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Chemical and mineralogical changes during basalt-seawater interaction: Site 223, Leg 23, D.S.D.P., north-west Indian Ocean

C. TH. PAPAVASSILIOU* AND M. E. COSGROVE

Department of Geology, The University, Southampton, SO9 5NH

ABSTRACT. The development of low- and high-temperature alteration products in a 23 m section of ocean-floor basalts is described. Analcime, calcite and dioctahedral smectite are ubiquitous. Trioctahedral smectite, smectite-chlorite mixed layers, chabazite and scolecite occur in the deeper sections with Fe^{3+} oxides/hydroxides progressively becoming more abundant in the upper regions. The upper layers of the sequence show marked chemical reduction. High-temperature chemical changes include Na and Mg enrichment accompanied by Ca and Fe^{2+} losses. Superimposed low temperature changes include gains in Fe^{3+}, K, Li, and Rb, and losses in Na, Ca, and Fe^{2+}. Many trace elements also show consistent behaviour.

DURING leg 23 of the Deep Sea Drilling Project in the Arabian Sea, basalts were collected beneath Palaeocene sediments from Site 223 (18° 44.98′ N., 60° 07.78′ E.) in the vicinity of the Owen Fracture Zone. About 23 m of igneous basement was penetrated; the upper 10 m or so being highly brecciated, the whole being progressively altered to a range of secondary minerals. Six core samples, representing the 23 m penetrated, were available for investigation (Table I). The igneous material, believed to represent a single flow, has been designated 'trachybasalt', being an alkali-rich rock atypical of both mid-ocean ridge and island arc environments (Whitmarsh *et al.*, 1974). More recent work shows the basement material to be a transitional basalt with strong sub-alkaline affinities (Papavassiliou, 1979).

Mineralogy and mineral chemistry. Secondary minerals in Site 223 basalts occur chiefly in fractures, vesicles or replacing interstitial groundmass material—mainly glass. Table I gives a semi-quantitative estimate of their distribution; analcime, smectite and calcite being the most abundant.

Analcime is common to abundant throughout the entire igneous sequence. Study of thin sections show that it occurs mainly in vesicles associated with palagonite, the vesicles being commonly rimmed with smectite (Papavassiliou, op. cit.). This type of occurrence suggests direct precipitation from a fluid phase of high salinity being rich in H_4SiO_4 and $Al(OH)_3$, and with a high Na:K ratio and a high pH. The existence of such fluids has been demonstrated by Jehl *et al.* (1977) in their study of ocean crust metamorphism in the N. Atlantic Ocean. They showed fluid salinity values up to five times that of normal seawater. Following the experimental work of Keene *et al.* (1976) a possible reaction for the formation of analcime might be:

$$Al(OH)_4(aq) + 2H_4SiO_4 + Na^+(aq) \rightleftharpoons NaAlSi_2O_6H_2O + 5H_2O$$

The ΔG (reaction) is negative at 25 °C (−19.053 kcal/mol), implying that thermodynamically, analcime can form spontaneously at 25 °C, given the necessary reactants.

The identification of analcime was confirmed by X-ray diffraction which also indicated the presence of the minor zeolites chabazite and scolecite (Table II) which only occur in small quantities in the lower samples. Analcime represents one-sixth of the total zeolite population in D.S.D.P. material from the Indian Ocean where it is present largely in 'basaltic volcanic sediments' (Iijima, 1978).

Smectite was identified by X-ray diffraction; orientated slide-mounts of bulk samples showing the characteristic smectite group expansion to 17 Å upon glycolation and contraction to 10 Å upon heating to 550 °C from the untreated (001) reflection between 14 Å and 14.6 Å. The X-ray results for non-orientated samples showed that throughout the igneous basement, smectites having (060) reflections in the range 1.50–1.52 Å are present, i.e. a dioctahedral variety. However, the lowest sample (41-2) also contains a more abundant smectite with

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* Present address: Laboratory of Mineralogy and Petrology, University of Athens, Ano Ilissia (Panepistimioupolis), Athens, Greece.

TABLE I. *Colour, secondary minerals, and oxidation coefficient of basalt core samples, Site 223*

Depth in bore below ocean floor	713-22 m		722-31 m			731-40 m
Sample No.	39-2 (46-48)	39-3 (132-134)	40-1 (60-62)	40-2 (15-17)	40-2 (105-107)	41-2 (12-14)
Colour	Red-brown, yellow with some green spots		Red-brown green spots	Grey-green with some red-brown spots		Green-grey
Hematite	*	*	*		*	
Geothite	*	**	**	**	*	*
Chabazite and scolecite				*	*	**
Analcime	****	***	****	***	***	****
Calcite	*	**	**	****	****	**
Smectite	****	****	***	***	***	**
Smectite-chlorite mixed layers				*	*	*
Oxidation coefficient	0.57	0.92	0.87	0.89	0.70	0.65

Depth to ocean floor: 3633 m.

