

Chapter 2

REVIEW OF THE MINERAL CHEMISTRY OF VOLCANIC ROCKS
FROM MAUI, HAWAII

R. V. Fodor

Department of Geosciences
North Carolina State University
Raleigh, North Carolina 27650

and

Klaus Keil

Department of Geology and
Institute of Meteoritics
University of New Mexico
Albuquerque, New Mexico 87131

INTRODUCTION

The Hawaiian Islands offer one of the world's best examples of the wide variety of distinctive basaltic rock types that can develop in a single volcanic province. Detailed petrologic studies have shown that three major rock suites, or parental magma types, exist on the Hawaiian Islands: the tholeiitic suite, usually SiO_2 -saturated rocks having low alkali contents; the alkalic suite, normally SiO_2 -undersaturated rocks forming a highly-differentiated series; and the nephelinitic suite, very undersaturated rocks rich in alkali contents (Macdonald and Katsura, 1962, 1964; Macdonald and Powers, 1968; Macdonald, 1968). Tholeiitic rocks form the main masses of the Hawaiian volcanic centers and are covered by a relatively small volume of alkalic lavas (<1%). The nephelinitic suite, composed of the youngest lavas, is separated from the other two suites by a pronounced unconformity.

The main criteria for establishing the three petrologic suites and their individual members were presented by Macdonald and Katsura (1964) and Macdonald and Powers (1968) as the SiO_2 and alkali contents, the normative mineralogy, and the modal mineralogy of the rocks. Among the most important rock types they defined are oceanite, olivine tholeiite, and tholeiite (tholeiitic suite); ankaramite, alkalic olivine-basalt, hawaiiite, mugearite, and trachyte (alkalic suite); and ankaratrite, basanitoid, basanite, and nephelinite (nephelinitic suite). All three suites are represented on all islands except the island of Hawaii, which has not yet evolved to the nephelinitic stage.

By the 1970's, more than 500 whole-rock analyses of Hawaiian rocks were available and the bulk compositions and field occurrences of the various rock types were well understood. Little, however, was known about the composition of their mineral components. On the basis of the wide compositional ranges of the rocks, there would presumably be an

equally wide range in mineral compositions, and probably certain compositional characteristics diagnostic of the different rock suites and members might be expected. Last, but not least, mineral compositions could contain information about genetic relationships between suites and individual members.

To investigate the relationships between mineral and bulk rock compositions of Hawaiian volcanic rocks, an extensive electron microprobe study was made of the mineral phases in 24 representative samples of the tholeiitic, alkalic, and nephelinitic suites of West Maui and Haleakala volcanic centers, Maui, Hawaii. Analyses were made of pyroxenes, olivines, feldspars, groundmass interstitial materials, and oxides in six tholeiitic, twelve alkalic and six nephelinitic rocks from the collection of G. A. Macdonald. The results were presented in a series of papers (Fodor et al., 1972, 1975, 1977; Keil et al., 1972). This report is a summary of the most pertinent observations of the mineral compositions of the volcanic rocks of Maui. The sample numbers, bulk chemical analyses, and localities are presented in Macdonald and Katsura (1964) and Macdonald and Powers (1968). Table 1 is a list of rock types and their respective volcanic series on Maui.

Mineral Chemistry

Pyroxene

Pyroxene compositions distinguish the tholeiitic, alkalic, and nephelinitic suites better than any other mineral phase analyzed. The differences lie mainly in the CaO contents of the pyroxenes and are best illustrated when the molecular amounts of CaO (expressed as wollastonite, Wo ; $CaSiO_3$), FeO (ferrosilite endmember, Fs ; $FeSiO_3$), and MgO (enstatite endmember, En ; $MgSiO_3$) in the pyroxenes are plotted in quadrilaterals (Fig. 1a).

Tholeiitic rocks contain augite, pigeonite, and bronzite. The high-Ca variety, augite, displays crystallization trends of increasing Fe and decreasing Ca and Mg contents (Fig. 1a). This trend is seen in both the compositional changes from phenocrysts to groundmass, and among groundmass pyroxenes highly variable in composition. A unique feature of tholeiitic pyroxene (high-Ca type) is that average compositions have less than about 42 mole percent Wo endmember, Wo_{42} (Fig. 1a).

Pyroxenes in some of the alkalic-suite members show affinities to those of the tholeiitic suite members. They have bronzite and/or compositional zoning of augite that is characteristic of tholeiitic rocks (Fig. 1a; samples C118, C125). On the whole, however, the differentiated alkalic suite has high-Ca pyroxene with its own crystallization trend. It begins with pyroxene in the basaltic members that compositionally overlaps in mole percent Wo content (augite with Wo_{40-42}) with tholeiitic pyroxene, but increases in Ca content, up to Wo_{48} , in hawaiiite and mugearite (differentiates of basalt). Finally, pyroxene in the most differentiated members, the trachytes, shows Fe-enrichment and is ferro-augite in composition (Fig. 1a, 1b).

