Carbonatization and Mobility of Ti, Y, and Zr in Ascot Formation Metabasalts, SE Quebec

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Abstract. The middle Ordovician Ascot Formation of southeastern Quebec consists of greenschist facies metamorphosed silicic to mafic pyroclastic rocks and lava flows and associated metasediments. Chemical analyses of lavas reveal a preponderance of metarhyolites and metabasalts, together with some porphyritic rocks with intermediate SiO_2 contents. The metabasalts exhibit wide ranges in concentrations of TiO_2 (0.25–2.0 wt.%), Y (9–46 ppm), and Zr (5–135 ppm). The extent of the ranges, and unusual inter-element ratios, suggest that the concentrations of these normally immobile elements have been affected by secondary processes.

There is a strong correlation between trace-element concentrations and the degree of carbonatization of the metabasalts. Low carbonate rocks are severely depleted in Ti, Y, and Zr whereas high carbonate rocks are depleted in Y and Zr and enriched in Ti. The differing movement of Ti can be explained in terms of variable chemical potential due to the various carbonatization reactions affecting titaniferous phases. Overall mobility of these generally 'immobile' elements is attributed to high CO_2 levels in the fluid phase during metamorphism.

Extrapolation of the two alteration trends to a common origin enables one to infer primary concentrations of the trace-elements. Primary inter-element ratios arrived at in this way are compatible with an island-arc origin for the Ascot Formation although TiO_2 concentrations are a little high (1.5 wt.%).

Introduction

Trace-element geochemistry is one of the most effective indicators of the chemical and tectonic affinity of volcanic rocks. In recent years much attention has been focussed on elements such as Ti, Zr, and Y, (e.g., Pearce and Cann 1973; Floyd and Winchester 1975) which are relatively immobile under most low- to medium-grade metamorphic conditions (Cann 1970) and are consequently of wider applicability in ancient terrains than more mobile elements. This paper reports the results of a study of metavolcanic rocks from the Ordovician Ascot Formation of southeastern Quebec in which these relatively immobile elements can be shown to have been very mobile indeed. The enhanced mobility is attributed to the presence of a CO_2-rich fluid during metamorphism.

In the Ascot Formation there is a range of metamorphic assemblages reflecting differing degrees of carbonatization, and a close relationship between the metamorphic assemblage and the relative enrichment or depletion in trace elements. The movement of Ti, whose host minerals are known, can be simply explained in terms of the reactions relating the various metamorphic assemblages. Despite the mobility of Ti, Y, and Zr it is possible to obtain a rough indication of their original concentrations that is useful as a paleotectonic indicator.

Geologic Setting and Field Relationships

The Ascot Formation is exposed in and around Sherbrooke, in the Eastern Townships of Quebec. It lies in the 'internal domain' of the Quebec Appalachians as defined by St. Julien and Hubert (1975), a zone of metamorphic and igneous rocks sitting SE of the wide zone of NW vergent nappes of the external domain. Rocks of the internal domain were themselves emplaced as nappes and then folded and cleaved, probably during Ordovician and earliest Silurian time (St. Julien and Hubert 1975).

The Ascot Formation consists of metamorphosed silicic pyroclastic rocks and lavas, and metamorphosed mafic lavas and tuffs together with a variety of metasedimentary rocks, particularly phyllites and chlorite-sericite schists (St. Julien and Lamarche 1965; Lamarche 1967). The age of the formation is not precisely known, but is thought to be middle Ordovician (St. Julien and Hubert 1975).

These rocks have been interpreted as the remains of a calc-alkalic volcanic arc, formed during the destruction of the early Paleozoic Iapetus ocean (St. Julien and Hubert 1975). They, with the correlative Weedon Formation further north, constitute the only such remains so far recognized in Quebec. Although the interpretation appears reasonable, doubts have been raised (Church 1977) because of a suggestion of bimodality and in particular because of high (up to 2.5 wt. %) TiO_2 contents in analyses of the metavolcanic rocks reported by Alsac et al. (1971). Results reported in this paper provide a possible explanation for the high TiO_2 contents, although the bimodality of the suite is still apparent.

Sampling for this study was conducted throughout the area of exposure of the Ascot Formation (St. Julien 1965) in an attempt to obtain the widest variety of rock types. A location map is available on request. Obvious tuffaceous rocks were avoided because of the possibility of contamination. In general, because of the intensity of the deformation and metamorphism, the pyroclastic rocks are highly schistose. Lavas can be recognized by their massive appearance. In the field, igneous primary structures are rarely observed, although some of the mafic lavas are pillowed. Many of the rocks sampled have relict primary petrographic features attesting to their igneous origin. However, some of the better cleaved samples have no primary features. It is therefore possible that they were tuffs. There is however no correlation between the degree of cleavage development and chemistry of the rocks, so that the presence of a non-igneous component in these rocks is thought unlikely.

Petrography

On the basis of primary textures and overall mineralogy the sampled rocks can be divided into three groups: porphyritic felsites, mafic to intermediate porphyritic rocks and non-porphyritic mafic rocks. The first and third groups constitute an overwhelming majority of the rocks present.

