

## Crystallization trend of titanomagnetites in an alkali basalt from Saint-Clément (Massif Central, France)

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**SUMMARY.** Three generations of homogeneous titanomagnetite in a hawaïte from Saint-Clément may be defined by differences in size, habit, or reflectance, and are believed to correspond to different crystallization stages of the lava. Chemical compositions were determined by electron microprobe, and by X-ray and thermomagnetic methods.

Larger crystals are of intratelluric origin and occur either as inclusions in phenocrysts of early clinopyroxene (generation 1) or separately in the groundmass (generation 2); in the latter case, they always show evidence of resorption. Post-eruptive titanomagnetite (generation 3) is smaller and so highly oxidized that it is better termed titanomaghemite. Since the maghemitization, which is a low temperature process, alters the metallic ratios (especially the Fe/Ti ratio) the metallic contents at the time of the high-temperature crystallization are exactly known only for the intratelluric titanomagnetites.

As intratelluric crystallization proceeds Ti content increases greatly (5 to 14 %); Mn also increases (but slightly), Al and Mg decrease, while results for Cr are inconclusive. Apparently these changes go on until the post-eruptive crystallization stage.

The titanium trend is contrary to common belief. However, it is in accordance with predictions from the Fe-Ti-O system and may be explained by a decrease in oxygen fugacity during magma ascent.

**RÉSUMÉ.** L'observation pétrographique d'un basalte alcalin différencié (hawaïte) permet de caractériser d'après leur forme, leur taille ou leur pouvoir réflecteur trois populations de titanomagnétites homogènes correspondant à diverses étapes de la cristallisation du magma.

La composition chimique des titanomagnétites a été déduite d'analyses à la microsonde électronique, de mesures de paramètres cristallins et d'études thermomagnétiques.

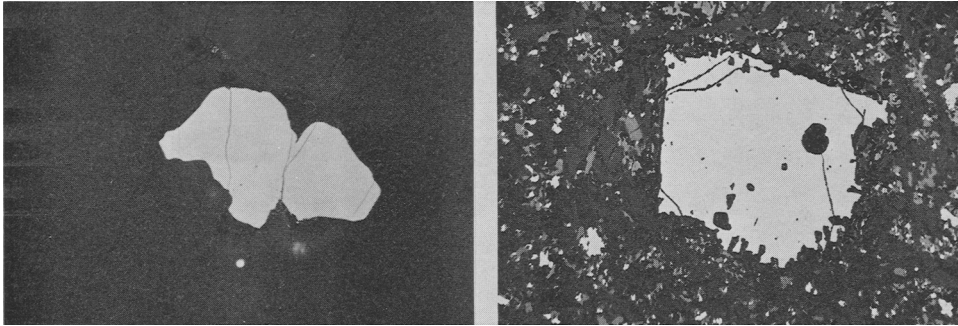
Les cristaux les plus grands, d'origine intratellurique, sont, soit inclus dans des phénocristaux de clinopyroxène précoce (génération 1), soit isolés dans la mésostase (génération 2). Dans ce dernier cas ils présentent toujours une corrosion périphérique. Les titanomagnétites post-éruptives (génération 3) sont des microcristaux fortement oxydés (titanomaghémites).

La maghémitisation modifiant à basse température les rapports métalliques (notamment le rapport Fe/Ti), les teneurs en métaux de la titanomagnétite originelle cristallisée à haute température ne sont connus avec précision, dans le cas de la coulée étudiée, que pour les titanomagnétites intratelluriques.

Au fur et à mesure que se développe la cristallisation intratellurique, la teneur en titane augmente fortement (de 5 à 14 %), celle du manganèse augmente légèrement, tandis que celles de l'aluminium et du manganèse diminuent. Apparemment, cette évolution se poursuit jusqu'au moment de la cristallisation post-éruptive.

L'évolution du titane est spectaculaire et contraire aux idées communément admises. Elle est en accord avec les données antérieurement fournies par l'étude expérimentale du système Fe-Ti-O et peut être due à une diminution de la fugacité de l'oxygène au cours de l'ascension du magma dans le conduit éruptif.