Table 1. Sample numbers and rock types examined from Haleakala (Ha) and West Maui (WM) volcanoes, Maui, Hawaii. For detailed locality and rock descriptions, and bulk chemical analyses, see Macdonald and Katsura (1964) and Macdonald and Powers (1968). v.s. stands for volcanic series

| Tholeiitic suite | | Alkalic suite | | Nephelinitic suite | |
|------------------|--|---------------|--|--------------------|---|
| C-93 | Tholeiite (WM), Wailuku v.s. | C-92 | Trachyte (WM), Honolua v.s. | C-130 | Basanite ^b (WM), Lahaina v.s. |
| C-100 | Tholeiite (WM), Wailuku v.s. | C-116 | Trachyte (WM), Honolua v.s. | C-135 | Basanitoid (Ha), Kula v.s. |
| C-111 | Tholeiite (WM), Wailuku v.s. | C-118 | Alkalic olivine basalt (WM), Uppermost part of Wailuku v.s. | C-136 | Basanitoid (Ha), Hana v.s. |
| C-120 | Tholeiitic hyper- sthene-bearing oli- vine basalt ^a (WM), Wailuku v.s. | C-124 | Alkalic basalt (Ha), Upper part of Honomanu v.s. | C-139 | Basanitoid (Ha), Hana v.s. |
| C-121 | Tholeiitic olivine basalt (Ha), Upper part of Honomanu v.s. | C-125 | Alkalic olivine basalt (Ha), Upper part of Honomanu v.s. | C-142 | Basanitoid (Ha), Hana v.s. |
| C-123 | Oceanite (Ha), Upper part of Honomanu v.s. | C-126 | Alkalic olivine basalt (Ha), Upper part of Honomanu v.s. | C-148 | Basanitoid (Ha), Hana v.s. |
| | | C-137 | Hawaiite (Ha), Kula v.s. | | |
| | | C-140 | Alkalic olivine basalt (Ha), Kula v.s. | | |
| | | C-141 | Mugearite (Ha), Kula v.s. | | |
| | | C-143 | Hawaiite (Ha), Kula v.s. | | |
| | | C-146 | Hawaiite (Ha), Kula v.s. | | |
| | | C-147 | Hawaiite (Ha), Kula v.s. | | |

^a Hypersthene was not found in the section studied here.

^b Nepheline was not found in the section studied here.

The characteristic feature of pyroxene in the nephelinitic suite is the high Ca content. The molecular percent Wo is over 50 in several nephelinitic samples (Fig. 1a).

The crystallization trends for each of the three suites are compared in Fig. 1b for combined individual analyses in each suite, and for average compositions in each rock.

Other relationships between pyroxene and whole-rock compositions are observed when using the highly characteristic Ca in the pyroxene as a basis for comparing changes in other elemental abundances in pyroxene. When comparing groundmass high-Ca pyroxene of the mafic members of each suite (i.e., excluding hawaiite, mugearite, and trachyte

