, 40-42	13.06	7.60	4.62	0.61	1.60	0.15
409-14-1, 51-53	12.18	7.90	3.40	0.43	0.80	0.06
409-15-3, 105-107	12.00	6.22	5.09	0.82	1.36	0.24
409-17-1, 36-40	12.41	8.56	2.90	0.34	0.55	0.61
409-21-2, 87-91	12.56	7.58	4.14	0.55	0.77	0.55
409-23-1, 111-114	11.61	6.90	3.94	0.57	1.08	6.14
409-24-1, 143-146	13.30	6.28	6.22	0.99	1.34	0.46
409-24-2, 87-90	12.14	8.28	2.94	0.36	0.83	0.01
409-24-3, 80-83	12.08	8.69	2.43	0.28	1.04	0.01
409-24-4, 89-92	12.36	8.82	2.56	0.29	0.46	0.04
409-25-1, 82-85	11.95	7.42	3.91	0.54	1.09	0.77
409-25-2, 35-38	11.53	6.34	4.49	0.71	1.40	0.66
409-25-3, 79-82					1.64	0.47
409-26-1, 29-32	12.70	6.63	5.33	0.80	1.69	0.26
409-28-1, 73-76	10.63	6.47	3.44	0.53	0.52	5.57
409-31-1, 121-124	12.35	6.48	5.15	0.79	1.80	0.24
409-31-2, 80-83	12.48	6.97	4.74	0.68	1.78	0.14
409-32-1, 135-138	11.20	7.53	2.83	0.38	0.79	0.19
410-39-1, 81-86	9.80	3.07	6.39	2.08	1.23	1.01
410-39-5, 90-93	8.43	4.36	3.59	0.82	1.26	0.66
410A-2-1, 48-52	9.28	5.39	3.29	0.61	1.60	0.12
410A-3-2, 43-45	9.52	3.93	5.15	1.31	1.86	0.70
410A-2-4, 55-60	9.24	4.86	3.84	0.79	0.66	0.11
410A-3-1, 76-78	9.00	3.52	5.09	1.45	1.04	0.06
410A-3-3, 120-123	8.76	4.07	4.24	1.04	1.83	0.13
410A-3-4, 120-123	9.03	3.72	4.90	1.32	2.68	0.18
410A-3-5, 33-38	8.92	3.52	5.10	1.45	2.88	0.31
410A-4-2, 87-90	9.00	3.87	4.70	1.21	1.46	0.22
410A-4-3, ?	8.73	4.01	4.27	1.06	2.73	1.54
410A-4-4, 65-70	8.76	3.83	4.50	1.17	1.21	0.41
410A-5-2, 110-115	8.95	4.18	4.31	1.03	0.75	0.49
410A-5-3, 38-45	8.52	3.35	4.80	1.42	1.44	1.89
410A-5-4, 95-106	8.87	5.17	3.13	0.61	1.51	0.90
410A-6-1, 118-126	9.24	4.74	3.97	0.84	1.08	0.89
411-1-1, 78-82	9.88	7.73	1.29	0.17	0.46	0.10
411-2-2, 2-13	9.87	7.48	1.56	0.21	0.59	0.11
411-3-1, 94-100					0.66	
411-4-1, 60-70	9.03	7.03	1.22	0.17	0.24	0.13

TABLE 1 — Continued

Sample (Interval in cm)	Total Fe as Fe ₂ O ₃	FeO	Fe ₂ O ₃	Fe ₂ O ₃ /FeO	H ₂ O ⁺	CO ₂
412A-1-1, 28-32	10.36	7.86	1.63	0.21	0.71	0.02
412A-2-2, 25-30	9.76	6.60	2.43	0.37	0.95	0.08
412A-3-1, 70-80	9.78	6.74	2.29	0.34	0.48	0.10
412A-3-2, 60-62	10.06	7.46	1.77	0.24	0.42	0.14
412A-3-2, 70-80	9.84	7.31	1.72	0.24	0.28	0.05
412A-4-1, 20-25	10.80	7.72	2.22	0.29	0.82	0.11
412A-5-1, 50-54	10.40	7.66	1.89	0.25	0.78	0.07
412A-6-1, 70-73	10.12	7.59	1.69	0.22	0.33	0.12
412A-7-1, 2-5	10.20	7.10	2.31	0.33	0.74	0.09
412A-7-2, 110-115	10.15	6.96	2.42	0.35	0.18	0.15
412A-8-1, 130-133	10.20	7.52	1.85	0.25	0.73	0.08
412A-8-2, 35-39	10.24	7.58	1.82	0.24	0.31	0.04
412A-9-1, 61-63	9.80	7.79	1.15	0.15	0.26	0.11
412A-10-1, 47-50	10.14	7.31	2.02	0.28	0.58	0.15
412A-11-1, 32-35	9.86	7.28	1.77	0.24	0.41	0.10
412A-11-2, 17-21	9.42	6.55	2.14	0.33	0.44	0.07
412A-13-1, 20-25	10.49	7.86	1.76	0.22	0.63	0.24
412A-13-2, 55-60	10.88	7.80	2.21	0.28	0.45	0.11
412A-14-1, 4-14	10.06	7.31	1.94	0.27	0.64	0.05
412A-14-2, 70-80	10.45	7.59	2.02	0.27	0.53	0.07
412A-14-3, 71-75	11.22	7.83	2.52	0.32	0.42	0.07

although the Leg 49 basalts — some of which were in fact recovered from ridge flanks — are not characterized by the higher water contents of ridge flank basalts. Even the least mineralogically altered samples of Leg 49 (smectite and palagonite) show a proportionate increase in H₂O⁺ and oxidation ratio. On the basis of such criteria as Fe₂O₃/FeO < 0.3 (Miyashiro et al., 1969) and weight percent H₂O⁺ < 0.3 (Hart and Nalwalk, 1970), considered essential for unaltered basalts, few of the Leg 49 samples can be described as really chemically fresh, especially with regard to the alkali elements. However, the freshest samples available are from the youngest sites, and contrast with the older basement basalts, all of which exhibit considerably higher values and greater dispersion, features corresponding to petrographic evidence of more severe alteration (smectite, palagonite, Fe and Ti oxides, carbonate, and zeolites).

Alteration and Time

A comparison of the averaged alteration parameters for the different holes (Table 2 and Figure 2) demonstrates that the older basaltic basement is not only more altered, but shows greater variation (as seen by an increase in the standard deviation, Table 2). Figure 2 indicates that significant hydration, oxidation, and carbonation may not take place until after about 1.5 m.y. of submarine weathering, when general alteration increases markedly. The relationship is apparently not a simple one of progressive alteration with time, however, and suggests that other, more local factors may also play a part. For example, the difference in the basal sedimentation rate (see Site Summary Chapters, this volume) could explain the relationship between the older crust of Holes 407 (sedimentation rate of 30 m/m.y.) and 408 (sedimentation rate of 4 m/m.y.). Although basement in Hole 407 is the oldest, the lack of extreme alteration may be a consequence of rapid initial sedimentation blanketing the basalts from the effects of seawater and limiting subsequent percolation. Differences between basement of similar age (Holes 410 and 410A) may reflect second-order factors such as the nature of the lavas — Hole 410 basalt is a pillow breccia, and thus more easily penetrated by oxygenated and

carbonated seawater than the packed pillow lavas of Hole 410A.

Time is probably one of the more important influences on the bulk chemistry of the basalts; aging accounts for most of the systematic alteration seen.

Effects on Magnetic Properties

Oxidation of the Ti-Fe oxides in ocean floor basalts may cause some variation in the magnetic properties of the rocks, such as an increase in the Curie temperature and a decrease in natural remanent magnetism (NRM) intensity (Johnson and Atwater, 1977).

As seen in Figure 3a, the Curie temperature (Faller, personal communication, 1977) of the Leg 49 basalts increases rapidly from about 100° to 300°C over a relatively low and narrow range of oxidation of 0.2 to 0.5. With further oxidation of older crust (10 m.y.), the Curie temperature remains essentially constant at the higher temperature. Progressive oxidation may also affect the inclination of the older basalt samples (Figure 3b). Normal polarity inclination shows a small decrease for Holes 408 and 410A, whereas a relatively well defined increase is exhibited by the reversed polarity of Holes 407 and 409 (with two trends developed) with progressive oxidation. There appears to be no clear systematic variation in the inclination with depth in any of the Holes (Figure 3b). The reduction in the NRM intensity with oxidation has been commented upon before (e.g., Johnson and Atwater, 1977), and is also illustrated by the Leg 49 basalts (Figure 3c). The older basement rocks clearly show the best correlation relative to the younger, and suggest that for a significant decrease in intensity the basalts must be at least 2.3 m.y. old (equivalent to Hole 409).