The porphyritic felsites contain phenocrysts of quartz and albite in a fine-grained quartzofeldspathic groundmass. The groundmass is commonly recrystallised but has a preserved trachytic texture in some cases. These rocks were probably soda-rich rhyolities.

The mafic to intermediate porphyritic rocks contain abundant phenocrysts of feldspar (now albite $\pm$ white mica) and a mafic mineral (now chlorite and/or actinolite) in a groundmass of albite, chlorite and epidote $\pm$ actinolite $\pm$ white mica $\pm$ calcite. The relative proportions of feldspar and mafite phenocrysts are very variable. Together they constitute typically 40 % of the rock by volume. Given the poor preservation of these rocks it is difficult to classify them. They may have been porphyritic basalts or andesites.

The non-porphyritic mafic rocks exhibit typical basaltic textures, dominated by roughly parallel-oriented plagioclase (now albite) laths. The form of original ferromagnesian minerals is generally obscured by chlorite $\pm$ actinolite overgrowths. Some of the finer grained mafic rocks contain actinolite pseudomorphs after quenched pyroxene grains. Many of these rocks contain small proportions of plagioclase phenocrysts. More rarely there are ferromagnesian phenocrysts (now chlorite or actinolite). Some of the rocks in this group are completely recrystallised with no trace of a former igneous texture. The non-porphyritic mafic rocks were originally basalts; a fact which is abundantly clear from their chemistry (see below).

From petrographic observations there is little evidence to suggest that the Ascot Formation consisted of a typical calc-alkalic igneous suite ranging from basalt through andesite and dacite to rhyolite. Rather, it appears to have consisted predominantly of basalts and rhyolites, with subordinate porphyritic rocks. The

possibility that intermediate lava types were erupted primarily explosively and are preserved as tuffs cannot, however, be excluded.

Present mineral assemblages in all rocks examined are in the greenschist facies. No primary minerals, other than quartz and perhaps albite in the metarhyolites, are preserved. Several different greenschist facies mineral assemblages occur, depending on the degree of carbonatization of the rocks. All mafic rocks contain chlorite, albite and quartz. The lowest carbonate assemblages contain in addition epidote (E), actinolite (A), and sphene (S). (The assemblage is referred to as EAS in what follows.) Many also contain small amounts of calcite. More carbonated assemblages contain no actinolite but have abundant calcite (C) together with epidote and sphene (ECS). A few rocks in this group contain no epidote (CS). Further carbonation produces the breakdown of sphene and production of rutile (R). Thus there are rocks with the assemblage epidote-calcite-sphene-rutile (ECSR), and rocks with the assemblage calcite-rutile (CR). Only one rock was observed with the assemblage ECR. All rocks contain chlorite, albite and quartz. Additional phases present in some rocks of all assemblages are phengitic mica and magnetite. Thus, the order of assemblages with increasing carbonatization is EAS, ECS or CS, ECSR, ECR, or CR. The sites of some of these minerals are firmly controlled by primary mineral sites. Albite pseudomorphs plagioclase, actinolite pseudomorphs pyroxene and the titaniferous minerals pseudomorph ilmenite. Quartz, calcite and epidote sites are not simply related to primary mineraloty. Phengitic mica occurs as a replacement of glagioclase.

Geochemistry

Thirty-nine rocks were analyzed for major elements, together with Rb, Sr, Zr, Y, and Nb (Table 1). Only three samples of the porphyritic felsites and all (four) of the mafic to intermediate porphyritic rocks that had been examined petrographically, were analysed. The analyses are therefore not proportionately representative of the field sampling, the felsites being particularly poorly represented. The rhyolitic character of the felsites is confirmed by their high SiO_2 contents (73–77 wt. %). The mafic to intermediate porphyritic rocks have SiO_2 contents ranging from 51 to 62 wt. %, reflecting the variable quantity and relative proportions of different phenocrysts. The non-porphyritic mafic rocks have SiO_2 contents between 48 and 57 wt. %, confirming their largely basaltic character. In view of the alteration these rocks have experienced, any more detailed comparison of the major

Table 1. Chemical analyses of Ascot Formation lavas. Analyses by XRF. Major element analyses (wt. %) are a combination of the author's and data from X-ray Assay Laboratories, Toronto. They are normalised to 100 % volatile-free. Rb, Sr, Y, Zr, and Nb (ppm) were analysed using a modification of the method of Webber and Newbury (1971). Nb values were generally below the detection limits (~5 ppm) and are not given. nd = not detected. Oxides in weight percent, trace-elements in ppm. Rocks 261, 251, 054, 241 are porphyritic intermediate to mafic; rocks 061, 032, 281 are felsic. All others are non-porphyritic mafic