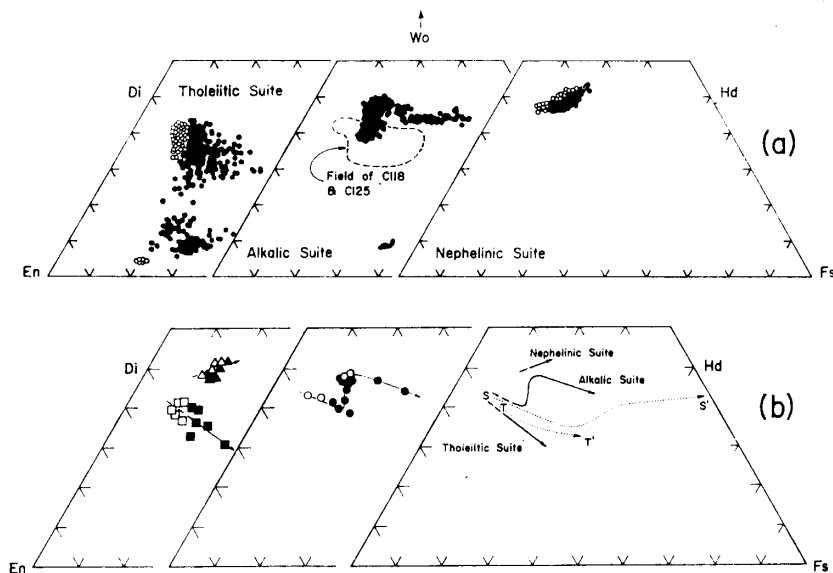


Figure 1. (a) Compilation of individual microprobe analyses of rocks of the tholeiitic, alkalic, and nephelinitic suites, showing overall differentiation trends. Because of the tholeiitic affinities of the alkalic olivine basalts C-118 and C-125, their high-Ca clinopyroxene is similar to that of the tholeiitic rocks and, hence, would confuse the trend for high-Ca clinopyroxene of genuine alkalic-suite rocks. Therefore, individual analyses for C-118 and C-125 are not plotted, and only their compositional range is shown by a dashed line. Open symbols, phenocrysts; closed symbols, groundmass grains. (b) Average compositions of clinopyroxene from rocks of the tholeiitic, alkalic, and nephelinitic suites, showing overall differentiation trends for each suite, compared to trends for the Skaergaard, S--S' (Brown and Vincent, 1963) and Thingmuli, Iceland, T--T' (Carmichael, 1967) provinces. Phenocrysts of the tholeiitic (\square), alkalic (\circ), and nephelinitic (Δ) suites, and their respective groundmass pyroxenes (\blacksquare , \bullet , \blacktriangle). Dashed lines, trend of phenocrysts; solid lines, trend of groundmass grains (after Fodor et al., 1975).

of the differentiated alkalic suite), there are increases in Al_2O_3 , Na_2O , and TiO_2 , and a decrease in MnO over the range 31 to 53 mole percent Wo (i.e., from tholeiitic through alkalic to nephelinic) (Fig. 2). Increases in Al_2O_3 , Na_2O , and TiO_2 are also noted throughout most of the differentiated alkalic suite, from basalt through mugearite.

The plots of certain oxides in pyroxene against the same ones in the bulk rocks help evaluate the influence of magma composition on mineral compositions. Examination of CaO_{rock} vs. CaO_{px} , for example, shows no strong influence of the concentration of CaO in a magma over CaO in pyroxene (Fig. 3a). Rather, the SiO_2 (and Al_2O_3) saturation of the original magma probably dictated the amounts of CaO that entered a high-Ca pyroxene: the lower the SiO_2 activity, the more CaO and Al_2O_3 will enter the crystal structure as $\text{CaAl}_2\text{SiO}_6$, or Ca-Tschermak's molecule. On the other hand, Na_2O in pyroxene is directly influenced by Na_2O (Fig. 3b). For tholeiitic rocks, $\text{FeO}/\text{FeO}+\text{MgO}+\text{CaO}$ ratios in high-Ca pyroxenes are dependent on the same ratios in the bulk rocks, but this relationship is obscured where there are appreciable alkali contents in the whole-rocks, as in nephelinic samples (Fig. 4).

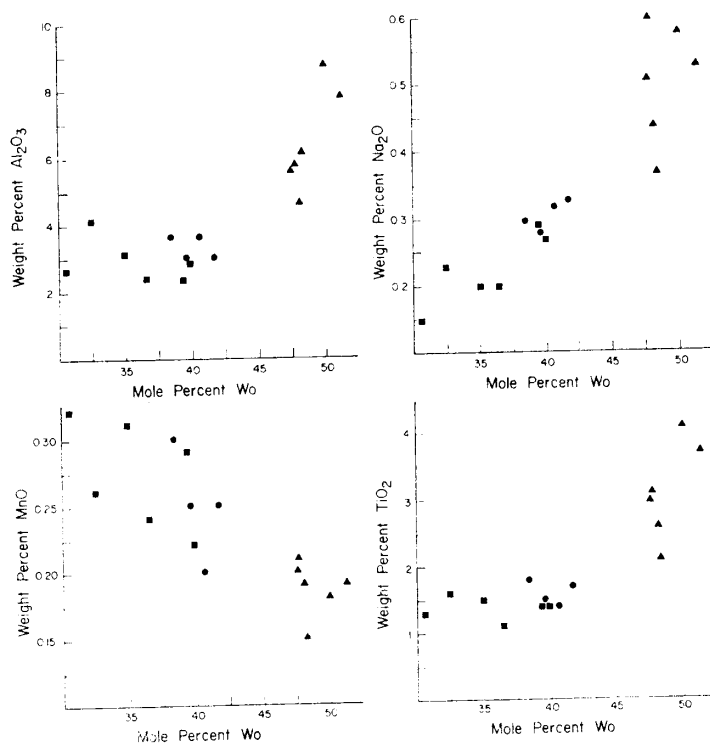


Figure 2. Plot of average weight percent Al_2O_3 , Na_2O , MnO , and TiO_2 in high-Ca groundmass clinopyroxene against their corresponding mole percent Wo contents for rocks of the tholeiitic, alkalic and nephelinic suites. Only mafic members of the alkalic suite (alkalic olivine basalt and alkalic basalt, except alkalic olivine basalt C-140 which is transitional to hawaiiite) are plotted. Symbols as in Fig. 1 (after Fodor et al., 1975).