THIS paper presents some results of an extensive study (Prévoit and Mergoïl, 1973) of several generations of intratelluric and post-eruptive titanomagnetites from an alkali basalt in which several kinds of homogeneous titanomagnetites coexist, corresponding to various stages of the crystallization of the magma. The host rock is a porphyritic basalt (hawaiite) from the Saint-Clément sequence (Velay, Massif Central), which consists of 11 lava flows showing a differentiation from hyalobasalts with olivine (bottom) to trachy-andesites (top). It is a rather thin flow (4 to 5 metres) with associated



FIGS. 1 and 2: FIG. 1 (left). Reflected light,  $\times 600$ , under oil. Generation 1 titanomagnetite inclusion in clinopyroxene (black) together with a small spherical pyrrhotine grain (white, lower centre). FIG. 2 (right). Reflected light,  $\times 100$ , in air, Titanomagnetites in the groundmass: larger crystal (generation 2), and microcrystals (generation 3).

basaltic tuffs lying below and above it. The phenocrysts (4 % of the whole rock) are of clinopyroxene, mostly 1 to 2 cm in size, compositionally intermediate between chromiferous augite (Huckenholz, 1965) and ferrisodic augite (Babkine, Conquére, and Vilminot, 1968), and they are thought to represent an intratelluric crystallization stage. They occur also in the tuffs associated with the flow. In both tuff and lava, they show peripheral corrosion, which therefore began during the intratelluric stage.

*Microscopic studies of the titanomagnetites.* Reflected light examination (up to  $\times 1000$  in oil) indicates that all the titanomagnetites are homogeneous. No ilmenite grains have been observed.

The larger titanomagnetite crystals are either included in clinopyroxene phenocrysts (generation 1) or occur separately in the groundmass (generation 2). Those in the pyroxene have a regular, sometimes almost spherical, shape and average  $150 \mu\text{m}$  in size. Rare small pyrrhotine grains occur also as inclusions in the clinopyroxene (fig. 1). The larger groundmass crystals range from  $100 \mu\text{m}$  to a few millimetres in grain size and show a peripheral corrosion (fig. 2). No systematic difference in reflectivity has been observed between the two groups.

Larger titanomagnetites have been also observed in the tuff, either included in clinopyroxene phenocrysts or located in the thin basaltic skin surrounding them, where they show evidence of magmatic corrosion, which therefore began prior to eruption. In the lava the smallest crystals of generation 2 are often located in cavities resulting from magmatic corrosion of the clinopyroxenes. As a whole, the larger

TABLE I. Examples of reflectivity measurements under oil for some larger titanomagnetite crystals (L; generations 1 and 2) and for some titanomagnetite microcrystals from the groundmass (M; generation 3). In both cases the extreme reflectivities are reported. Standard: Si C; oil: Leitz  $n = 1.515$

$\lambda$ (Å)	4200	4400	4600	4800	5000	5200	5400	5600	5800	6000	6200	6400	6600	6800	7000
L	4.30	4.28	4.17	4.06	4.17	4.17	4.28	4.22	4.32	4.45	4.47	4.57	4.58	4.70	5.02
	4.72	4.67	4.47	4.45	4.47	4.62	4.71	4.63	4.72	4.78	4.82	4.85	4.82	4.90	5.40
	3.80	3.85	3.70	3.76	3.73	3.71	3.66	3.72	3.78	3.74	3.70	3.78	3.78	3.54	3.68
	3.98	4.10	4.00	3.98	4.07	4.12	4.07	4.10	4.17	4.25	4.21	4.20	4.35	4.27	4.20
M	5.50	5.41	5.20	5.02	5.13	5.01	4.93	4.97	5.02	5.08	5.00	5.06	5.08	5.30	5.24
	5.77	5.47	5.28	5.23	5.20	5.24	5.30	5.45	5.56	5.80	5.90	5.88	5.93	5.90	5.87
	5.00	5.07	4.84	4.85	4.90	4.92	5.00	5.17	5.32	5.50	5.60	5.50	5.62	5.52	5.42
	5.42	5.57	5.36	5.40	5.41	5.45	5.47	5.54	5.63	5.74	5.75	5.72	5.82	5.68	6.40

groundmass titanomagnetites correspond to a later crystallization stage, or at least they continued growing longer than the crystals included in pyroxene.

Microcryst titanomagnetite of the groundmass is always less than 20  $\mu\text{m}$  in grain size. Crystals are euhedral and have higher reflectivity than the larger crystals (Table I). They correspond to a post-eruptive crystallization stage (generation 3).