Rock	161	056	171	111	201	191	083	174	057	222
Metamorphic assemblage	CR	CR	CS	EAS	CR	EAS	ECS	ECSR	CR	EAS
SiO_2	48.44	49.12	49.31	49.86	50.03	50.59	50.98	51.45	51.45	51.50
Al_2O_3	17.59	19.17	17.80	16.34	15.77	17.77	17.90	17.59	17.69	17.89
TiO_2	0.60	1.85	1.57	0.83	1.01	0.70	1.46	1.66	1.44	0.72
FeO	9.58	10.36	9.41	8.44	9.75	7.20	9.10	9.48	9.56	7.45
MnO	0.31			0.25		0.27				0.21
MgO	9.54	7.61	8.47	9.36	9.42	8.62	8.21	7.50	6.81	9.21
CaO	9.21	6.50	9.37	12.31	9.80	10.51	9.53	7.20	7.84	8.73
Na_2O	4.46	4.69	1.38	2.50	2.05	3.13	2.64	4.50	4.52	3.28
K_2O	0.31	0.55	2.54	0.06	2.13	1.15	0.07	0.47	0.56	0.98
P_2O_5	0.06	0.16	0.15	0.04	0.04	0.04	0.11	0.15	0.13	0.04
Rb	nd	7	40	nd	25	12	3	8	7	10
Sr	159	78	107	282	124	227	149	151	116	360
Y	15	19	22	24	24	25	36	29	26	21
Zr	6	91	110	12	24	17	118	125	108	18

Rock	181	271	011	221	172	082	133	088	232	173
Metamorphic assemblage	EAS	EAS	ECR	CR	ECSR	ECS	EAS	ECS	EAS	ECSR
SiO_2	51.65	51.71	51.73	51.78	52.53	52.55	52.72	52.73	52.73	52.86
Al_2O_3	17.91	17.60	18.83	15.52	17.26	16.89	14.97	16.33	17.96	18.02
TiO_2	1.23	1.12	0.46	2.05	1.76	1.45	0.83	1.80	0.62	1.56
FeO	8.21	10.22	7.65	14.90	9.91	9.35	7.77	10.67	12.18	9.58
MnO	0.24	0.31					0.28	0.28	0.28	0.27
MgO	7.07	7.62	4.87	5.76	7.45	7.80	9.94	7.65	5.73	6.29
CaO	8.95	7.34	9.35	5.54	6.20	9.39	9.84	9.48	8.44	6.80
Na_2O	2.35	3.90	6.90	4.10	4.64	2.24	3.28	0.84	1.95	3.02
K_2O	2.27	0.04	0.05	0.20	0.13	0.20	0.32	0.02	0.03	1.44
P_2O_5	0.12	0.13	0.17	0.15	0.14	0.12	0.05	0.19	0.06	0.17
Rb	28	nd	nd	4	8	nd	2	nd	nd	27
Sr	205	216	175	92	126	163	175	152	381	151
Y	30	30	9	43	21	27	21	38	16	34
Zr	120	46	12	74	97	108	16	115	7	134

element analyses with those of modern volcanic rocks is considered unwise. It is worth noting, however, that discriminant analysis of the non-porphyritic mafic rocks using the method of Pearce (1976) shows most of these rocks have the major element 'fingerprints' of mid-ocean ridge basalts. Their lithological association makes a mid-ocean ridge origin very unlikely, and the comparison demonstrates the dangers of using data from altered basalts.

Alteration problems have been avoided for many ancient basalts by concentrating only upon relatively immobile elements such as Ti, Y, Zr, and P. However, a remarkable feature of mafic rocks of the Ascot Formation is the extreme range in concentrations of these elements for very small ranges in major element content (Fig. 1). Several lines of reasoning suggest

that these ranges in concentration are not primary in origin. First, the ranges exhibited (almost an order of magnitude) are much greater than observed within the mafic part of fresh volcanic suites. Second, the lowest contents of TiO_2 and Zr observed (0.25 wt. % and 5 ppm respectively) are unusually low. Third, there is no simple correlation between TiO_2 and Zr content and the extent of differentiation (as reflected, very roughly, by FeO/MgO - Fig. 2). Finally, the rocks plot over a broad field on Pearce and Cann's (1973) Ti - Y - Zr plot (Fig. 3), many lying well outside the fields defined by Pearce and Cann for modern basalts. In the following discussion it is assumed that most of the variation in Ti, Zr, and Y is secondary in origin, although a small amount may be primary.

Table 1 (continued)

Rock	132	131	141	084	272	153	031	085	081	091
Metamorphic assemblage	EAS	EAS	EAS	EAS	EAS	EAS	EAS	EAS	ECS	EAS
SiO_2	53.07	53.36	53.68	54.20	54.29	54.52	54.62	54.87	55.00	55.00
Al_2O_3	15.08	12.72	16.24	17.08	16.44	16.85	17.78	17.45	13.90	13.90
TiO_2	0.83	0.82	1.16	0.39	0.58	0.99	0.52	0.38	0.25	0.25
FeO	7.43	8.14	10.86	9.79	9.42	12.45	10.52	8.57	9.13	9.13
MnO		0.31	0.30	0.30		0.25	0.27	0.24		
MgO	8.55	12.41	4.51	8.44	7.19	5.83	6.30	7.45	9.51	9.51
CaO	11.32	8.29	7.81	7.85	7.64	5.03	7.20	7.75	8.84	8.84
Na_2O	3.08	3.00	4.96	1.87	4.33	3.62	2.69	3.18	3.14	3.14
K_2O	0.58	0.91	0.39	0.03	0.04	0.36	0.03	0.04	0.20	0.20
P_2O_5	0.06	0.04	0.09	0.05	0.06	0.09	0.06	0.05	0.02	0.02
Rb	6	6	1	nd	nd	2	nd	nd	1	2
Sr	263	137	295	147	197	86	95	56	130	63
Y	21	23	29	10	12	30	10	11	46	09
Zr	37	23	42	10	26	56	5	14	114	14