ALTERATION AND ELEMENT COHERENCE AND MOBILITY

Studies of the effect of alteration on ocean floor basalts (see summaries in Hart et al., 1974, and R.A. Hart, 1976b) have demonstrated that in most cases K, Rb, Cs, B, U, Ca, Mg, Fe, Mn, etc. may be mobilized, whereas Ti, Zr, Y, Nb, Cr, Co, Sr, and the rare-earth elements are generally "immobile," or at least little affected. Apart from comparing fresh and weathered portions of a sample, the mobility of an element can be determined in a suite of rocks by a number of simple chemical methods: (1) By comparing element variability with a general alteration parameter (such as H_2O^+) and observing any correlation with progressive alteration. (2) By demonstrating a lack of or disruption of correlation between a pair of elements that are closely associated (coherent) in magmatic rocks. In such cases, even if both elements are mobile, coherence is usually lost because of the effects of differential mobility. (3) By comparing element variability relative to an "immobile" element (e.g., Zr). In this situation any correlation may reflect both stability and the effects of magmatic processes, e.g., high-level crystal fractionation, in causing systematic variation in both the elements.

These methods are illustrated here, although only a few elements have been plotted, and they are used primarily as examples of alteration effects.

Zr and Nb

Both these elements are generally considered stable in altered rocks (Cann, 1970), and exhibit strong covariance in a cogenetic suite (Erlank and Kable, 1976). This last feature is illustrated in Figure 4a, where the two separate trends

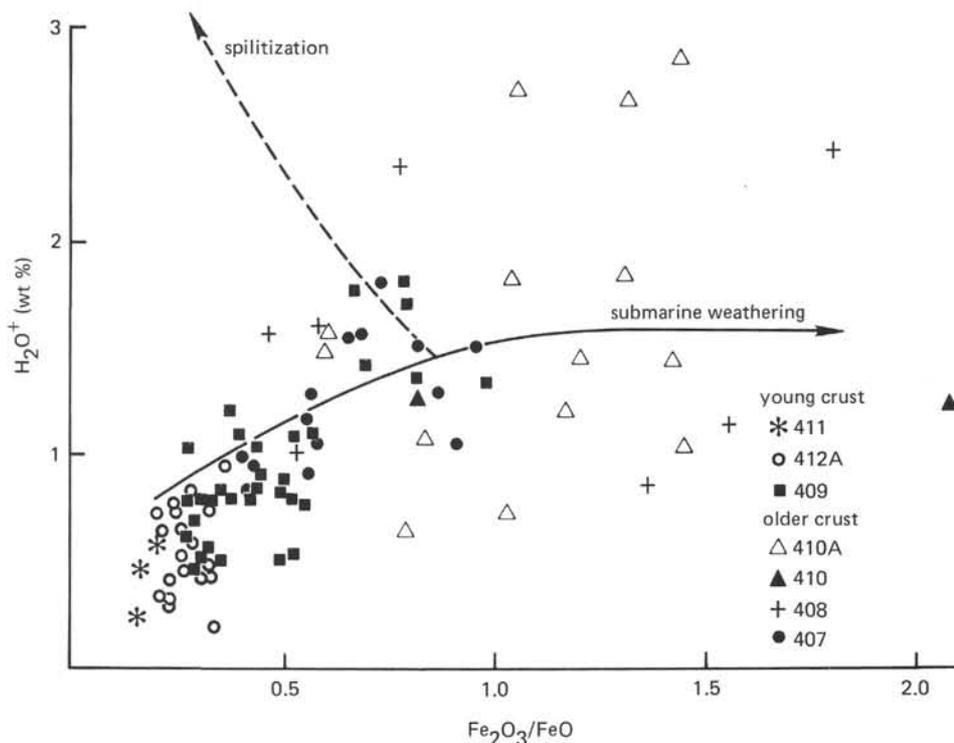


Figure 1. Variation of oxidation (as Fe_2O_3/FeO) and hydration (H_2O^+) in Leg 49 basalts. Data for generalized submarine weathering trend and spilitization trend from Miyashiro et al. (1971) and Cann (1969), respectively.

TABLE 2
Average Values (X) and Standard Deviation (S) of Alteration
Parameters in Leg 49 Basalts From Different Holes, Listed
According to Age

Hole	411	412A	409	410A	410	408	407
FeO	X 7.41 S 0.35	7.40 0.41	7.50 0.71	4.15 0.64	3.72 (0.91)	5.75 1.69	7.49 1.35
Fe ₂ O ₃	X 1.36 S 0.18	1.98 0.33	3.53 1.00	4.38 0.65	4.99 (1.98)	5.18 1.32	4.92 0.99
Fe ₂ O ₃ /FeO	X 0.18 S 0.02	0.27 0.05	0.49 0.18	1.09 0.29	1.45 (0.89)	1.02 0.55	0.66 0.18
H ₂ O ⁺	X 0.49 S 0.18	0.53 0.21	0.98 0.39	1.62 0.71	1.25 (0.02)	1.61 0.59	1.32 0.39
CO ₂	X 0.11 S 0.02	0.10 0.05	0.53 1.37	0.57 0.57	0.84 (0.25)	0.75 0.86	0.10 0.09
Number of samples	4	21	35	14	2	8	15
Oldest sediment	Pleistocene	Pleistocene	Upper Pliocene	Upper Miocene	Upper Miocene	Lower middle Miocene	Lowermost Oligocene
Site age (m.y.)	1.0	1.5	2.3	10	10	20	36-38
Site	Median valley of MAR (FAMOUS)	Fracture zone in MAR (FAMOUS)	West crest Reykjanes Ridge	MAR crest 45° N	MAR crest 45° N	West flank Reykjanes Ridge	West flank Reykjanes Ridge

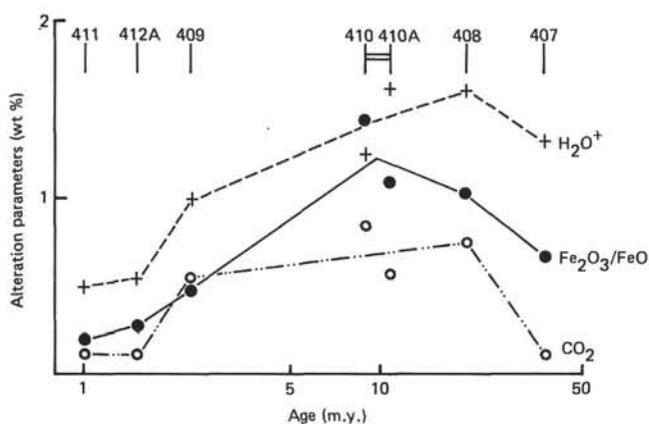


Figure 2. Variation of average values for hydration, oxidation, and carbonation with age of the basaltic basement.

developed are unrelated to the degree of alteration or the age of basement. Instead, they represent separate locations (crest and flanks of the Reykjanes Ridge; 45°N and FAMOUS areas of the Mid-Atlantic Ridge) with different Zr/Nb ratios. The characteristic ratios are still clearly defined and unaffected by progressive alteration (Figure 4b).

K and Rb

K and Rb are characteristically low for typical MORB, although the K/Rb ratios are unusually low (300 to 600) for a large proportion of the Leg 49 samples. This may indicate alteration (S.R. Hart, 1969; Hart and Nalwalk, 1970), or, on the other hand, the low K/Rb ratios may represent a primary feature of some "transitional" basalts that show LIL-enriched characters.

In general, the older crustal basement is higher in K (and H₂O⁺) than the younger basalts (Figure 5a) and suggests adsorption of K with time. A progressive increase in K with hydration is also reflected by the relatively young 2.3-m.y.-old Hole 409 samples. The youngest material (Holes 411 and 412A), however, shows a wide variation of K and again may indicate variable mobility, even when hydration is relatively

low. This is partly borne out by the lack of good correlation with Zr at any particular Hole or within any one geochemical unit (Figure 5b).

Rb is uniformly low and does not show the general enrichment with age like K; thus, the most altered samples do not have the lowest K/Rb ratios, as might be expected. As shown in Figure 5c, there is considerable overlap between the K/Rb ratios of young and older crustal basalts; the former, irrespective of oceanic environment, has the lowest such ratio. It seems likely that some of these low K/Rb ratios reflect initial values, although it is equally likely that they also indicate some early extensive Rb adsorption or more probably, K depletion of young, poorly hydrated crust. There appear to be differences in the behavior of K and Rb in the young crust basalts relative to the older crust basalts. S.R. Hart (1969) demonstrated that submarine weathering caused a lowering of the K/Rb ratio, with concomitant increase in K, relative to chemically fresh ocean floor basalts (MORB) of uniform K/Rb ratios and variable K contents. Figure 6 confirms the negative K/Rb-K relationship (S.R. Hart, 1969) for the older crust, but also shows a very scattered positive relationship for the low-K/Rb young crust. This later feature may be primary, although Hart and Nalwalk (1970) found a similar trend for Puerto Rico trench basalts and attributed it to alteration.

In conclusion, because of the non-MORB characteristics of some elements in the basalts from FAMOUS (Holes 411, 412A) and from 45°N (Holes 410, 410A) (Erlank and Kable, 1976; Tarney et al., this volume), the generally low K/Rb ratio of the younger basement could reflect primary values, although their wide variation suggests early variable mobility of K and Rb. With time, however, Rb is differentially enriched relative to K, such that the negative K/Rb-K relationship of the older crust is produced (Figure 6).