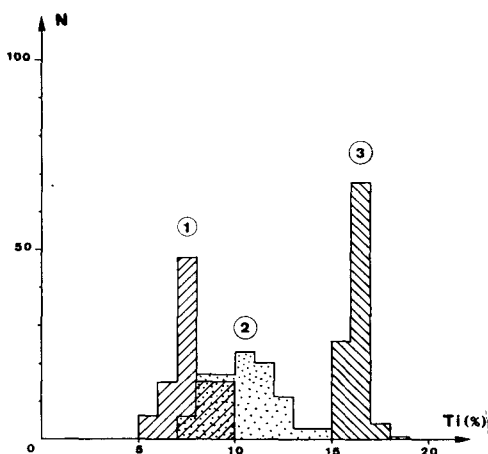


FIG. 3. Histograms of the titanium content (corrected value in wt %) for the three generations of titanomagnetites (normalized for 100 grains from each population). For details about the method of correction see Prévot and Mergoil, 1973. 1, crystals included in clinopyroxenes (Generation 1); 2, larger crystals in the groundmass (Generation 2); 3, microcrystals in the groundmass (Generation 3).

peak, probably because the crystallization of these titanomagnetites corresponds to a long and poorly delimited period, which overlapped the last crystallization stages of generation 1. Moreover, not all the titanomagnetite grains that crystallized before the clinopyroxene occur as inclusions.

*Chemical composition of the titanomagnetites.* Electron-microprobe analysis, X-ray measurements, and thermomagnetic studies have been carried out to determine the chemical composition of the three titanomagnetite generations. Experimental procedures are described in detail elsewhere (Prévot and Mergoil, 1973). All the crystals, even when showing evidence of magmatic corrosion, are chemically homogeneous.

The titanium content of 30 to 40 titanomagnetite grains from each of three populations has been determined by electron-microprobe analysis. Titanium concentration increases considerably from generation 1 to 3 (fig. 3). Generations 1 and 3 have a well defined mean titanium content. For generation 2, the Ti content varies more broadly and does not show a clearly defined

More complete electron microprobe analysis have been carried out for 23 grains from the three populations (Table II). As titanium content increases it appears that Al, Mg, and Cr contents decrease whereas Mn content increases slightly. The increasing in titanium is considerable:  $x$  (defined in Table II) varies from 20 to about 80%. To interpret these trends as the result of crystallization at high temperature we must ascertain whether or no the metallic contents of the titanomagnetite crystals have

TABLE II. *Electron microprobe analyses of the titanomagnetites*

		Fe	Ti	Al	Mg	Mn	Cr	$x$
Titanomagnetite inclusions in clinopyroxenes (generation 1)	1	47.5%	5.1%	7.7%	5.8%	0.1%	2.6%	20.8
	2	54.4	6.9	4.0	2.8	0.3	0.4	31.0
	3	52.7	7.2	4.0	2.1	0.3	1.3	33.2
	4	52.0	7.2	4.3	2.3	0.4	0.7	33.3
	5	52.9	7.5	3.7	2.6	0.2	1.3	34.1
	6	49.5	9.5	6.4	3.2	0.2	0.9	40.4
Larger titanomagnetite crystals in the groundmass (generation 2)	7	49.9	7.3	5.9	8.4	0.4	0.4	28.1
	8	52.0	8.1	4.7	4.4	0.4	0.7	34.4
	9	50.2	10.1	3.6	4.1	0.4	0.0	44.6
	10	50.1	10.5	3.5	3.6	0.5	0.0	46.9
	11	53.0	11.1	4.2	3.5	0.5	0.0	46.8
	12	52.5	12.4	1.5	0.7	0.6	0.7	59.3
	13	54.0	13.3	1.3	1.2	0.6	0.5	61.1
	14	52.3	13.6	1.3	1.0	0.6	1.0	63.6
	15	51.5	13.7	2.3	1.3	0.6	1.2	62.1
	16	49.7	13.8	1.7	1.5	0.6	1.8	64.1
	17	51.1	13.9	1.9	0.7	0.5	1.2	65.1
Titanomagnetite microcrysts in the groundmass (generation 3)	18	46.8	15.5	2.0	1.2	0.7	0.1	74.7
	19	47.1	15.8	1.2	1.7	0.6	0.5	75.6
	20	48.3	15.9	1.8	1.2	0.6	0.6	74.6
	21	47.1	17.0	0.4	1.7	0.7	0.3	81.8
	22	49.8	17.3	0.9	0.5	0.6	0.3	81.9
	23	49.5	18.4	0.7	1.7	0.7	0.6	82.9

$x$ : molecular percentage of ulvöspinel in the pure and non-oxidized equivalent titanomagnetite is calculated as follows:

— first, Al, Mg, Mn, and Cr atoms are replaced by Fe. So we obtain the chemical composition of the 'pure equivalent titanomagnetite' corresponding to the titanomagnetite studied.