Oxidation coefficient = Fe_2O_3/Fe_2O_3+FeO. Value for fresh mid-ocean ridge basalts = 0.156; average for off-ridge basalts (D.S.D.P., Legs 1-25) = 0.465 (Kharin, 1976; Hart, 1976).

Key:
* rare
** present
*** common
**** abundant

a 1.535 Å reflection indicating a trioctahedral variety. It was not possible to separate and analyse the smectites from this core.

Smectites separated from the upper samples (39-2 and 39-3) were analysed. The results, together with a calculation of the formula of both clays is presented in Table III. Both are iron-bearing dioctahedral montmorillonites showing a characteristic octahedral cation sum greater than 2.0 as the tetrahedral Al is greater than 0.5 (Weaver and Pollard 1973). Alkali values are high with K > Na. This K dominance has been reported in smectites associated with deep-sea basalts from various localities (Andrews *et al.*, 1977; Melson and Thompson, 1973; Scheidegger and Stakes, 1977). As the Na : K ratio of seawater is about 28 and the Na : K ratio in the analysed smectites is about 0.5, it is clear that such K-rich smectites could be an important trap for potassium in the ocean environment.

Small amounts of smectite-chlorite mixed layers which occur in the lower samples were identified by X-ray diffraction.

Calcite is obvious in the original core material, while X-ray diffraction studies show it to be a low-Mg variety. The Ca required for its formation was presumably derived from the basalt while the necessary CO_2 was evidently available as part of the magmatic event. A CO_2-rich environment accelerates breakdown of glass and pyroxenes as compared with felspars (Bass *et al.*, 1973), a pattern clearly shown in thin sections of Site 223 samples.

Geothite, hematite, and amorphous Fe^{3+} oxides/hydroxides are progressively more abundant in the upper samples, their presence being mainly responsible for the major colour change in the samples from grey-green to red-brown and yellow. Such variation in colour is clearly related to the increase in oxidation coefficient from the lower to higher samples (Table I), reflecting the supply of oxygen in the circulating fluids and their greater availability in the upper, more brecciated basalts. The smectites also show a change in colour from grey-green in the lower samples to red-brown in the upper material. This change has been explained (Bass, 1976) as due to Fe^{2+} in the octahedral lattice layers of first-formed smectites being oxidised to Fe^{3+} as oxygenated fluids penetrate the rock. During this process, the Fe^{3+} cannot be continuously incorporated in the octahedral lattice and is expelled to form independent non-silicate Fe^{3+} minerals.

TABLE II. *X-ray diffraction data for Site 223 zeolites*

d Å	*I*	ch.	sc.	an.
9.30	W	*		
6.61	W		*	
5.86	W		*	
5.59–5.62	S			*
4.98	W	*		
4.84	M			*
4.40	W		*	
4.33	W	*		
3.87	W	*		
3.66	W			*
3.58	W	*		
3.425–3.437	VS			*
2.91–2.93	S	*	*	*
2.86	W	*	*	
2.79	W			*
2.69	M			*
2.499–2.506	M			*
2.422	W			*
2.221	W			*
1.897	M			*
1.868	M			*
1.738–1.739	M			*
1.711	W			*
1.624	W			*
1.591	W			*
1.495	W			*
1.358	M			*

I (Intensity)

Key: VS = very strong
S = strong
M = medium
W = weak

ch. = chabazite
sc. = scolecite
an. = analcime

Whole-rock chemistry. The chemical analyses of the six original core samples are shown in Table IV. Major elements were determined on fused (lithium metaborate flux) rock powders using a Telsec Betaprobe, while trace elements were analysed by atomic absorption spectroscopy on rock digests or by Philips PW1212 X-ray spectrometer on rock powder pellets. Carbon dioxide was determined using an infra-red gas analyser and FeO by titration.

In order to gain more meaningful analytical values for comparison and discussion of the alteration products and processes, the original analyses were recalculated on a ($CaCO_3 + H_2O$)-free basis. These new analyses are shown for three individual samples (39-2, 39-3, 41-2) in Table V. The values for the three samples from core 40 (40-1, 40-2 (15–17), 40-2 (105–107)) have been averaged and are shown in core sequence in Table V under the heading 40-1, 40-2. The averaging of these three samples is justified since the individual recalculated analyses were very similar and in any case, they were taken within the same 2 m of core material.