K and Ba

Although Ba may be captured by K-rich host minerals, these elements only show a positive correlation, typical of magmatic coherence, in the younger crust and the least-altered older crust (Hole 407) basalts. This is essentially a reflection of the mobility of K with progressive alteration since the correlation of Ba with an immobile element like Zr is fairly good for all Holes (Tarney et al., this volume). As shown in Figure 7, the younger basalts maintain relatively constant Ba values with progressive hydration and are characteristic for each hole. The Ba-enriched nature of the 45°N samples (Hole 410A) is also apparent, although some of the variation seen may be a result of secondary as well as primary processes.

Sr

Sr is often considered to be relatively immobile in altered oceanic basalts (Pearce and Cann, 1973; S.R. Hart, 1971). Figure 8a shows that there is some degree of correlation with Zr and the existence of two or more trends. Individual holes have retained essentially constant Sr contents with progressive hydration (Figure 8b). Variable Sr values within any one hole of the older crust (e.g., 410A and 407) suggest the presence of different magma batches rather than the effects of alteration.

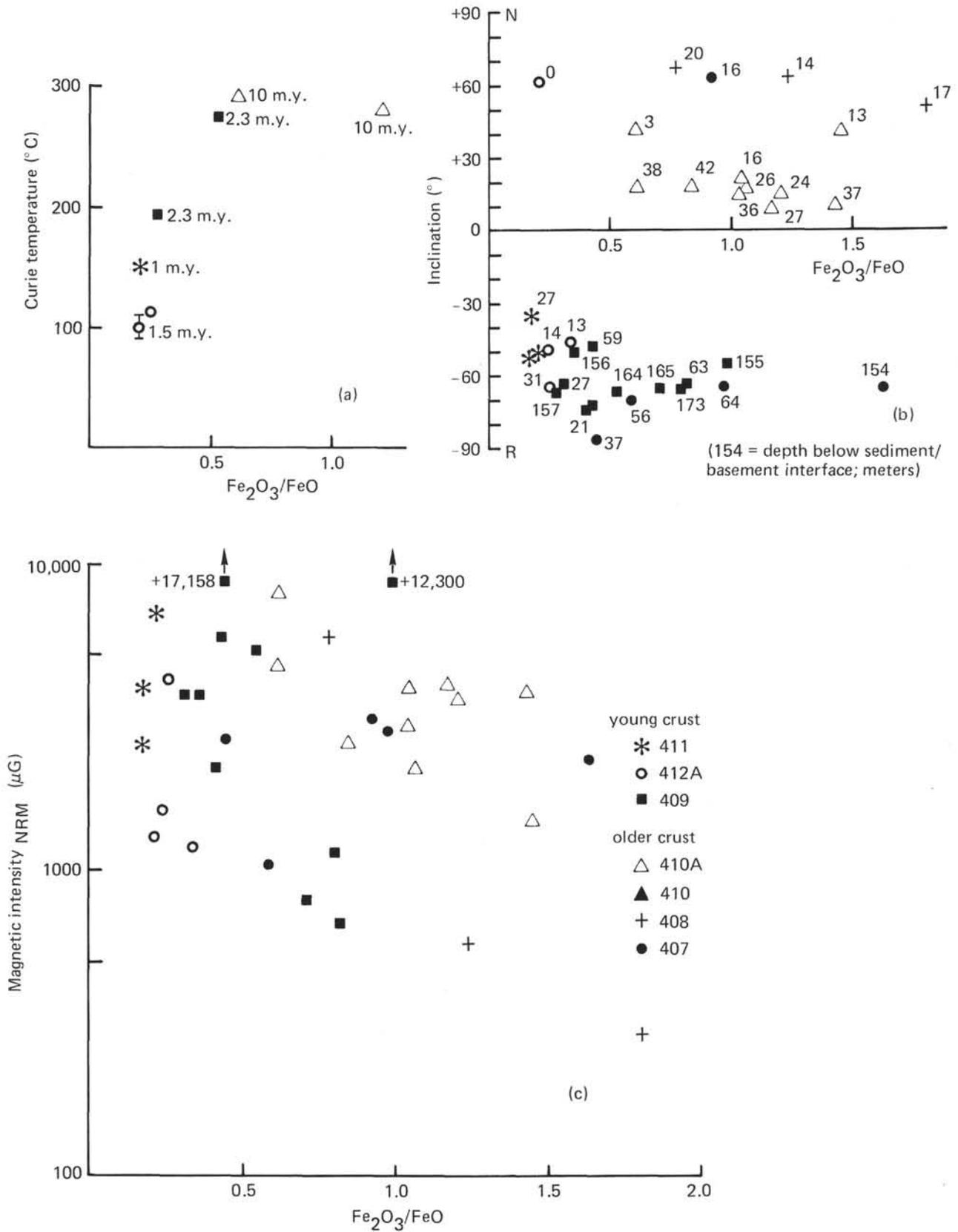


Figure 3. Variation of Curie temperature (a), normal and reversed inclination (b), and intensity of normal remanent magnetism (c), with progressive oxidation.

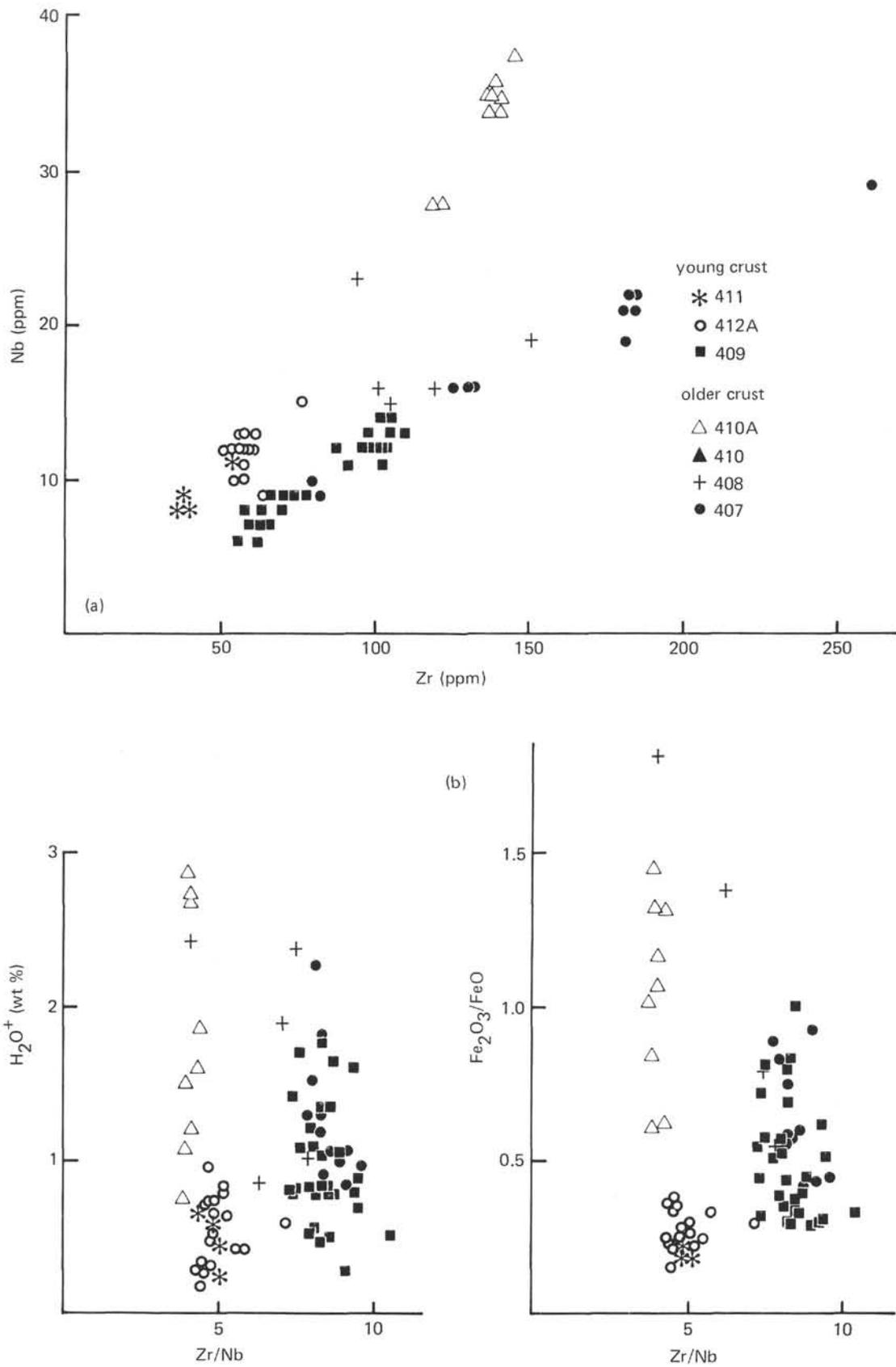


Figure 4. Systematic relationship between Zr and Nb (a) and the lack of variation of specific Zr/Nb ratios with progressive hydration and oxidation (b).