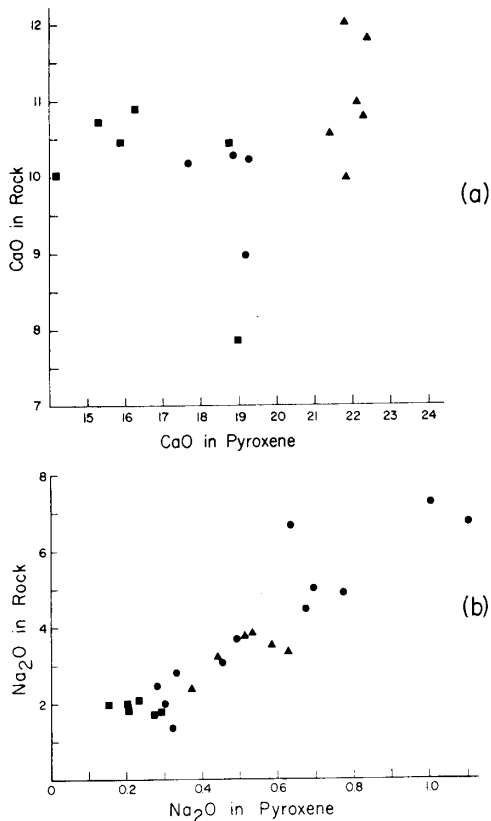


Figure 3. (a) Plot of bulk-rock CaO content (Macdonald and Katsura, 1964; Macdonald and Powers, 1968; Fodor et al., 1975 for C-121) against average CaO content of high-Ca groundmass clinopyroxene for rocks of the tholeiitic, alkalic, and nephelinitic suites (in wt.%). Only mafic members of the alkalic suite (alkalic olivine basalt and alkalic basalt, except C-140, an alkalic olivine basalt transitional to hawaiite) are plotted. The two samples with about 8% and 9% bulk rock CaO are cumulates (C-118; C-123). Symbols as in Figure 1. (b) Plot of bulk-rock Na₂O content (Macdonald and Katsura, 1964; Macdonald and Powers, 1968; Fodor et al., 1975 for C-121) against average Na₂O content in high-Ca groundmass clinopyroxene for rocks of the tholeiitic, alkalic, and nephelinitic suites (in wt.%). Symbols as in Figure 1 (after Fodor et al., 1975).

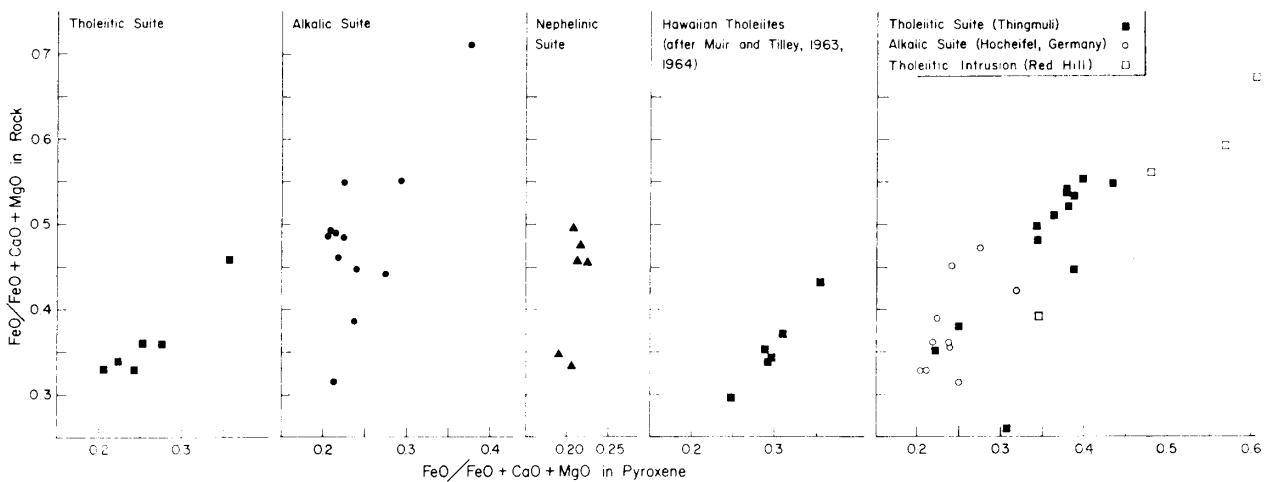


Figure 4. Plot of bulk rock FeO/(FeO+CaO+MgO) (Macdonald and Katsura, 1964; Macdonald and Powers, 1968; Fodor et al., 1975 for C-121) against the same ratio in high-Ca groundmass clinopyroxene, calculated from weight percent oxide contents. Data for tholeiitic, alkalic and nephelinitic suites are for rocks from Maui; Thingmuli tholeiites (Carmichael, 1967); Red Hill tholeiites (McDougall, 1962; Hocheifel alkalic suite (Huckenholz, 1965) (after Fodor et al., 1975).