Rock	086	151	261	251	054	241	061	032	281
Metamorphic assemblage	EAS	EAS	EAS	EAS	EAS	EAS	CR	CR	CR
SiO_2	55.55	56.67	50.97	55.62	59.89	61.83	73.43	76.42	77.26
Al_2O_3	16.19	15.62	20.33	17.60	17.55	16.91	13.72	13.17	13.40
TiO_2	0.35	0.93	0.90	0.59	0.70	0.62	0.29	0.27	0.08
FeO	8.14	11.79	10.12	9.29	7.23	5.79	4.17	2.37	1.17
MnO	0.28	0.23	0.31	0.24	0.28		0.17		
MgO	7.17	6.58	5.98	5.25	3.76	3.50	0.53	0.19	0.40
CaO	8.94	3.87	5.43	5.61	3.81	5.61	0.81	0.26	0.43
Na_2O	3.05	4.02	2.12	2.82	5.40	2.16	6.73	7.21	2.97
K_2O	0.28	0.20	3.67	2.84	1.19	3.48	0.08	0.09	4.27
P_2O_5	0.04	0.10	0.18	0.12	0.19	0.09	0.07	0.03	0.03
Rb	nd	1	101	84	26	86			
Sr	82	75	237	198	210	393			
Y	11	26	22	22	24	18			
Zr	9	48	146	145	167	99			

Element Mobility and Degree of Carbonatization

There is a clear correlation between the trace-element contents and the degree of carbonatization of mafic rocks of the Ascot Formation. The low carbonate rocks, with assemblage EAS, have generally low contents of TiO_2 and Zr, in strong contrast to rocks with the assemblages CS, ECS, and ECSR (Figs. 1, 2, 4). This correlation provides further support for the secondary origin of the variation, and suggests that the amount of CO_2 in the fluid phase has a bearing on the mobility of these elements.

The contrast between the highly mobile behaviour of Ti and Zr in the Ascot Formation and their general immobility during metamorphism is most simply attributed to the presence of significant CO_2 in the fluid phase. Although the factors controlling dissolution of cations in a fluid phase are complex it is clear that cations such as Ti^{4+} and Zr^{4+} tend to form weakly bonded complexes with ligands such as CO_3^{2-} because of the high electronegativities of these high valence cations (e.g., Rösler and Lange 1972; Langmuir 1979). Thus the general immobility of these cations in aqueous solutions is understandable. A possible explanation for the enhanced mobility of these cations when CO_2 levels are high lies in the formation of high ligand-number complexes. Such complexes are favoured by high ligand concentration in the fluid and are more prevalent for high valence cations (Langmuir 1979). Thus a high CO_2 content in the fluid phase may favour the formation of high-order carbonate complexes with Ti^{4+}, Zr^{4+} and other high valence cations, while having little effect on the solubility of lower valence cations.

Systematics of Dissolution Process

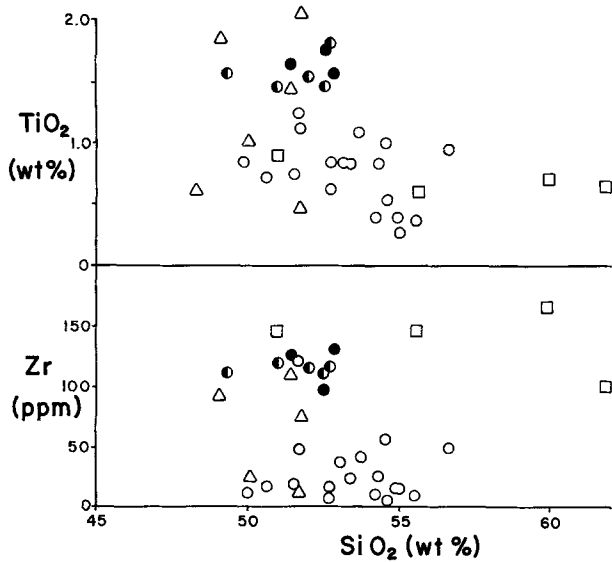Element mobility may be modelled by considering a fluid passing through the rock, selectively removing

Fig. 1. TiO$_2$ and Zr variation with SiO$_2$ in mafic rocks of the Ascot Formation. Non-porphyritic mafic rocks distinguished by metamorphic assemblage: o EAS; ○ CS and ECS; ● ECSR; △ CR and ECR; □ porphyritic intermediate to mafic rocks
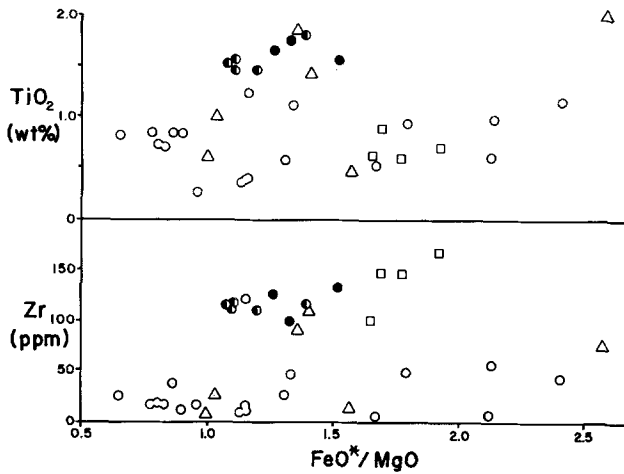