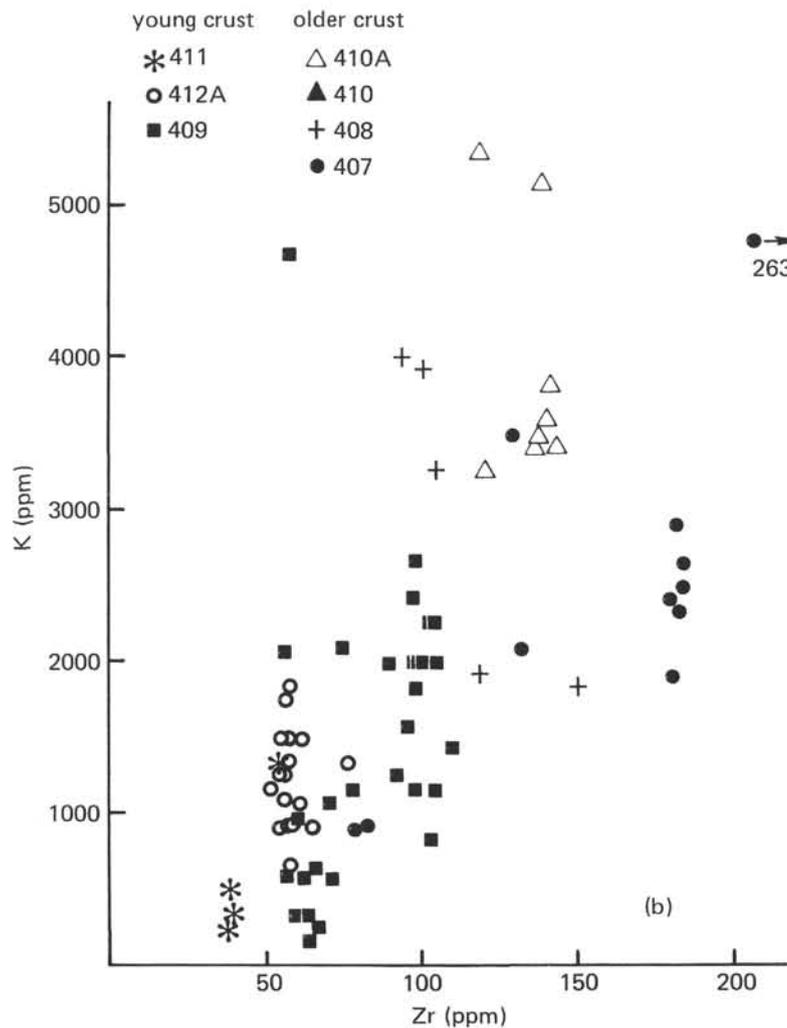
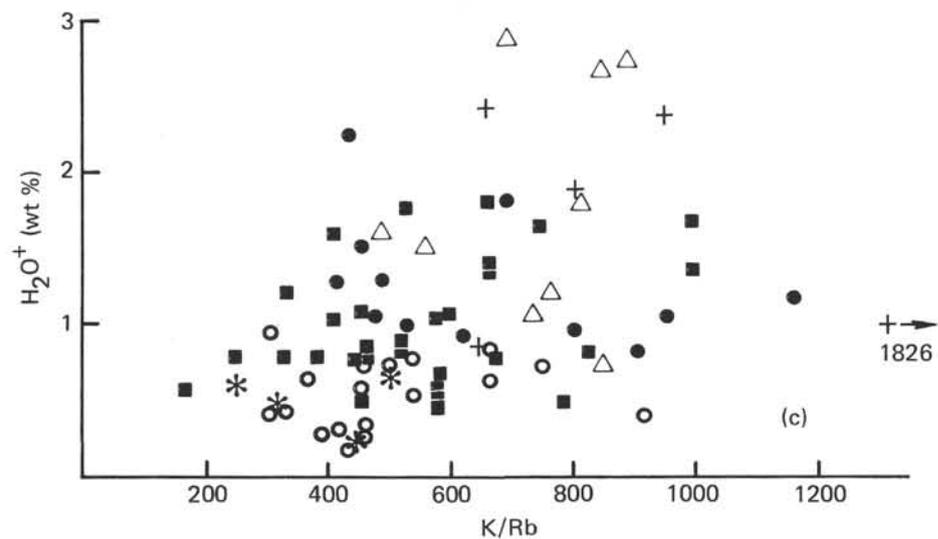
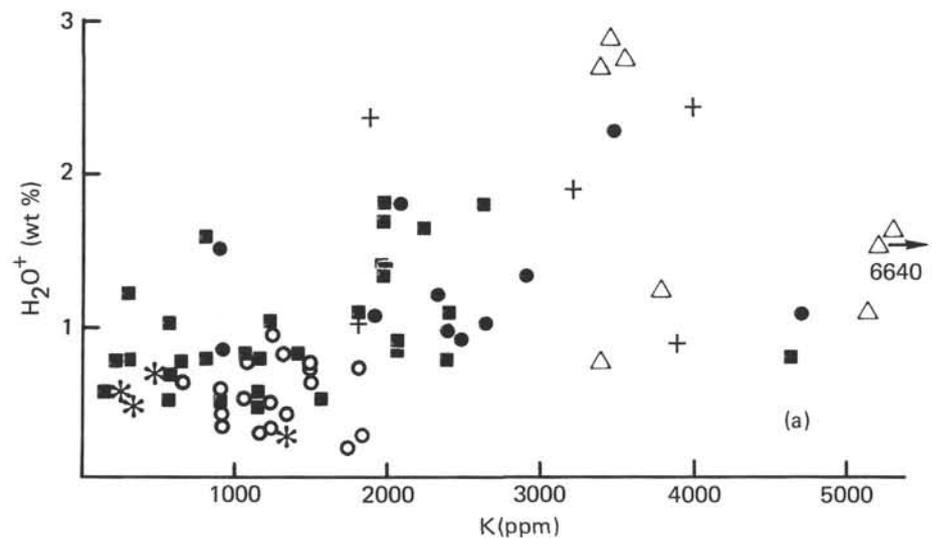


Figure 5. Variation of K content with progressive hydration (a) and Zr content (b). Variation of K/Rb ratio with progressive hydration (c).

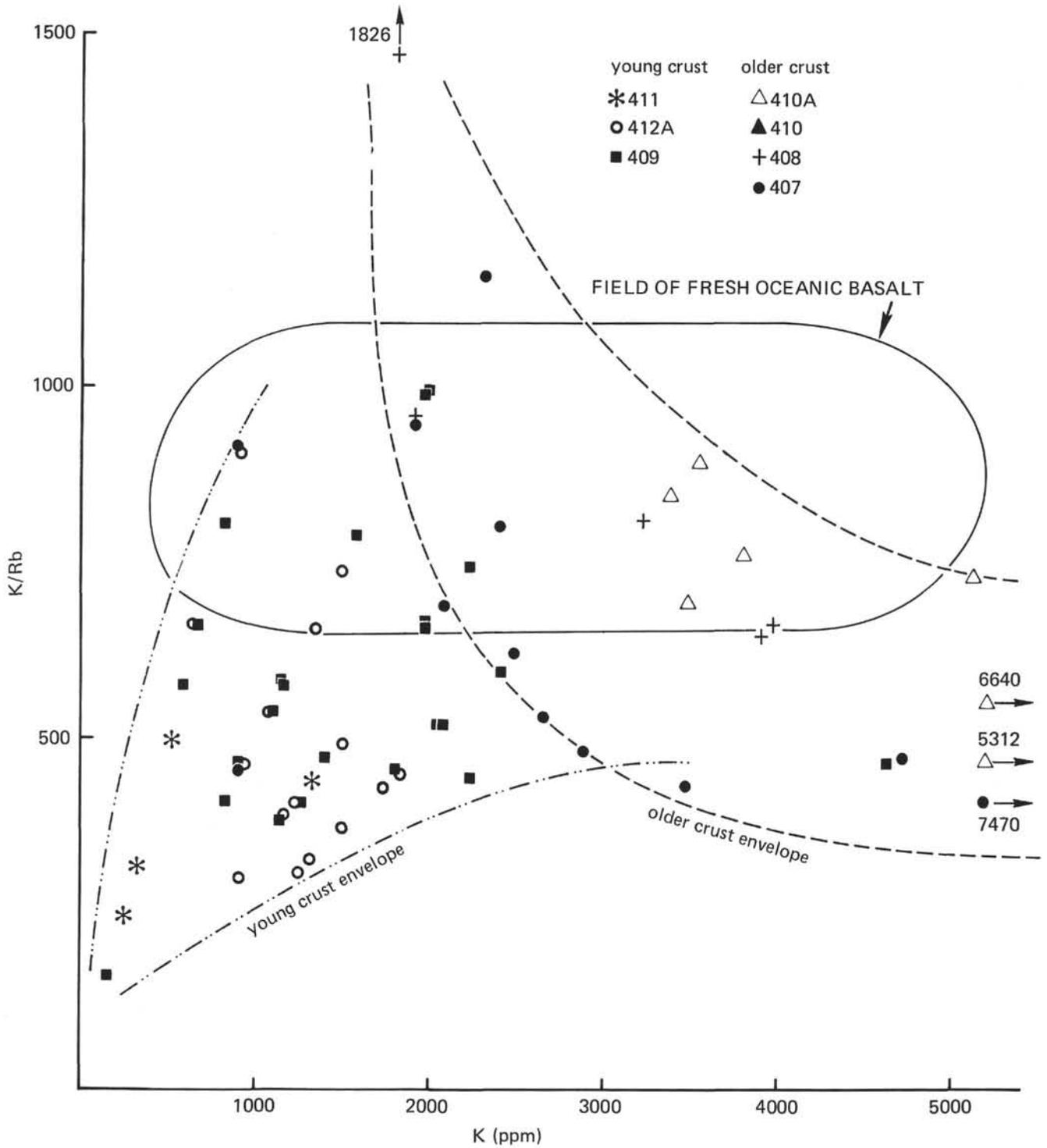


Figure 6. Varying systematic alteration trends for K and K/Rb ratio in young and older basalts. Fresh oceanic basalt field (typical MORB) from S. R. Hart (1969).