There are very few differences between the olivine in the mafic rocks of the tholeiitic, alkalic, and nephelinic suites. The mole percent Fo (forsterite, Mg_2SiO_4) ranges between 70 and 85 for basalts of all types (Fig. 5). One compositional distinction, although small, is in the slightly higher CaO contents in the groundmass olivine of the nephelinic suite compared to the groundmass olivine of the tholeiitic and alkalic basalts (Fig. 5a). Also, olivine from tholeiites is slightly richer in NiO (Fig. 5c).

Most notable in olivine compositions are the variations throughout the differentiated alkalic suite. The mole percent Fo endmember of the olivine decreases drastically from about 80 to 15 from basalt to trachyte, and is attended by increasing MnO and CaO, and decreasing NiO contents (Fig. 5).

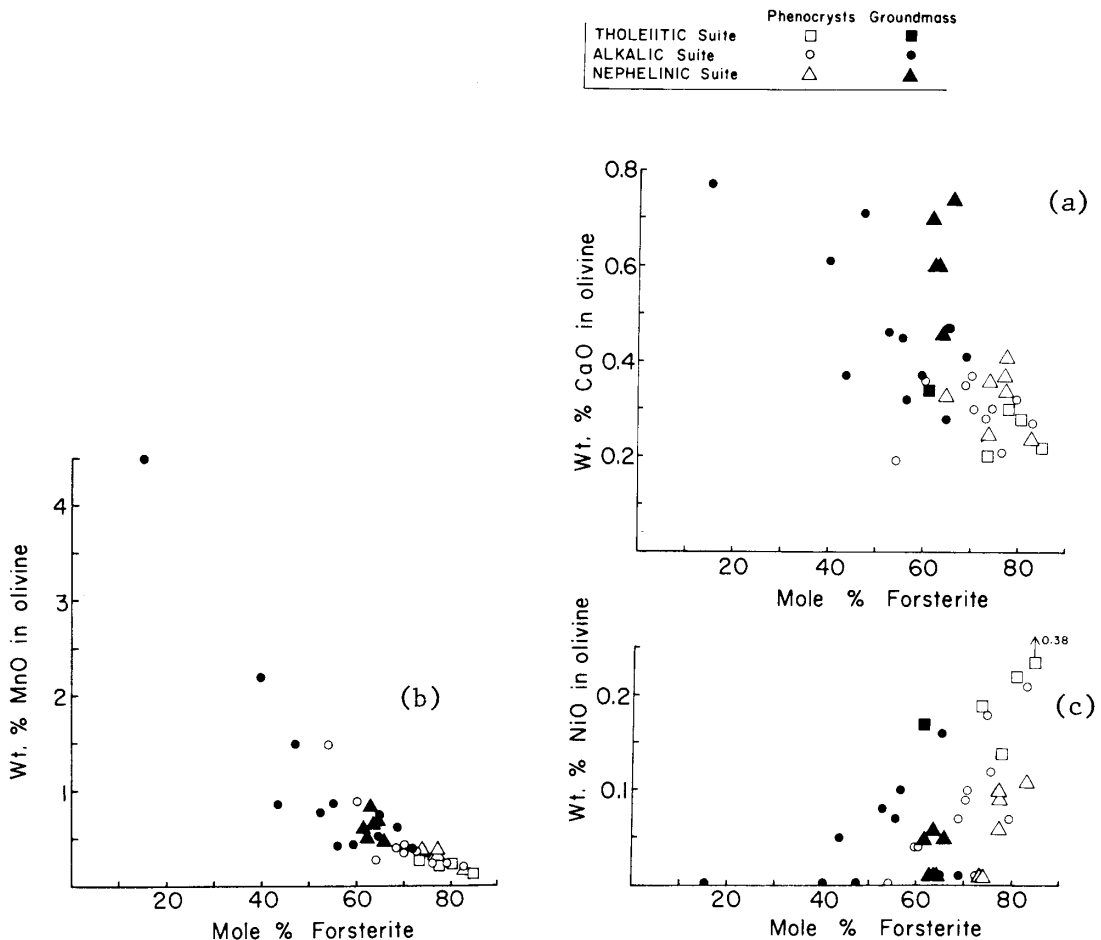


Figure 5. Mole percent Fo ($Mg SiO_4$) plotted against a) weight percent CaO in olivine; b) weight percent MnO in olivine; c) weight percent NiO in olivine for rocks from the tholeiitic, alkalic and nephelinic suites (after Fodor et al., 1977).