During the recalculation procedure no account was taken of the likely association of Mn and Sr with calcite. No correction of their values was possible, since the degree of association was not known. The reliability of the recalculated Mn and Sr values in Table V must therefore be in doubt.

Table V also shows the intervals down core between the analysed samples. Precise measurements are not possible due to the incomplete core-barrel sections. Sample 39-2 (the highest) is within 1.5 m of the upper surface of the basalt; core 40 crosses the breccia-lava boundary at about

TABLE III. *Chemical composition and structural formulae of smectites from altered basalts, Site 223*

Sample	39-2 (46–48) %	39-3 (132–134) %
SiO_2	53.39	50.45
TiO_2	1.40	2.49
Al_2O_3	17.03	15.88
Fe_2O_3	9.29	10.70
FeO	—	1.04
MgO	7.51	9.18
MnO	0.21	0.27
CaO	1.05	1.06
Na_2O	1.11	0.85
K_2O	1.82	1.65
H_2O^+	6.30	5.43
Total	99.11	99.00
Tetrahedral ions		
Si^{4+}	3.459	3.350
Al^{3+}	0.541	0.650
Octahedral ions		
*Ti^{4+}	0.068	0.125
Al^{3+}	0.760	0.593
Fe^{3+}	0.453	0.535
Fe^{2+}	—	0.058
Mg^{2+}	0.725	0.909
Mn^{2+}	0.012	0.015
	2.018	2.235
Interlayer ions		
Ca^{2+}	0.073	0.075
Na^+	0.139	0.109
K^+	0.150	0.140
	0.362	0.324

* Ti may occupy some tetrahedral sites. Trace quantities of leucoxene may also be present.

TABLE IV. *Chemical analyses of the six original core samples*

Sample	39-2 (46–48)	39-3 (132–134)	40-1 (60–62)	40-2 (15–17)	40-2 (105–107)	41-2 (12–14)
SiO_2	48.46	39.12	43.79	23.73	30.22	43.37
TiO_2	0.46	0.82	1.18	0.46	0.92	1.02
Al_2O_3	16.58	12.67	14.71	7.24	10.04	14.08
Fe_2O_3	4.13	12.68	8.88	5.25	5.49	5.99
FeO	3.10	1.08	1.30	0.64	2.38	3.25
MgO	4.38	7.90	5.79	3.78	4.00	5.90
CaO	5.63	8.90	5.76	28.58	22.49	9.41
Na_2O	3.17	2.57	4.09	2.31	2.75	4.34
K_2O	2.30	1.41	1.55	0.95	1.34	1.03
P_2O_5	0.03	0.05	0.07	0.04	0.10	0.08
L.o.I.	11.25	13.31	12.74	26.95	20.48	10.83
Total	99.49	100.51	99.86	99.93	100.21	99.30
CO_2	1.8	4.6	2.2	20.4	14.9	2.7
ΣFe as Fe_2O_3	7.58	13.88	10.33	5.96	8.13	9.60
Li	47	50	10	10	15	12
S	182	160	232	191	174	107
V	72	152	154	119	194	216
Cr	65	182	101	27	24	43
Mn	1382	2049	1026	2457	2215	1350
Ni	64	92	109	49	36	39
Cu	56	126	47	39	49	35
Zn	51	234	97	39	65	65
Ga	17	15	14	6	12	14
Rb	46	17	27	10	n.d.	13
Sr	62	54	42	108	43	374
Y	18	14	14	19	14	20
Zr	59	56	78	60	38	74
Nb	12	5	8	9	4	9
Ba	83	86	110	105	165	100
La	13	18	13	n.d.	n.d.	n.d.
Ce	17	21	11	6	9	22
Pb	3	4	6	3	3	4

Major elements in percentage; trace elements in parts per million. L.o.I. = loss on ignition; ΣFe as Fe_2O_3 = total Fe expressed as Fe_2O_3 as determined by Betaprobe; n.d. = not detected.

10 m depth and sample 41-2 (the lowest) occurs between 14 and 21 m below the surface (Whitmarsh *et al.*, 1974).

It is immediately obvious on inspection of Table V that while the upper sample (39-2) is substantially different in composition from the others, the lower three analyses form a group which show distinctive chemical trends. For example, Fe_2O_3, MgO (and K_2O) increase in abundance upwards from right to left as do the trace elements Li, Cr, Ni, Cu, Zn, Ga, Rb, and La. Further, FeO, CaO, Na_2O (and P_2O_5) show a decrease in abundance upwards as do Sr (and V). The values for SiO_2, TiO_2, and Al_2O_3 are very similar in this lower group of three and it is perhaps significant that during the alterations producing the changes in the other components mentioned above, these three are virtually unchanged. Alumina and TiO_2 in particular have often been considered as the least mobile components amongst the major elements.