— second, we calculate the chemical composition of the 'pure and non-oxidizing equivalent titanomagnetite', which is the member of the  $x\text{Fe}_2\text{TiO}_4$ ,  $(1-x)\text{Fe}_3\text{O}_4$  solid solution series with the same Fe/Ti ratio as the 'pure equivalent titanomagnetite'.

been modified by any low-temperature process. Now, it has been shown (Prévo, Rémond, and Caye, 1968; Marshall and Cox, 1972; Prévo and Mergoil, 1973) that low-temperature oxidation of titanomagnetites (maghemitization) alters the cation ratios. In particular the Fe/Ti ratio decreases, sometimes by 30% (Prévo, Rémond, and Caye, 1968). For the 'minor' elements the evolution seems to be variable and erratic. Thus the cation ratios obtained for a titanomaghemite are not representative of the crystallization state at high temperature (before maghemitization). It is therefore necessary to know whether the titanomagnetites studied are oxidized or not.

The degree of oxidation  $z$  of the titanomagnetites (O'Reilly and Banerjee, 1966) has been determined by using the cell-edge calculation method (Prévoit and Poix, 1971; Prévoit, 1971). The separation was carried out by a combination of hand picking, heavy liquids, and wet-magnetic techniques. It was successful for titanomagnetites of generations 2 and 3, not for those of generation 1. An attempt to separate these from a powder of clinopyroxene extracted from the whole rock led to a mixture of material from generations 1 and 2. This was because the titanomagnetites of generation 1 are scarce and weakly magnetic, as a result of their high degree of Al, Mg, and Cr substitution, and because some crystals of generation 2 occur inside the corrosion cavities of the clinopyroxenes.

TABLE III. Mean chemical, crystallographic, and thermomagnetic data for the three generations of titanomagnetites

	Generation 1	Generation 2	Generation 3	
Metal ions, wt %	Fe	51.5	51.7	48.1
	Ti	7.2	10.4	16.7
	Al	5.0	3.5	1.2
	Mg	3.1	3.7	1.3
	Mn	0.2	0.5	0.7
	Cr	1.2	0.4	0.4
Ulvöspinel percentage	$x$	31.9	45.1	78.7
Crystallographic data	$a$	—	$8.404 \pm 0.005$	$8.449 \pm 0.005$
	$a_0$	8.36	$8.40_1$	$8.48_4$
Thermomagnetic data	$\theta_c$	—	260 °C	140 °C
	$T_c$	$\approx 220$ °C	$\approx 250$ °C	$\approx 140$ °C
Inferred oxidation degree	$z$	—	0	$0.35 \pm 0.05$
Oxides contents (wt %) for generation 1, assuming $z = 0$ (see text)	FeO	35.2	38.5	33.9
	Fe <sub>2</sub> O <sub>3</sub>	34.5	31.1	31.1
	TiO <sub>2</sub>	12.0	17.4	27.9
	Al <sub>2</sub> O <sub>3</sub>	9.5	6.6	2.3
	MgO	5.1	6.1	2.2
	MnO	0.4	0.6	0.9
	Cr <sub>2</sub> O <sub>3</sub>	1.8	0.6	0.6
Total	98.5	100.9	98.9	

$a$  is the measured cell-edge,  $a_0$  the calculated cell-edge deduced from mean cation contents, assuming  $z = 0$ ;  $z$ , the degree of oxidation of the titanomagnetites (calculated using the cell-edge method), is the fraction of the total Fe<sup>2+</sup> ions of the pure and non-oxidized equivalent titanomagnetite that must be converted to Fe<sup>3+</sup> to obtain the chemical composition of the pure equivalent titanomagnetite;  $\theta_c$  is the measured Curie point and  $T_c$  an estimated Curie point determined from experimental data for synthetic titanomagnetite and based on the mean cation contents and the value of  $z$ ;  $x$  is defined in Table II.