Feldspar and Groundmass Interstitial Material

The feldspar in the rocks from Maui shows decreasing An endmember (anorthite, $\text{CaAl}_2\text{Si}_2\text{O}_8$) and increasing Or endmember (orthoclase, KAlSi_3O_8) from phenocrysts, to microphenocrysts, to groundmass feldspar, to interstitial material of feldspar composition. When feldspar phenocrysts are present in basaltic rocks, they almost invariably fall within the compositional field of bytownite (70-90 mole % An) in composition (Fig. 6a-c). Only in the highly differentiated rocks of the alkalic suite, mugearite and trachyte, is the feldspar alkali-rich; groundmass laths are andesine (30-50 mole % An) and anorthoclase $[(\text{Na},\text{K})\text{AlSi}_3\text{O}_8]$, and phenocrysts in one trachyte are oligoclase (10-30 mole % An) (Fig. 6b).

Interstitial material is present in nearly all samples as anhedral patches between groundmass grains of plagioclase, pyroxene, and olivine. It represents the residual liquids in cooling lavas and, accordingly, has variable compositions with respect to alkali contents. In tholeiitic rocks, interstitial material is commonly feldspar of intermediate composition, only slightly richer in Na and K than the coexisting groundmass feldspar (Fig. 6a). One tholeiite was noted to contain interstitial high- SiO_2 glass (SiO_2 75 wt. %, Na_2O 1.3%, K_2O 4.9%) rather than feldspar, and another contains material of sanidine composition (Fig. 6a). This latter rock is interpreted as transitional to the alkalic suite because a characteristic feature of alkalic rocks is the presence of interstitial material rich in alkali contents (Fig. 6b). Similarly, alkalic rocks transitional to the tholeiitic suite have interstitial material not very rich in Na and K, and like that of true tholeiitic samples (Fig. 6b; samples C125, C126).

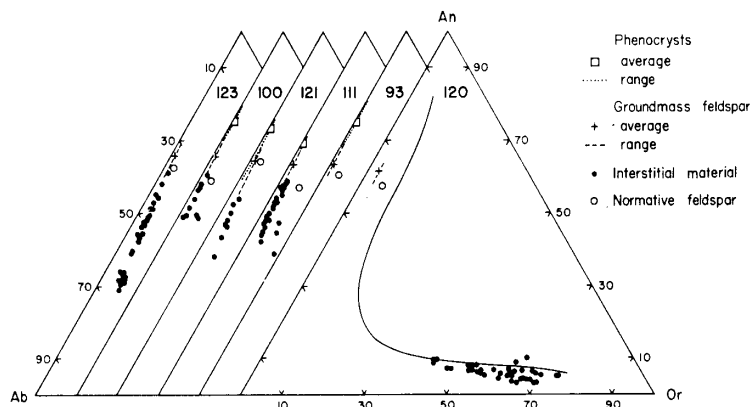


Figure 6a. Compositions of feldspar phenocrysts, groundmass feldspar, interstitial material of feldspar composition, and normative feldspar (calculated from bulk chemical analysis), for six rocks of the tholeiitic suite, expressed in terms of endmembers An, Ab, and Or. Solid line gives the boundary for the two-feldspar region (after Keil et al., 1972).