The upper sample (39-2), closest to the surface of the basalt, shows large increases in SiO_2, Al_2O_3, K_2O, and Rb, and falls in TiO_2, Fe_2O_3, MgO, and P_2O_5 compared with the lower group. Further, the upward decreasing trends of FeO, CaO, and Na_2O in the lower group are reversed as are the upward increasing trends for Li, Cr, Ni, Cu, Zn, and La. Most significantly perhaps is that sample 39-2 has the lowest total Fe value and oxidation coefficient of all samples.

Discussion. The mineralogical and chemical evidence is complementary and indicates the varying nature of alteration of the basalt throughout the penetrated thickness of 23 m. The lower samples, in addition to major analcime, smectite, and calcite contain small quantities of chabazite, scolecite and smectite-chlorite mixed layers. This mineral assemblage clearly indicates that the lower parts of the section have been subjected to high temperature alteration, probably in the 150-200 °C range. Many would regard such an assemblage as truly metamorphic, representing the lowest phases of the zeolite facies (Miyashiro *et al.*, 1971; Miyashiro and Shido, 1970).

The lowest sample (41-2) is the nearest approximation to unaltered basalt both in terms of chemistry and mineralogy. However, it has a very high Na_2O value in excess of 5.0% which, in all probability, greatly exceeds the original concentration. Such Na enrichment is explained by abundant analcime and other zeolites—chabazite and scolecite, both of which (but especially the former) can be Na-rich. In addition, more relatively unaltered basalt with (Na-enriched) plagioclase is present. Thus the lowest material in the igneous section already shows substantial chemical change, where it is believed that the Na gain is the major manifestation of the relatively high-temperature reactions between fresh basalt and downward percolating ocean water.

As described in the previous section, the lower group of three analyses (Table V) show systematic chemical changes representing progressive alteration upwards to sample 39-3. The increase in Mg and loss in Ca and Fe^{2+} and to some extent Si are characteristic changes for high-temperature (hydrous metamorphic) alteration (Tomasson and Kristmannsdottir, 1972; Hart, 1973). The increasing trends of Fe^{3+}, total Fe, K, Li, and Rb in the same group of samples are characteristic changes for low-temperature alteration (halmyrolysis) (Hart, S. R., 1969; Hart, 1976; Melson and

TABLE V. *Chemical analyses recalculated and restructured on a ($CaCO_3+H_2O$)-free basis (see text)*

Sample and distance between	39-2 2.36 m	39-3 > 4.5 m	40-1, 40-2 > 4.0 m	41-2
SiO_2	56.04	48.39	50.71	50.59
TiO_2	0.53	1.01	1.30	1.19
Al_2O_3	19.18	15.67	16.46	16.42
Fe_2O_3	4.78	15.69	10.24	6.99
FeO	3.56	1.36	2.28	3.79
MgO	5.07	9.77	7.17	6.88
CaO	3.86	3.77	4.93	6.96
Na_2O	3.67	3.18	4.76	5.06
K_2O	2.66	1.74	2.02	1.20
P_2O_5	0.03	0.06	0.11	0.09
Oxidation coefficient	0.57	0.92	0.82	0.65
ΣFe as Fe_2O_3	8.77	17.17	12.77	11.20
Li	54	62	19	14
S	211	198	323	125
V	83	188	252	252
Cr	75	225	72	50
Mn	1598	2535	3363	1575
Ni	74	114	97	69
Cu	65	156	73	41
Zn	59	289	102	76
Ga	20	19	17	16
Rb	53	21	18	15
Sr	72	67	117	436
Y	21	17	27	23
Zr	68	69	94	86
Nb	14	6	12	10
Ba	96	106	208	117
La	15	22	5	—
Ce	20	26	14	26
Pb	3	5	6	5

Major elements in percentage; trace elements in parts per million.

Thompson, 1973). These researchers also record loss in Na, Mg, Ca, and Fe^{2+} as further characterization of low temperature change. Thus Ca and Fe^{2+} are lost whatever the temperature of alteration, whereas a low-temperature alteration following a high-temperature change would reverse the roles of Na and Mg, having been gained during initial high temperature change and lost later.

In the group of samples under study, we find the consistent changes for Ca and Fe^{2+}, a persistent increase in Mg values upwards (compatible with high-temperature alteration), and a persistent decrease in Na values compatible with low-temperature alteration. This pattern probably reflects the differing stabilities of the main early formed minerals containing these components where Mg-rich smectites resist later low-temperature changes while Na-rich analcime is more susceptible to low-temperature change or K for Na substitution.