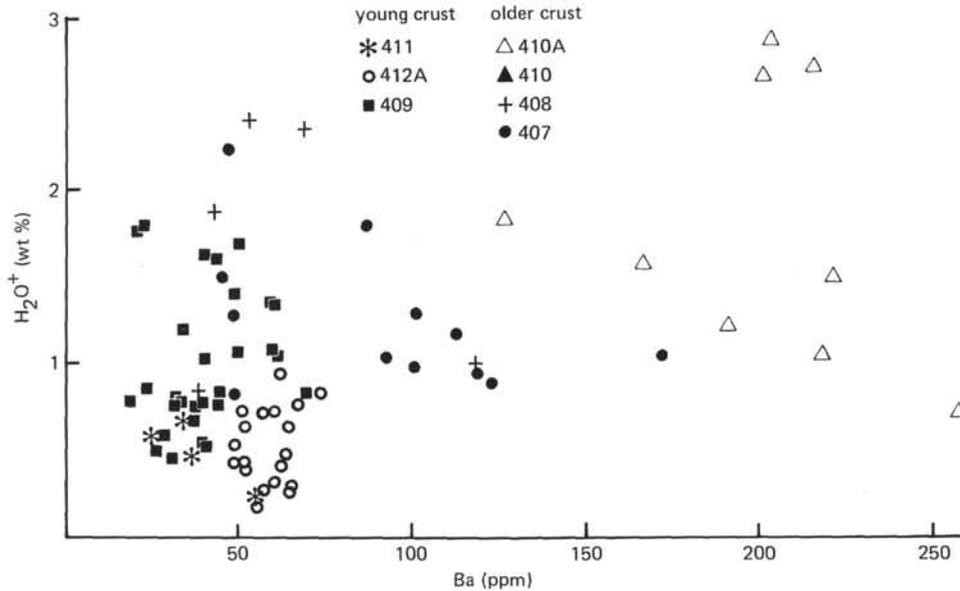


Figure 7. Variation of Ba with progressive hydration.

Na₂O

Altered basalts often have higher Na₂O contents than relatively fresh material (Miyashiro et al., 1971; R.A. Hart, 1970). In general, this appears to be the case here (Figure 9), where the more altered older basalts show greater variability. Within this group there is also a tendency for Na₂O to decrease with progressive hydration in any one hole. Variation within the younger basalts essentially reflects the composition of individual magma batches.

In conclusion, one of the main features to emerge is that some elements (e.g., K, Rb) show mobility in very young oceanic crust, even when mineralogical alteration is at a minimum, whereas others only show mobility at increased levels of alteration. Although this has been demonstrated previously, it has been confirmed here by comparing the behavior of an element in young, relative to older, crustal basalts.

BASEMENT PROFILE VARIATION

Elemental addition and subtraction during submarine alteration affect the material balance of the ocean water-basement system (R.A. Hart, 1973), and have led to various models suggesting the operation of cyclic hydrothermal cells in the vicinity of the mid-ocean ridges (Spooner et al., 1974; Stern et al., 1976; Bonatti et al., 1976; Wolery and Sleep, 1976; Spooner et al., 1977a). In general, cold ocean water descends at the flanks, and at depth is heated by magmatic activity before returning to the surface via fractures. Element interchange, with solution and deposition, together with low-grade metamorphism of the basalts, takes place at varying depths.

This section examines the overall variation of alteration parameters and element distribution with depth in the basement basalts. Alteration profiles in young crust have been compared with those of older crust. So that sample depths in each hole are comparable, the depth below the basement/

sediment interface has been plotted on the diagrams (Figures 10 and 12).

We were particularly interested to determine the depth and timing of maximum alteration in the basement profiles, although the limited depth of penetration in a few of the older basement holes restricted us from drawing any firm conclusions. Previous studies of the depth of submarine weathering, based on sonic velocity data (R.A. Hart, 1973; 1976b), indicate that alteration can affect the upper 500 meters of Layer 2 crust, although the upper 100 meters or so are generally the most altered in the older basement sections. Seawater usually penetrates to far greater depths, however, as indicated by the oxygen isotopic composition of hydrated metabasalts from ridge axes (Muehlenbachs and Clayton, 1972) or ophiolite complexes (Spooner et al., 1977a), and eventually becomes part of the hydrothermal circulation pattern of the deep crust.

Variation of Oxidation Ratio With Depth (Figure 10a)

A clear distinction with depth is evident between the young crust and the older crust profiles. The young crust has essentially "constant" oxidation ratio with depth, whereas the older crust shows a highly variable ratio in the upper 50 meters of the profile before decreasing to a more constant value with increasing depth. In individual down-hole profiles, however, the variation with depth shows a "saw-tooth" distribution (e.g., Hole 409) related to second-order effects of the flow units (e.g., oxidized flow tops relative to less oxidized centers). The same type of variation is also evident in deeper basement profiles from Leg 37 (e.g., Hole 332B; Blanchard et al., 1976). The variation of oxidation with depth is apparent in Holes 407 and 408, both of which can be divided into an upper oxidized zone and a more reduced pyrite-bearing lower zone.

The profiles can best be explained by the downward penetration of oxygenated seawater, which caused considerable

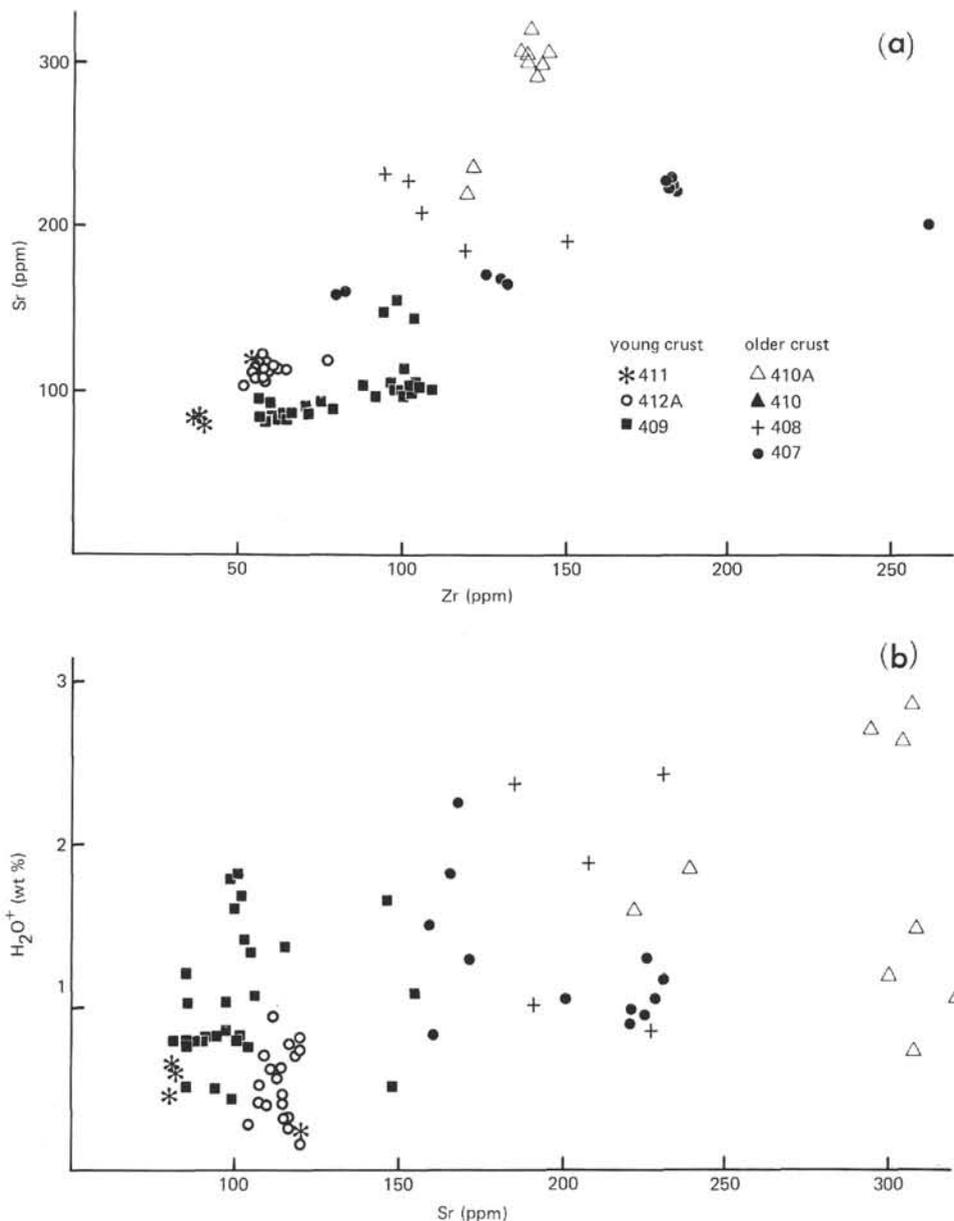


Figure 8. Variation of Sr with Zr content (a) and progressive hydration (b).

oxidation in the upper 50 meters but became reduced with depth. However, some millions of years (~ 2.5 m.y.) were required before wholesale oxidation developed in the upper part of the profile. The general decrease in oxidation with depth to relatively constant lower values can also be seen in thick ophiolite sections (Coish, 1977; Spooner et al., 1977b).