The results obtained for titanomagnetites of generations 2 and 3 are listed in Table III. The mean chemical compositions have been estimated by combining data from fig. 3 and Table II. For generation 2, the measured cell edge  $a$  is not significantly different from the cell edge  $a_0$  calculated from the mean chemical composition, assuming the titanomagnetite is not oxidized ( $z = 0$ ). An estimated Curie point  $T_c$  has been deduced from the chemical composition,  $z$  being taken equal to zero, by considering experimental Curie points for titanomagnetites and substituted magnetites.

The measured Curie point  $\theta_c$  is close to  $T_c$ , which supports the conclusion that the larger crystals in the groundmass are non-oxidized titanomagnetites. Probably this conclusion holds also for the titanomagnetites included in the clinopyroxenes (together with pyrrhotine grains), which would be protected from subsequent oxidation. Indeed their reflectivity is the same as for the titanomagnetites of generation 2.

For the titanomagnetites of generation 3  $a$  is clearly smaller than  $a_0$ . The calculated cell edge is equal to  $a$  for  $z = 0.35$ . Using the data of Ozima and Sakamoto (1971) an estimated Curie point of about 140 °C was found, in perfect accordance with  $\theta_c$ . So the microcrysts of the groundmass are highly oxidized titanomagnetites (titanomaghemites).

Thus we must conclude that only the cation contents measured in the intratelluric titanomagnetites correspond exactly with the chemical composition of the minerals at the time of their high temperature crystallization.

*Conclusions and discussion.* As the intratelluric crystallization proceeds the chemical composition of the titanomagnetites evolves as follows (figs. 3 and 4): the titanium content increases markedly, the aluminium and magnesium contents decrease; the manganese content increases slightly; but the chromium content shows no systematic variation.

Apparently these trends continue into the crystallization stage of post-eruptive titanomagnetites. In particular the increase in titanium from generation 2 to 3 is too large to be ascribed to the maghemitization process alone.

Four main conclusions emerge:

In a basaltic magma the Al and Mg contents in titanomagnetites show a systematic decrease with progressive crystallization; this agrees well with the few results so far obtained (Babkine *et al.*, 1965; Carmichael and Nicholls, 1967) although the variation is considerably greater in the Saint-Clément basalt.

It seems that the increase in Mn content noted for the titanomagnetites from the Saint-Clément basalt has not yet been observed in other basaltic lava. This result, however, agrees with the fact that the Mn content is normally lower in basaltic lava than in more differentiated rocks: the trend in manganese is therefore probably correlated with the progressive differentiation of the residual magma.

Behaviour of Cr as the titanium content increases is not clearly established. It can be said only that early titanium-poor titanomagnetites are sometimes considerably more chromiferous than the late titanium-rich titanomagnetites. But the Cr content varies greatly from one crystal to another of generations 1 and 2, some of them having no detectable Cr in spite of their relatively high Al and Mg contents. A possible explanation is that some of these larger titanomagnetite crystals have replaced pre-existing spinel phases of quite different Cr content. Early spinel phases in an undifferentiated alkaline basalt from the Devès (Velay) have been studied by Babkine *et al.* (1965). They show that the spinels are either highly chromiferous, when of basaltic or peridotitic origin, or contain only Al, Mg, and Fe (ferrian ceylonite) when originating from pyroxenite inclusions. Cr-free crystals in the Saint-Clément basalt might have grown from such ferrian ceylonites.

The crystallization trend of pure titanomagnetites in basaltic liquids has been studied theoretically by Carmichael and Nicholls (1967) assuming that the  $\text{Fe}_2\text{O}_3/\text{FeO}$  ratio in the liquid is the determining factor that controls the appearance of a spinel phase. As the residual liquid would seem, in general, to become progressively more