Fig. 2. TiO$_2$ and Zr variation with FeO*/MgO in mafic rocks of the Ascot Formation. Symbols as for Fig. 1

Fig. 3. Ti–Y–Zr (ppm) diagram for mafic rocks of the Ascot Formation. Symbols as for Fig. 1. Fields A to D are from Pearce and Cann (1973). Within-plate basalts fall in field D, low-potassium tholeiites (island-arc) fall in field A, and calc-alkalic basalts fall in field B. The large cross is the intersection of 'original' Ti/Zr and Ti/Y ratio-lines determined from Figs. 5 and 6 (see text)
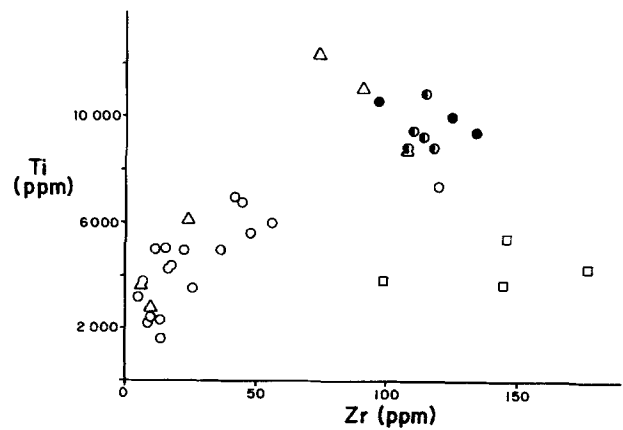
Fig. 4. Ti vs Zr for mafic rocks of the Ascot Formation. Symbols as for Fig. 1

and adding elements. If the distribution coefficient D_i (concentration of element i in fluid/concentration of element in rock) is assumed constant for any two elements, and the mass of the rock is held constant, it can be shown (c.f., derivations by Allegre et al. 1977, for fractional crystallization processes) that, during a progressive metasomatic process

$$\ln\left(\frac{C_1}{C_2}\right) = \left(\frac{D_1}{D_2} - 1\right)\ln C_2 + A$$

where C_i is the concentration of element i, A is a constant and D_i is positive for leaching, negative for

deposition of element i. The assumption that D_i are constant is reasonable if the fluid is at all times saturated with the elements concerned. The rock will then undergo 'incongruent' dissolution, the ratios of cations in solution being different from those in the rock and determined by the chemistry of the complexing.

Plots of $\ln C_1/C_2$ versus $\ln C_2$ can be used to evaluate D_1/D_2. Such plots are not sensitive to small variations in C_i. Igneous suites do not, therefore, show much variation on these plots unless the complete spectrum of rocks from mafic through silicic is
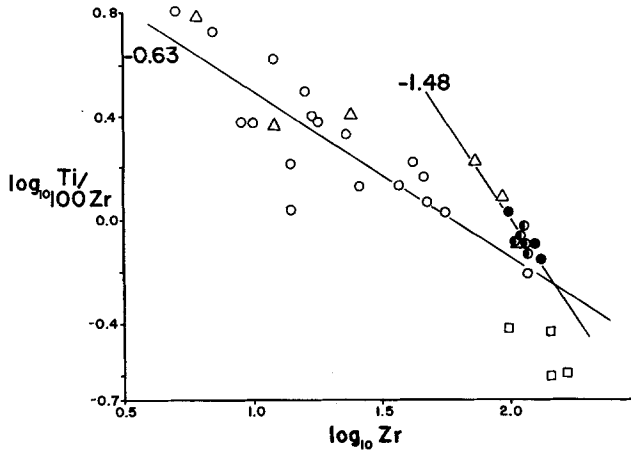
Fig. 5. LogTi/100 Zr vs log Zr. Symbols as for Fig. 1. *Straight lines* are linear best fits to two data sets one of which consists of all rocks in the assemblage EAS, and three rocks with ECR/ER, and the other of which consists of all rocks with ECS, CS, ECSR and the remaining rocks with ECR/ER. The highly porphyritic rocks were not considered. *Numbers* beside each line give the slope of the line
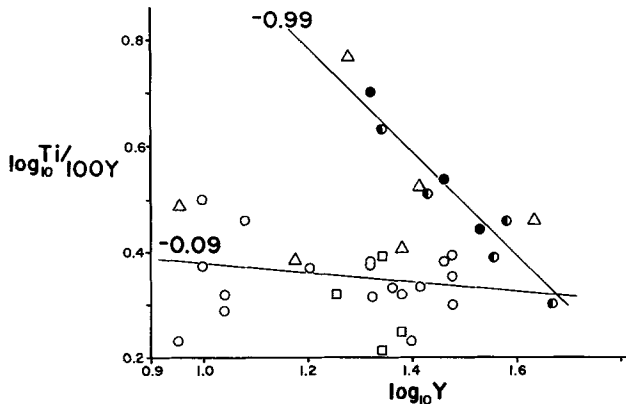