Variation of Hydration With Depth (Figure 10b)

A distinction can again be seen between the down-hole variation for young crust relative to older crust, together with maximum variation in the upper 50 meters of the later profile. One important difference, relative to the oxidation profiles, is that H₂O⁺ appears to increase in depth in both young and older basement samples. A similar but more irregular increase in hydration with depth occurs in some of the Leg 37 holes (Blanchard et al., 1976). Although some high values at depth can be related to specific parts of some lava units, the

increasing trend with depth appears to be a first-order feature, and may reflect hydrothermal fluids rising from below. Deeper profiles are required, however, to confirm any continuing trend with depth.

Variation of Carbonation With Depth (Figure 10c)

The distribution of CO₂ is more variable than the other alteration parameters, and correlates closely with second-order features of individual flows. For example, high CO₂ at depth in relatively young crust can be related to calcite infillings of highly vesicular units. In general, the upper 50 meters of the older crust profile have the greatest variation, indicating that considerable time is required before physicochemical conditions in this portion allow precipitation of considerable carbonate from seawater. This may be related to a change in the pH of seawater circulating in the basement, caused by earlier alteration (oxidation and element exchange), such that the solubility of CaCO₃ is decreased.

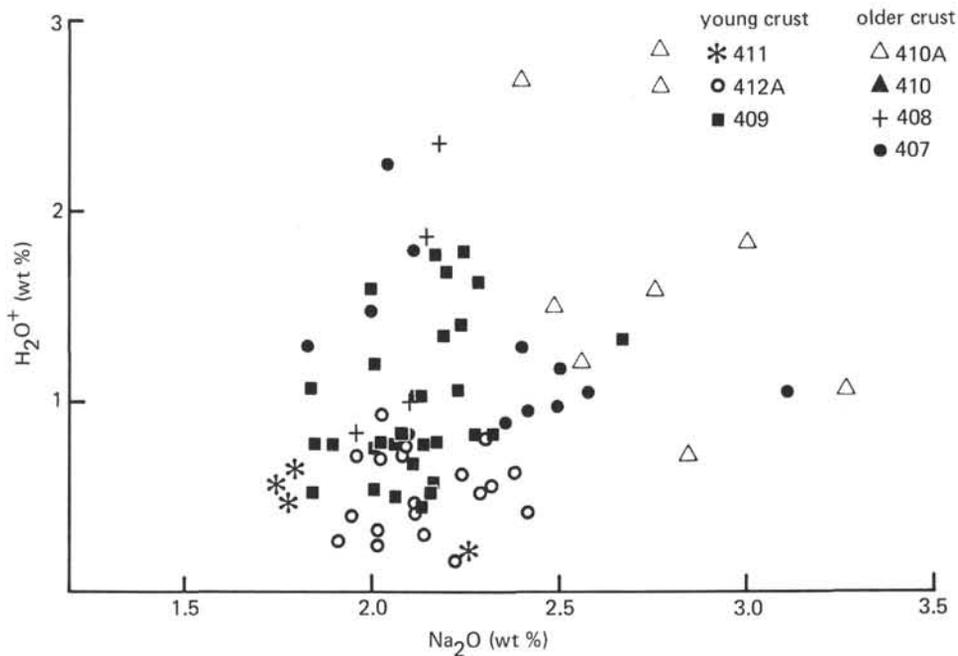


Figure 9. Variation of Na_2O with progressive hydration.

Petrographic studies indicate that deposition of carbonate is one of the last alteration effects to occur.

Element Variation With Depth

The variation with depth of the general alteration parameters (above) may also be reflected by the more mobile elements. The less mobile or "immobile" groups are more likely to reflect the specific characteristics of petrographic units or groups. For example, crystal fractionation or variation in source magma composition may produce trends of variation or definite breaks in composition with depth.

Variation with depth caused by both alteration and specific magma batch composition can be seen in the profile of Hole 407. On the basis of distribution of Zr relative to other elements, four distinct chemical units can be distinguished in the basalts (Tarney et al., this volume). Although there are few samples in Units I and II, total Fe (as Fe_2O_3), K_2O , MgO , and Ni all show increasing scatter within each of the chemical units with depth (Figure 11). The mobility of the ferromagnesian elements in the lowest units may be related to the progressive hydration of olivine in the basalts.

Figure 12 shows depth profiles for a few elements in all the holes sampled. The K/Rb ratio shows wide variation at all depths, although the slightly lower values in the upper portion of the young crust profile may indicate early K leaching relative to Rb or may on average be near primary values. Elements such as Ba, Sr, and Na are all higher in the older crust profiles; the greatest variation in each hole occurs in the top 50 meters. However, this variation indicates both minor alteration (e.g., Ba decreases toward the top of the profile in Hole 410A, whereas Na_2O is more irregular) and specific magma compositions (Sr variation is marked by distinct groupings within separate holes). The young crust basalts show little systematic variation with depth for Ba, Sr, or Na_2O , and probably show original magmatic values.

CONCLUSIONS

1. Few basalt samples from the Leg 49 holes can be considered completely chemically fresh, and most show the effects of submarine weathering.

2. As previously recorded, the older basement is generally more altered than the young basement. However, initial sedimentation rate and possibly cover thickness may affect the rate of subsequent alteration with time.

3. Oxidation and hydration occur very rapidly after extrusion and cause changes in the most mobile of the elements, whereas extensive carbonation takes longer. Leached elements may be responsible for changing the pH of the local aqueous environment of the basement solutions, and may eventually allow precipitation of carbonate.

4. The apparently low K/Rb ratios of the young crust may in part reflect original magmatic values, although their variation probably indicates variable mobility of K and Rb at an early stage. Subsequent aging of the crust causes the basalts to absorb K and some Rb.

5. Differences in alteration with depth occur in the basement between young and older crust profiles. The young crust shows very little variation with depth; the older crust shows extensive alteration in the top 50 meters of basement. The relative ages of the sites drilled suggest that about 2.5 m.y. are required before this extensive alteration zone develops. Detailed "saw-tooth" variation in both young and older profiles are related to specific flow-unit features.

6. The profiles indicate that all the alteration is caused by seawater percolating down through the lava pile from above. As time passes, prolonged contact causes extensive alteration and element mobility. At this crustal thickness (maximum of 230 m in Hole 409), there is little evidence for uprising hydrothermal fluids, although there is a tendency for water to increase with depth.