The bottom 19 m or so of the 23 m of sampled basement has thus been subjected to high-temperature alteration which developed a characteristic zeolite-smectite-calcite assemblage with the appropriate chemical changes. Superimposed on this, a low-temperature phase brought about changes in the Na content and caused the development of Fe oxides/hydroxides and Fe^{3+}-rich smectite as described earlier. The progressive upward increase in oxidation coefficient clearly indicates the growth of Fe^{3+} over Fe^{2+}, this change being associated with an increase in total Fe.

The abrupt drop in total Fe abundance between sample 39-3 and the highest (near surface) sample 39-2 is perhaps the most striking change in the over-all differences in the chemistry of this top sample. The large drop in oxidation coefficient provides the vital clue to the chemical history of this sample, as clearly it has suffered a late stage reduction causing abundant $Fe^{3+} \rightarrow Fe^{2+}$ accompanied by the fall in total Fe. This must be the last event in the alteration history of the igneous basement and presumably relates to the sealing-off of the basalt from the open ocean waters by overlying clays which would also penetrate the heavily brecciated upper layers of basalt. Thus sample 39-2 could well have been in an active reducing environment induced by the enclosing sediments. Earlier-formed Fe^{3+} would be reduced to Fe^{2+} which could then be carried in solution to lower levels to be re-oxidised by remaining oxygenated interstitial waters. This would account for both the change in oxidation coefficient and the reduction in total Fe.

CaO and Na_2O show insignificant changes in the upper sample compared with sample 39-3, but MgO with a large decrease, and K_2O a substantial increase reflect previously recorded low temperature changes, perhaps enhanced here in the upper layers where shattering and rapid cooling was intense. P_2O_5 and TiO_2 are also much lower in the upper sample which suggests that these components are also removed as a result of intensive low-temperature alteration.

The net result of these changes recorded in sample 39-2 is to reduce significantly the total chemical components other than SiO_2 and Al_2O_3, thus increasing the SiO_2 and Al_2O_3 percentages to maintain the 100% total. This is reflected in the over-all abundances of the secondary aluminosilicates, smectite and analcime.

The large reductions in abundance of certain trace elements in sample 39-2 as compared with lower samples, in particular V, Ni, and Zn together with an increase in Rb are compatible with other recorded low-temperature changes (Hart, 1976).

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REFERENCES

Andrews, A. J., Barnett, L. R., MacClement, B. A. E., Fyfe, N. S., Morrison, G., Macrae, N. D., and Starkey, J. (1977). *Initial Reports of D.S.D.P.* **37**, Washington D.C., U.S. Govt. Printing Office. 795–810.

Bass, M. N., Moberly, R., Rhodes, J. M., Shih, C. S., and Church, S. E. (1973). Ibid. **17**, 429–503.

——(1976). Ibid. **34**, 393–432.

Hart, R. A. (1973). *Can. J. Earth Sci.* **10**, 799–815.

——(1976). *Initial Reports of D.S.D.P.* **34**, 301–39.

Hart, S. R. (1969). *Earth Planet. Sci. Lett.* **6**, 295–303.

Iijima, A. 1978. In *Natural Zeolites*, Sand, L. B., and Mumpton, F. A. (eds.) Oxford–New York (Pergamon Press). 175–98.

Jehl, V., Poty, B., and Weisbrod, A. (1977). *Bull. Geol. Soc. France*, **7**, 1213–21.

Keene, J. B., Claque, D. A., and Nishimori, R. K. (1976). *J. Sed. Petrol.* **46**, 647–53.

Kharin, G. N. (1976). *Initial Reports D.S.D.P.* **38**, 685–715.

Melson, G. W. and Thompson, G. (1973). *Geol. Soc. Am., Bull.* **84**, 703–16.

Miyashiro, A. and Shido, F. (1970). *Lithos*, **3**, 251–60.

————and Ewing, M. (1971). *Phil. trans. R. Soc.* **A 268**, 589–603.

Papavassiliou, C. T. (1979). Unpubl. Ph.D. thesis, University of Southampton.

Scheidegger, K. F. and Stakes, D. S. (1977). *Earth Planet. Sci. Lett.* **36**, 413–23.

Tomasson, J. and Kristmannsdottir, H. (1972). *Contrib. Mineral. Petrol.* **36**, 123–34.

Weaver, C. E. and Pollard, L. D. (1973). *The Chemistry of Clay Minerals.* Amsterdam (Elsevier).

Whitmarsh, R. B., Weser, O. E., Ross, D. A. *et al.* (1974). Initial Report D.S.D.P. **23**.

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