Fig. 7. Log SiO_2/TiO_2 and log CaO/TiO_2 vs log TiO_2. Symbols as for Fig. 1

Fig. 6. LogTi/100Y vs log Y. Symbols as for Fig. 1. *Straight lines* are linear best fits to two data sets as for Fig. 5. *Numbers* beside each line give the slope of the line

considered (compare, e.g., Pearce and Norry 1979). However the mafic rocks from the Ascot Formation show wide variation due to the metasomatic effects. The existence of a linear trend due to metasomatism does not confirm the assumption of constant D_i, since constant D_1/D_2 will have the same effect. Furthermore the graphs are insensitive to the effect of small changes in D_i. However the relative signs of D_i can be unambiguously determined from such graphs.

Plots of log Ti/Zr against log Zr (Fig. 5) and log Ti/Y against log Y (Fig. 6) distinguish clearly between the low Ti, Zr and high Ti, Zr rocks of the Ascot Formation. Rocks with the assemblages ECR/ER fall partly into the high Ti and partly into the low Ti set. The distribution of points in each set is roughly linear on both graphs. The steep ($\ll -1$)
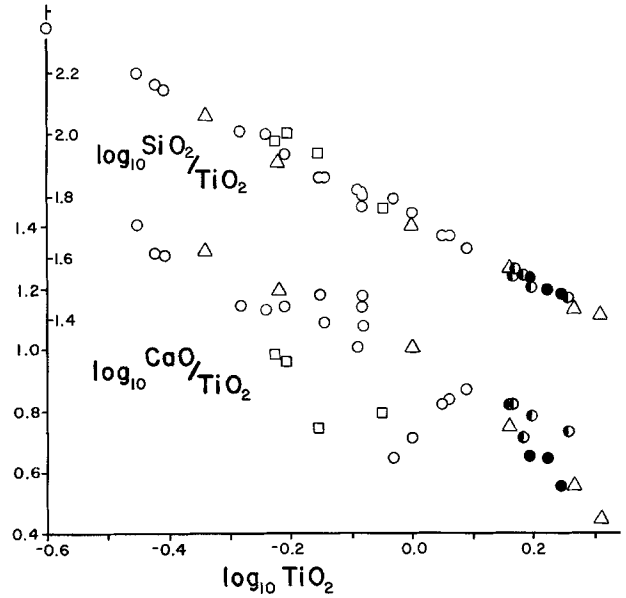
slope of the distribution of high carbonate rocks on Fig. 5 implies that D_{Ti} and D_{Zr} for this set had opposite signs, i.e., one of Ti, Zr was being leached and the other deposited. Given the high TiO_2 concentrations in these rocks it is most probable that Ti was being deposited and Zr was being leached. The slope near -1 for the high carbonate set on Fig. 6 implies that Y was moved much more effectively than Ti ($D_y \gg D_{Ti}$). For the carbonate-poor rocks the slopes of the distributions are shallow on both figures showing that all three elements were either leached or deposited. The very low values of Ti and Zr in these rocks clearly suggest that they were leached.

Log (SiO_1/TiO_2) against log TiO_2 (Fig. 7) gives an almost perfect straight line with a slope of -1 for all the rocks, showing that D_{Si} was very much less than D_{Ti}. This may reflect the much higher concentration of SiO_2 in the rock compared with TiO_2, rather than a much lower concentration of SiO_2 in the fluid. It shows how the effective mobility of these two elements has been reversed in the Ascot Formation, compared with the normal situation. Log CaO/TiO_2 (Fig. 7) gives a wide scatter, but with some suggestion of Ca-enrichment, along with Ti, in the carbonate-rich assemblage.

Controls on the Direction of Movement

Given that the mobility of Ti, Zr, and Y is due to high CO_2 content in the fluid, and that the amounts and directions of movement are related to the metamorphic assemblages present, it should be possible to

Table 2. Mineral compositions used to balance reactions discussed in text. All minerals are ferric-iron free. Actinolite and chlorite are pure ferrous iron end members