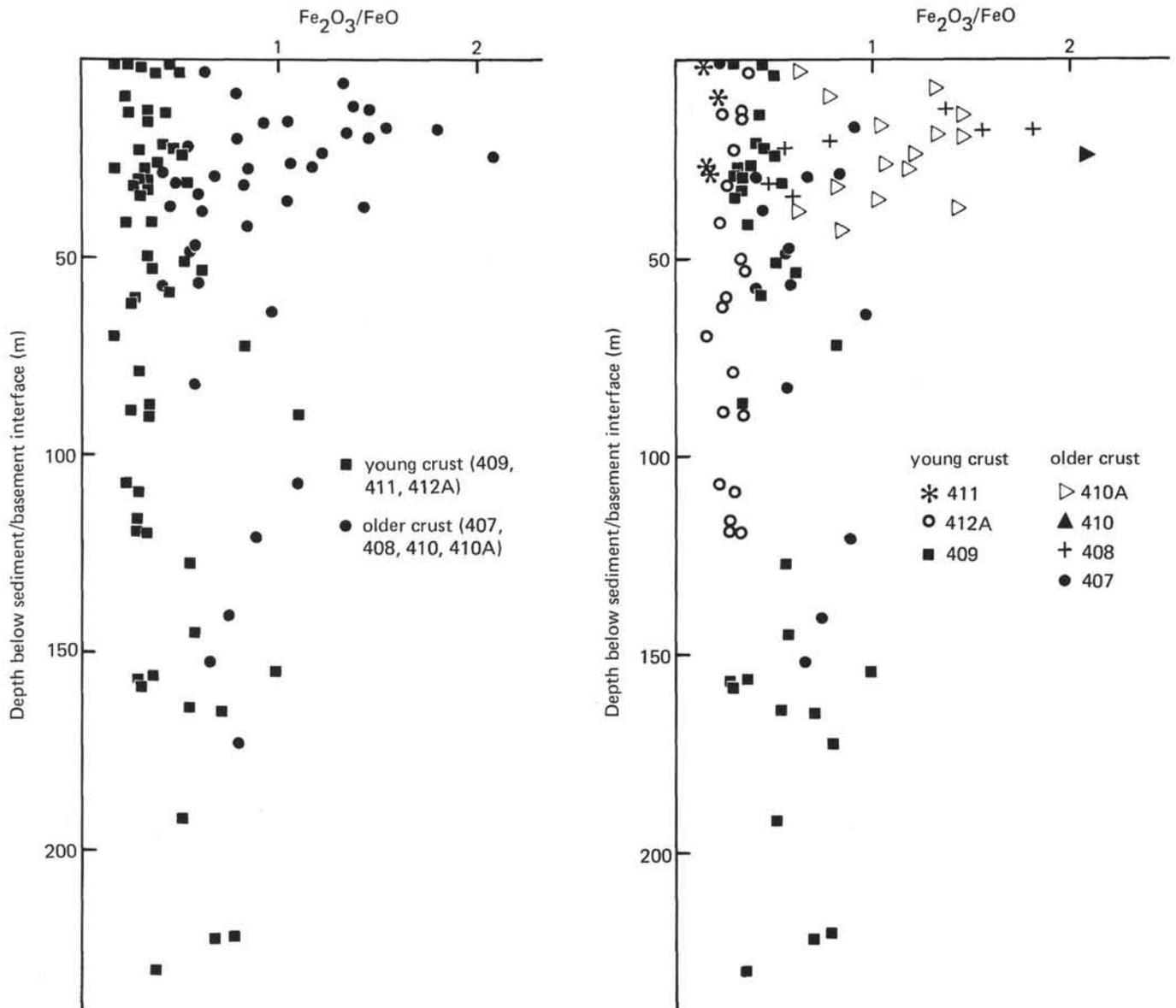


Figure 10a. Variation of oxidation with depth in the basaltic basement profile. Differences are evident between the young and older profiles in each case.

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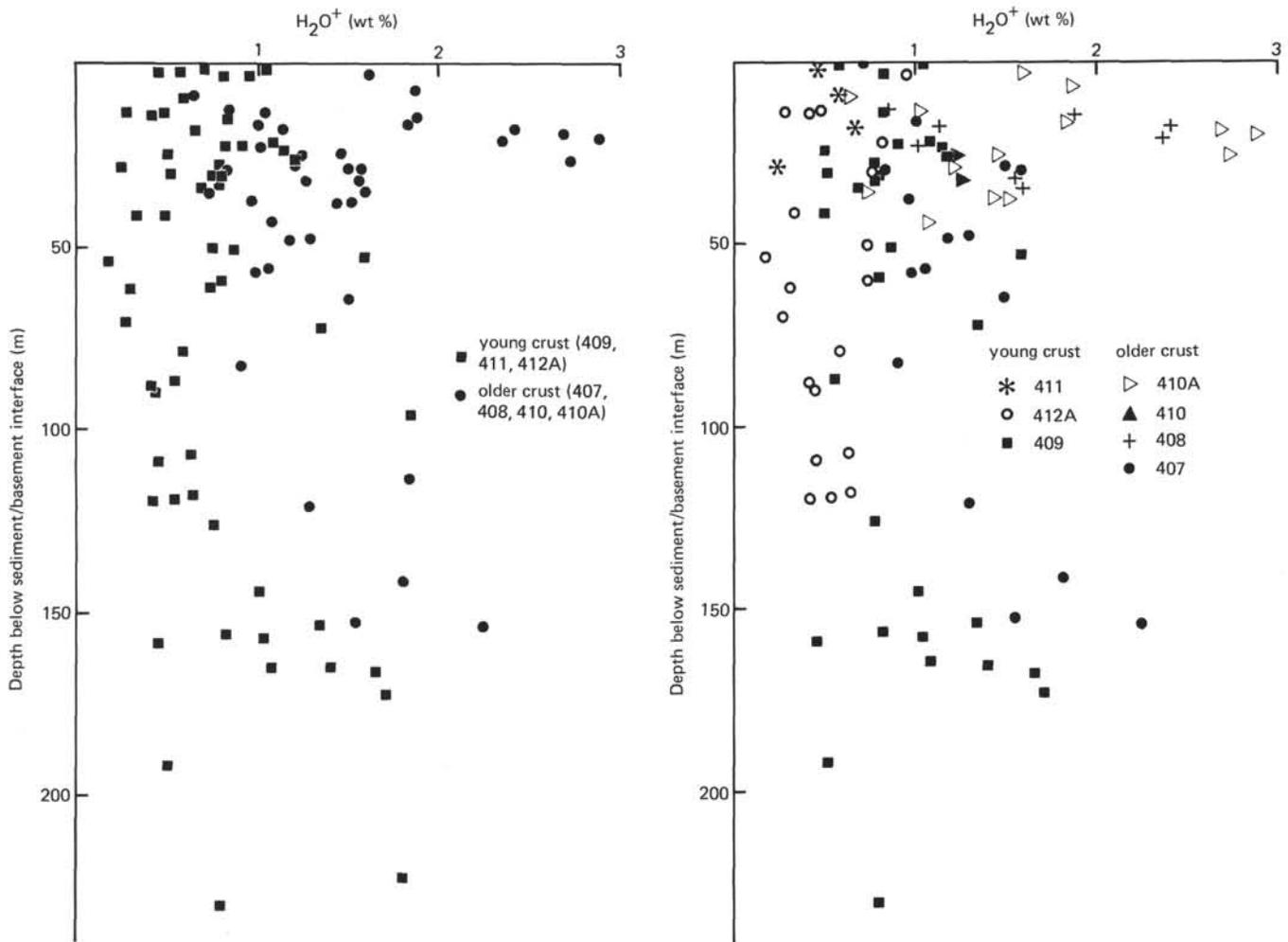


Figure 10b. Variation of hydration with depth in the basaltic basement profile. Differences are evident between the young and older profiles in each case.

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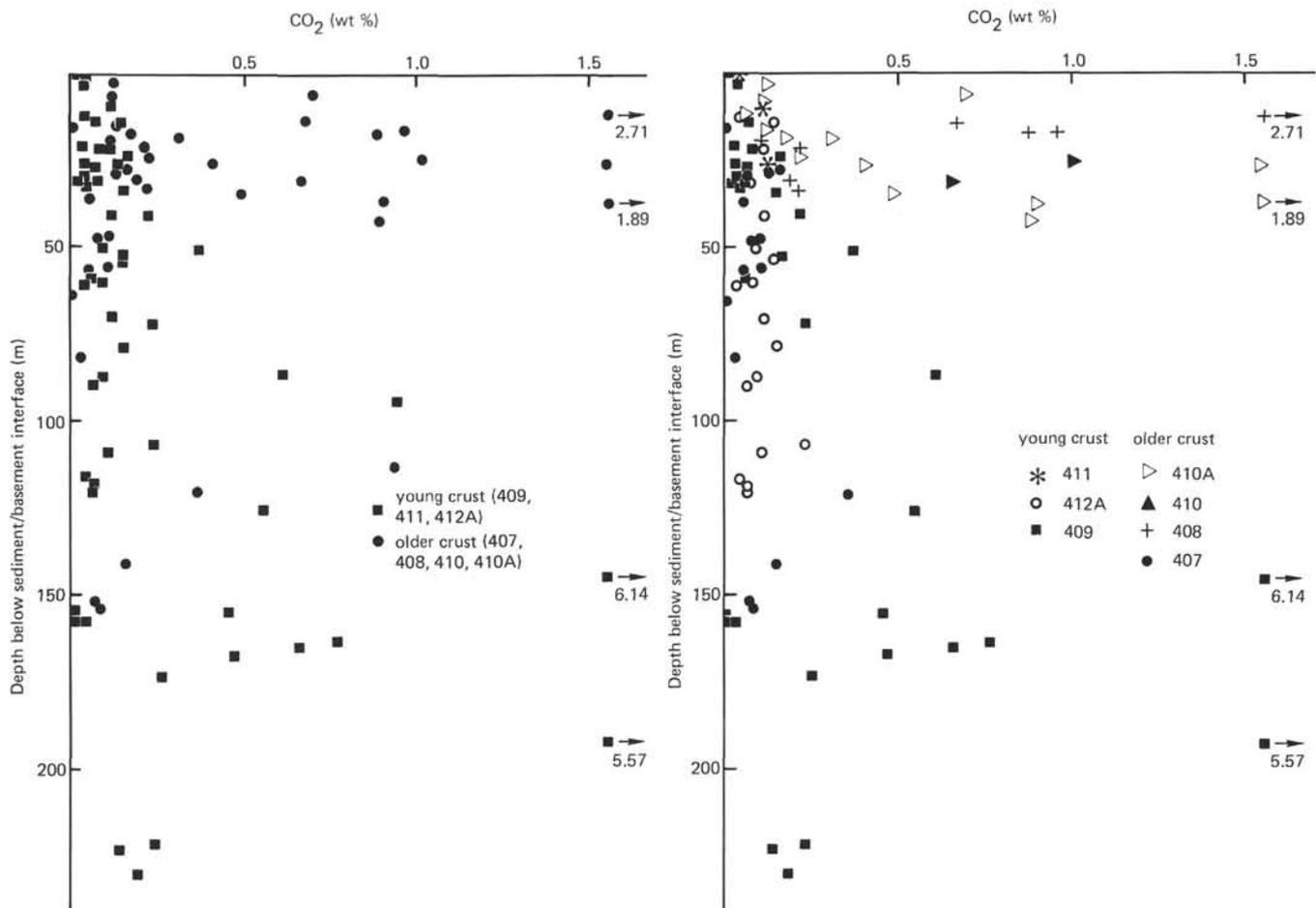


Figure 10c. Variation of carbonation with depth in the basaltic basement profile. Differences are evident between the young and older profiles in each case.