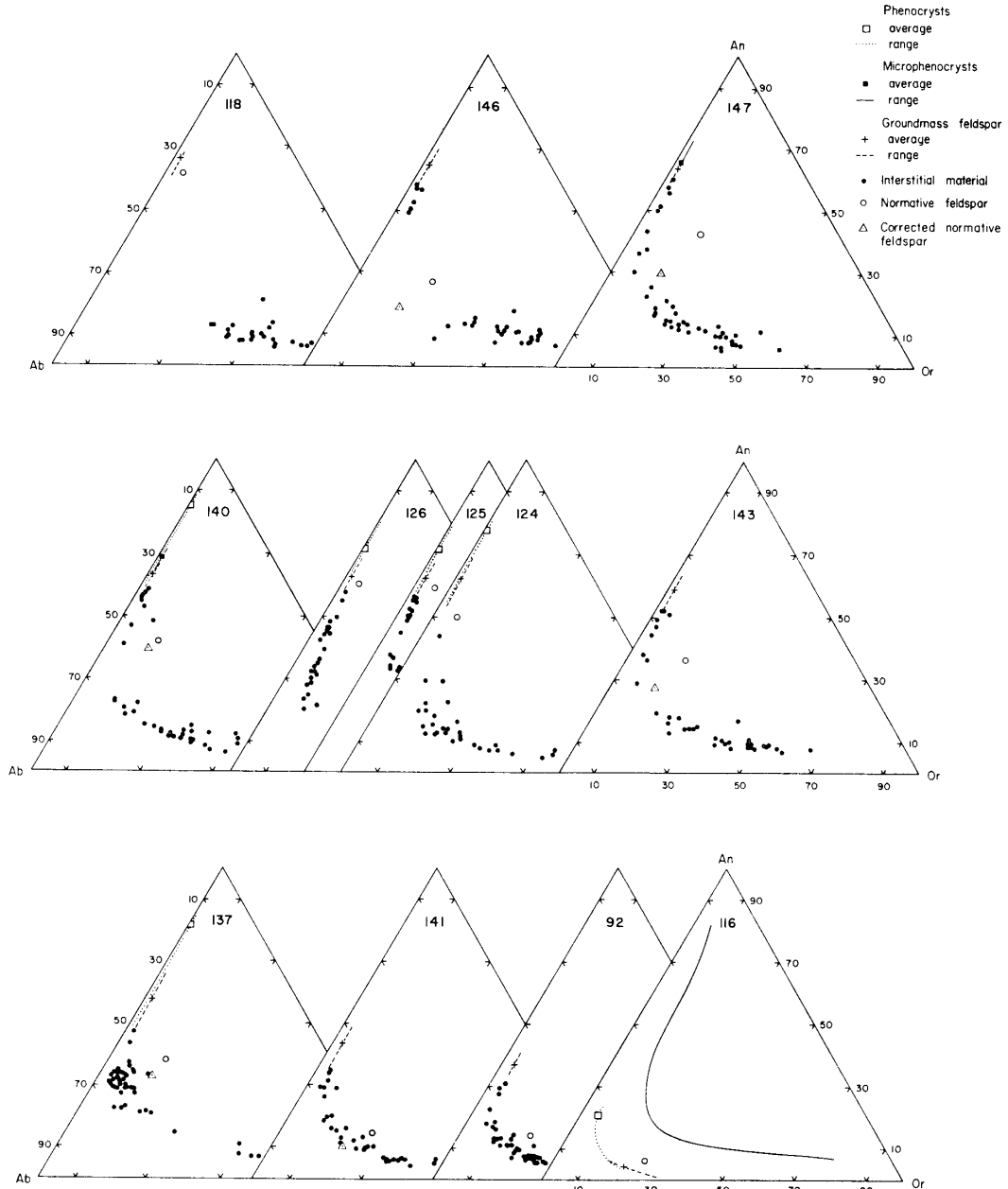


Figure 6b. Compositions of feldspar phenocrysts, microphenocrysts, groundmass feldspar, interstitial material of feldspar composition, normative feldspar (calculated from bulk chemical analysis), and normative feldspar corrected for nepheline, for 12 rocks of the alkalic suite, expressed in terms of endmembers An, Ab, and Or. Solid lines gives the boundary for the two-feldspar region (after Keil et al., 1972).