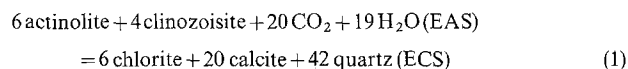| Mineral	Formula
Actinolite	$Ca_2Fe_5Si_8O_{22}(OH)$
Calcite	$CaCO_3$
Chlorite (daphnite)	$Fe_5Al_2Si_3O_{10}(OH)_8$
Epidote (clinozoisite)	$Ca_2Al_3Si_3O_{12}(OH)$
Ilmenite	$FeTiO_3$
Rutile	TiO_2
Sphene	$CaTiSiO_5$
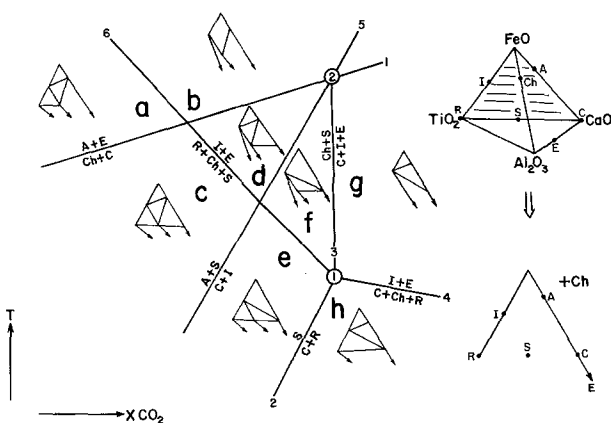
Fig. 8. Petrogenetic grid in $T - X_{CO_2}$ space for mafic rocks from the Ascot Formation. Numbered reactions are given in complete form in the text. Mineral assemblages in each field are represented on a ternary diagram which is a projection from chlorite onto $TiO_2 - CaO - FeO$ in $TiO_2 - CaO - FeO - Al_2O_3$ as illustrated on the right. Chlorite, albite, quartz and a fluid are present in all cases. A actinolite; C calcite; Ch chlorite; E epidote; I ilmenite; R rutile; S sphene

explain, at least qualitatively, why some rocks have lost certain elements and others have gained them. In this discussion Ti is used, because it is the element that is gained by some and lost by other rocks and because it is the only element among those discussed whose major mineral-sites are unequivocally known.

If it is mobile, a component will travel down the gradient of its chemical potential. A restatement of this is that a component will tend to move into another domain if there is, in that domain, another component with which it can react to produce a lower free energy assemblage (compare Thompson 1959), A petrogenetic grid in $T - X_{CO_2}$ space for the assemblages of the Ascot Formation can be used, with this principle, to explain why Ti moves as it does.
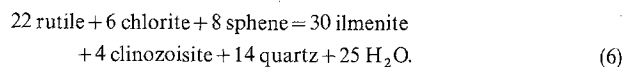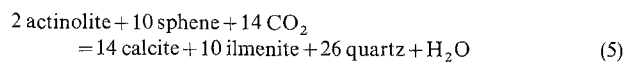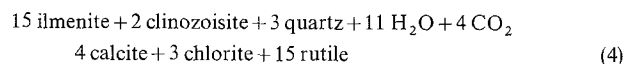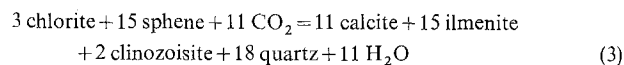
Simple carbonation reactions can be written relating the various metamorphic assemblages. The balanced reactions given below use the idealised mineral compositions of Table 2. (The system is treated

as ferric-iron free, and only the iron end-members of chlorite and actinolite are included in the reactions.)

$6\,actinolite + 4\,clinozoisite + 20\,CO_2 + 19\,H_2O\,(EAS)$
$\quad = 6\,chlorite + 20\,calcite + 42\,quartz\,(ECS)$ (1)

$4\,sphene + 4\,CO_2\,(ECS) = 4\,calcite + 4\,rutile + 4\,quartz$
$\quad + 3\,H_2O\,(ECR)$ (2)
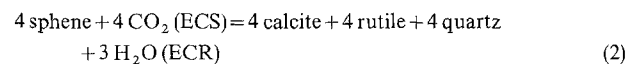
CS and CR are compositionally degenerate rocks in ECS and ECR respectively. ECSR is the assemblage on reaction 2.

A petrogenetic grid (Fig. 8) has been constructed about the two isobarically invariant points calcite-chlorite-clinozoisite-ilmenite-rutile-sphene (1) and actinolite-calcite-chlorite-clinozoisite-ilmenite-sphene (2) in the system $FeO - Al_2O_3 - CaO - SiO_2 - TiO_2 - Na_2O - CO_2 - H_2O$. Quartz, albite and fluid are considered in excess. The four additional reactions on the figure are:

$3\,chlorite + 15\,sphene + 11\,CO_2 = 11\,calcite + 15\,ilmenite$
$\quad + 2\,clinozoisite + 18\,quartz + 11\,H_2O$ (3)

$15\,ilmenite + 2\,clinozoisite + 3\,quartz + 11\,H_2O + 4\,CO_2$
$\quad 4\,calcite + 3\,chlorite + 15\,rutile$ (4)

$2\,actinolite + 10\,sphene + 14\,CO_2$
$\quad = 14\,calcite + 10\,ilmenite + 26\,quartz + H_2O$ (5)

$22\,rutile + 6\,chlorite + 8\,sphene = 30\,ilmenite$
$\quad + 4\,clinozoisite + 14\,quartz + 25\,H_2O.$ (6)

The six reactions were arranged about the invariant points using Schreinemaker's principles (Zen 1966). The slopes of reactions (positive or negative) were deduced using Greenwood's (1967) method and, in the case of reactions 3 and 5, standard molal entropy data from Robie (1966) and Helgeson et al. (1978). For reaction 3 ΔS is so small that the slope was treated as vertical. The actual slopes of the reaction lines are dependent on the X_{CO_2} positions of the invariant points and on the activities of the pure phases considered, in the real phases in the rocks. Thus, the actual slopes may be different from what is shown, but the topology will remain the same. The following arguments depend only on the topology.