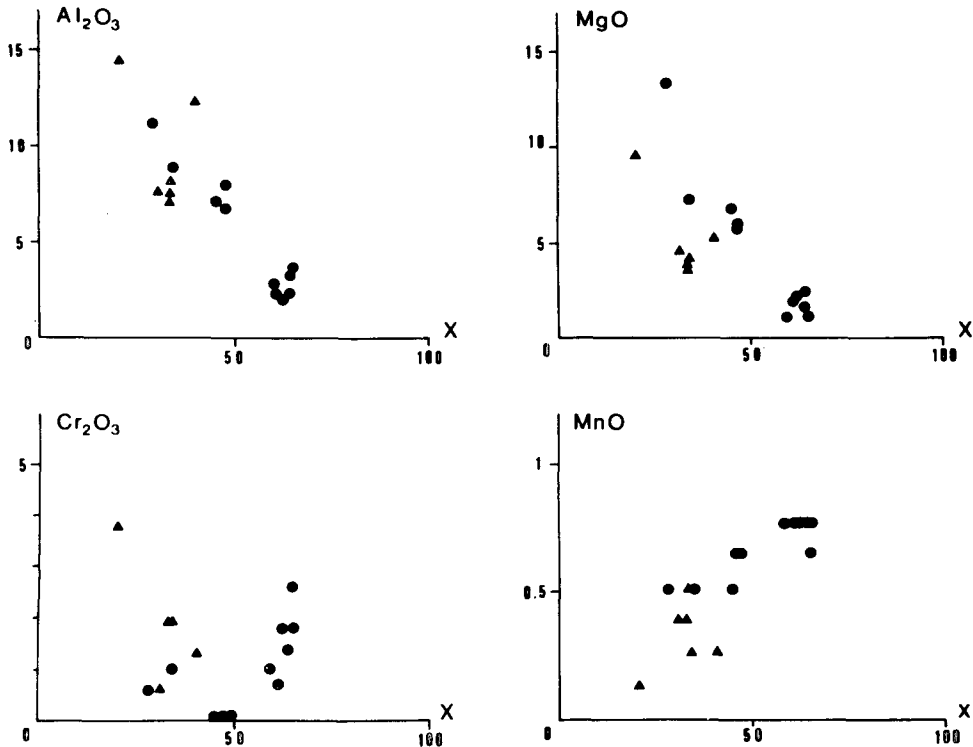


FIG. 4. Variations of the  $\text{Al}_2\text{O}_3$ ,  $\text{MgO}$ ,  $\text{Cr}_2\text{O}_3$  and  $\text{MnO}$  concentrations (wt %) with  $x$  in 17 macrocrysts from the Saint-Clément basalt. Triangles: Generation 1; circles: Generation 2. Data from table II.

'oxidized' as fractionation proceeds, they conclude that successive titanomagnetites must be poorer in the ulvöspinel molecule. Only a few analyses of coexisting homogeneous titanomagnetites have been carried out (Babkine *et al.*, 1965; Carmichael and Nicholls, 1967). The results are conflicting and in all cases the variation in titanium content is rather small. This is not the case for the titanomagnetites from the Saint-Clément lava: their ulvöspinel content increases considerably as crystallization proceeds. Probably this trend is not exceptional in alkaline lavas. Anderson (1968) observed that the ulvöspinel content in zoned titanomagnetite 'micro-phenocrysts' from alkaline basalts of Tristan Da Cunha is higher near the outer margins of crystals. He found also that the highest ulvöspinel contents occur in groundmass titanomagnetites. Increasing titanium content in titanomagnetites as crystallization proceeds is therefore probably a common trend in alkaline basalts. A similar trend may also occur in some tholeiitic magmas (Anderson and Wright, 1972).

How to explain this trend? We may note that it is supported by results from the  $\text{FeO} \cdot \text{Fe}_2\text{O}_3 \cdot \text{TiO}_2$  system (Taylor, 1963): it corresponds to the slope of the liquidus surface in the spinel field in this system. However, the distribution of Fe, Ti, and O between basaltic melts and Fe-Ti oxides involves many factors (for example the effect of alkalis) that cannot be neglected *a priori*. Another possible explanation is resorption of phenocrysts of oxy-kaersutite. Such 'resorbed' phenocrysts are quite common in the basalts of the Massif Central (Darvich-Zad, 1971), and a few completely 'resorbed' phenocrysts of oxykaersutite have been observed in the Saint-Clément porphyritic basalt. The problem is that, to be efficient, this 'resorption' must release significant quantities of titanium in the magma, but it is in fact an alteration to a mixture of crystals, some of them titaniferous.

The most plausible explanation is a decrease in oxygen fugacity. If differences in composition between co-existing titanomagnetites arise as a result of the changing composition of the liquid as crystallization proceeds, the trend in titanium indicates that the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  ratio in the residual liquid decreases progressively. Thus, the effect of the decrease in oxygen fugacity would be more important than the effect of increase in alkali content, which, according to Carmichael and Nicholls (1967), would tend to increase the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  ratio as crystallization proceeds. This decrease in oxygen fugacity can be attributed, as suggested by Anderson and Wright (1972) for some Kilauea basaltic magmas, to the effervescence and loss of gas (water and  $\text{SO}_2$ ) during magma ascent, and may be accompanied by an increase in temperature.

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