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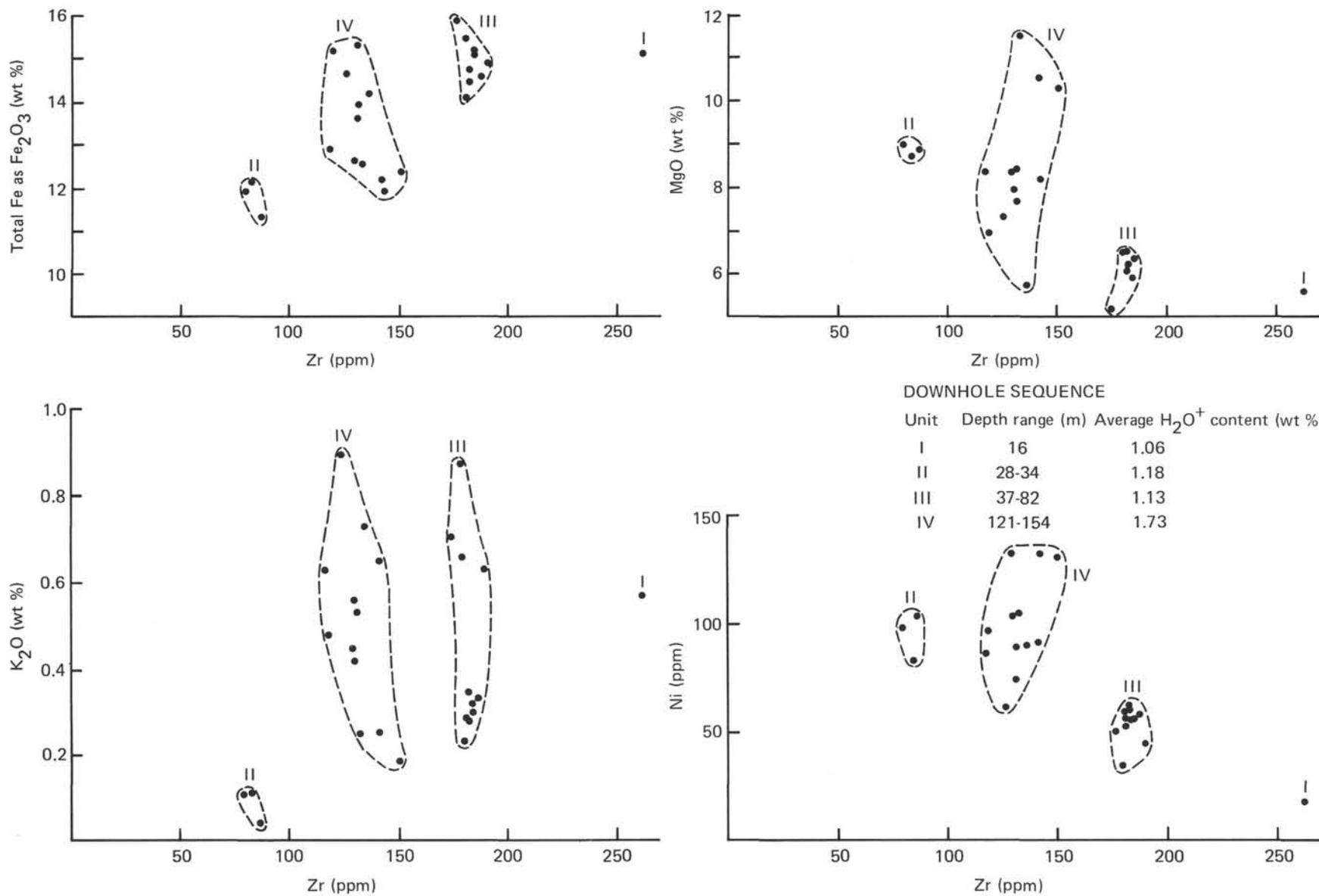


Figure 11. Increasing chemical scatter of total Fe, K₂O, MgO, and Ni within the four Zr-based units of Hole 407 with depth.

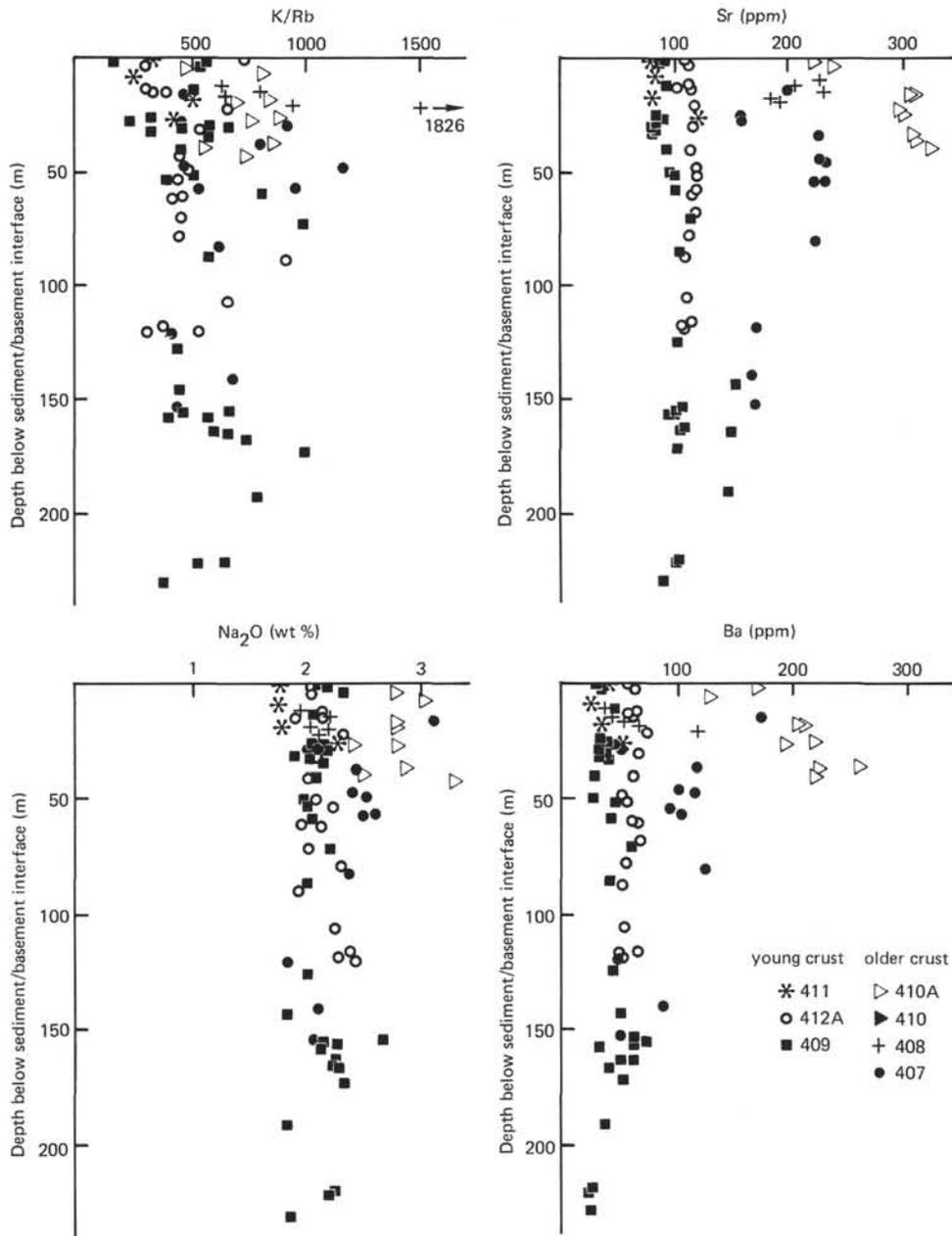


Figure 12. Variation of K/Rb, Sr, Ba, and Na₂O with depth in the basaltic basement.