Excluding quartz, albite and fluid, there are 4 phases in each isobarically divariant field on Fig. 8. In the case of the Ascot metabasalts, one of these is always chlorite. Phase relationships are therefore most simply represented by a projection from chlorite onto the $FeO - CaO - TiO_2$ face, in the tetrahedron $Al_2O_3 - FeO - CaO - TiO_2$ (Fig. 8). Using this projection, the $T - X_{CO_2}$ fields for the various metamorphic assemblages in the Ascot formation can be determined. Thus, assemblage EAS belongs in field a or b; ECS and CS belong in fields c to f; ECSR on reaction 2; and ECR and CR in field h.

In fields c and e a rock containing calcite would

react with TiO_2 (rutile) to produce more sphene, according to reaction 2. In field *a* this reaction is no longer possible, because calcite is not present. In fields *d* and *f* a rock containing sphene would react with TiO_2 to produce ilmenite and clinozoisite according to reaction 6. In field *a* the reaction is again not possible because sphene is not stable. However, in field *g* TiO_2 could react with clhorite and calcite according to reaction 4. Thus the chemical potential of TiO_2 is lower in fields *c* to *g* than in fields *a*, *b* and *h*. If TiO_2 is mobile it should be enriched in rocks in fields *c* to *g*, and depleted in fields *a*, *b* and *h*. This is in general what is observed in the Ascot Formation, with EAS, from field *a* or *b*, being depleted, and ECS, CS and ECSR from fields *c* to *f*, being enriched in TiO_2.

According to these arguments, rocks in field *h* should also be depleted in TiO_2. In fact, however, some lie on the enrichment trend and some on the depletion trend of Fig. 5 and 6. Those that lie on the enrichment trend show evidence of rutile growth after ilmenite. Their enrichment may be a reflection of metasomatism while in field *g*, at which time they would have been enriched in TiO_2, followed by retrograde reaction in field *h*.

Movement of TiO_2 between the basalts of the Ascot Fm. can, then, be simply explained by chemical potential gradients for TiO_2 as a result of the carbonization state of the rocks. A similar analysis of the movement of Y and Zr cannot be made without further knowledge of their sites.

Inference of Original Trace-Element Concentrations

In altered and metamorphosed metabasalts trace-element concentrations have been used with considerable success to distinguish rocks from different tectonic settings (Pearce and Cann 1973) although there are problems with rocks from transitional tectonic settings (Morrison 1978). For rocks from the Ascot Formation, it is clear that trace-element data must be used with extreme caution. Most of the rocks have trace-element concentrations affected by metasomatism. However, since there are two different trends for the metasomatism of the Ascot metabasalts some indication of the primary values can be obtained by extrapolating the trends to a common origin. This method has been attempted with the data of Figs. 5 and 6, by fitting straight lines to each set of data and determining their intersection. The two graphs give the following 'primary' values for the suite:

Fig. 5, Ti/Zr = 57.9;   Zr = 146 (Ti = 8454);
Fig. 6, Ti/Y = 208;   Y = 47 (Ti = 9796).

The two ratios have been used to produce a 'primary' point on Pearce and Cann's Ti $-$ Y $-$ Zr diagram (Fig. 3). It lies just within the field restricted to calc-alkalic basalts.

These 'primary' values obviously are very imprecise, but they serve to illustrate that the original inter-element ratios of these rocks may have been compatible with the proposed island-arc origin for these rocks. Despite this, the inferred primary levels of Ti in the Ascot Formation are still high for island-arc volcanic rocks, although much lower than many of the analyses reported by Alsac et al. (1971). The only other tectonic setting with which the inferred primary ratios are compatible – mid-oceanic ridges – may however be excluded because of the general lithological association of the Ascot Formation.

Conclusions

The ranges in concentrations of Ti, Y, and Zr exhibited by the mafic rocks of the Ascot Formation are probably caused by the movement of a CO_2-rich fluid through the rocks. This fluid has effected significant transport of these normally immobile elements. In general, rocks that have high contents of carbonate are enriched in Ti and depleted in Zr and Y, whereas rocks that have low carbonate contents are depleted in all three elements. However, some of the most carbonatized rocks are also depleted in Ti. The net movements of Ti can be explained in terms of the chemical potential gradient of TiO_2.

It is particularly important to note that the rocks most severely depleted in Ti, Y, and Zr, the low carbonate rocks, appear very little 'altered' in thin section. The high carbonate rocks, which are enriched in TiO_2, would be avoided in geochemical surveys by many geologists, although their concentrations of trace-elements are proportionately closer to the primary levels than those of the low-carbonate rocks.

Secondary enrichment in TiO_2 during carbonatization may explain the high concentrations of TiO_2 in the Ascot Formation previously reported in the literature. The inferred primary levels of TiO_2 in the Ascot metabasalts – around 1.5 % – are high for an island-arc setting, although inter-element ratios are compatible with such a setting. Based on the inferred primary ratios a 'within-plate' setting is very unlikely; and the lithological association precludes an origin at a mid-oceanic ridge. An island-arc origin therefore must remain the favoured tectonic environment for deposition of the Ascot Formation.

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