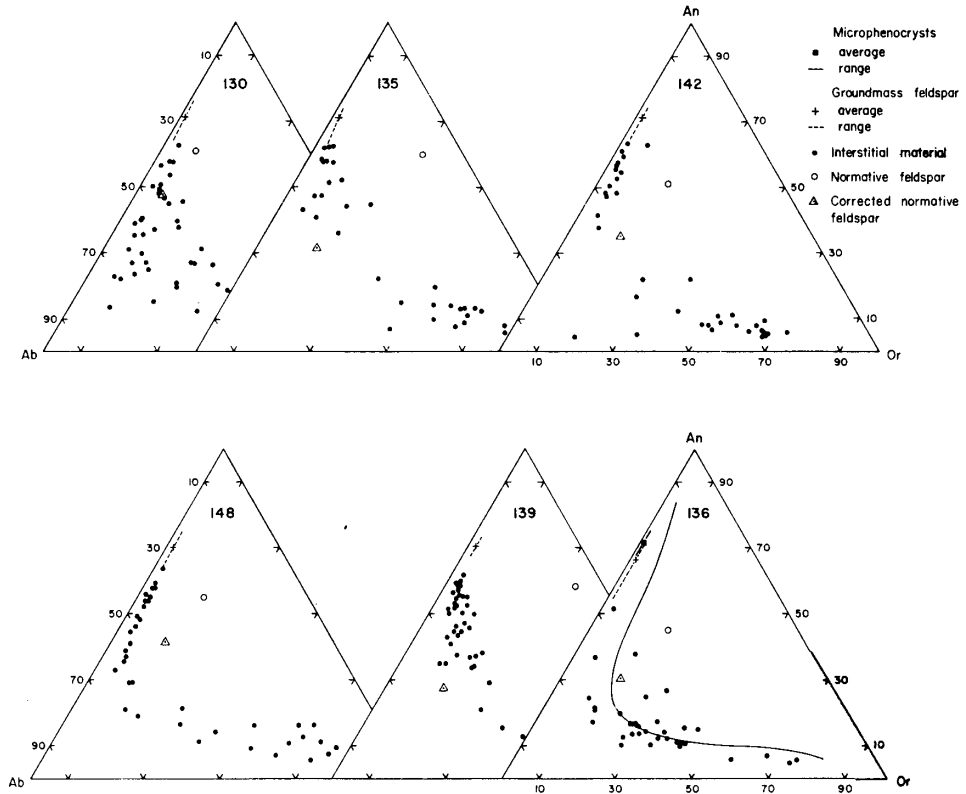


Figure 6c. Compositions of feldspar microphenocrysts, groundmass feldspar, interstitial material of feldspar composition, normative feldspar (calculated from bulk chemical analysis), and normative feldspar corrected for nepheline, for 6 rocks of the nephelinic suite, expressed in terms of endmembers An, Ab, and Or. Solid line gives the boundary for the two-feldspar region (after Keil et al., 1972).

Nephelinic rocks have abundant alkali-rich interstitial material, but not all of it is stoichiometric feldspar (Fig. 6c). Rather, some of it may be glass.

Feldspar compositional features that distinguish rock suites and types are Ca and K concentrations in the groundmass feldspar. When expressed as An and Or, respectively, the higher CaO content of feldspar in rocks of the nephelinic suite, and the lower K₂O content of feldspar in rocks from the tholeiitic suite clearly separate the three suites (Fig. 7). As with high-Ca pyroxene, the higher Ca in the rocks of the nephelinic suite reflects the lower SiO₂ feldspar will have higher CaO and Al₂O₃ as An content. Within the differentiated alkalic suite, increasing Or content separates the rock types hawaiiite, mugearite, and trachyte (Fig. 7).

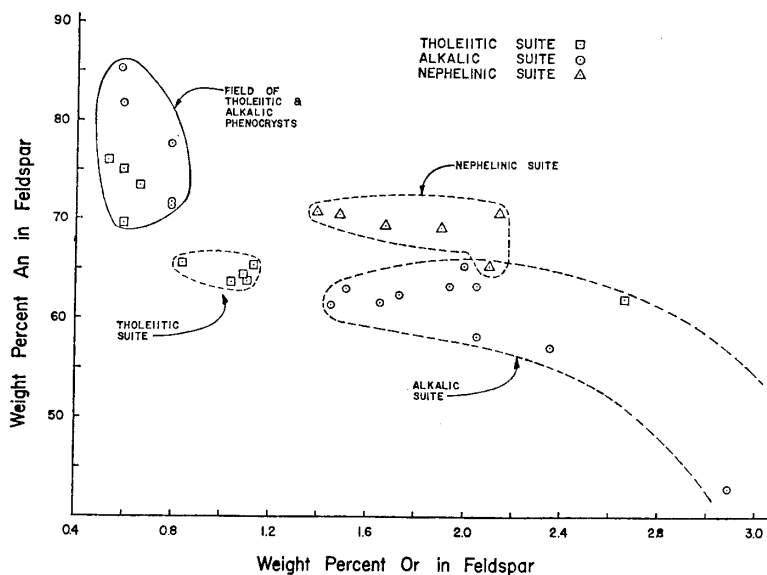


Figure 7. Plot of weight percent An vs Or in feldspar. Phenocrysts of rocks of the tholeiitic and alkalic suites are similar in composition. However, in general, rocks of the three suites can be distinguished on the basis of their An and Or contents in groundmass feldspar: rocks of the tholeiitic have lowest Or and moderate An contents; rocks of the nephelinitic suite have highest An and high Or contents; and rocks of the alkalic suite have low to very low An and high to very high Or content (the two trachytes are not plotted) (after Keil et al., 1972).

Oxides

Titaniferous magnetite is one oxide present in all rocks examined. It occurs as phenocrysts, microphenocrysts, and groundmass grains. Ilmenite is restricted to a groundmass phase in tholeiites and alkalic olivine-basalts (sometimes as lamellae in titaniferous magnetite). Cr-spinel is present only in tholeiitic basalts, alkalic olivine-basalt, and nephelinitic basalts, as inclusions in olivine phenocrysts.

The major elemental components of the titaniferous magnetites, Fe and Ti, do not distinguish rock suites or rock types: average molecular ulvospinel (Fe_2TiO_4) values of the tholeiitic suite are 68 to 71%; for the alkalic suite, 54 to 74%; and for the nephelinitic suite, 55 to 71%. In contrast, the minor elements, Mn and Al, in titaniferous magnetite distinguish between the tholeiitic and nephelinitic suites (Fig. 8). These two elements also separate the different members of the alkalic suite, both Mn and Al being richer in fractionated members than in the mafic members (Fig. 8).

Spinel grains, where present, are variable in composition. The grains in some rocks show a continuous gradation between Cr-spinel and titaniferous magnetite, where FeO, Cr_2O_3 , Al_2O_3 , and MgO decreases, while TiO_2 increases (Fig. 9).

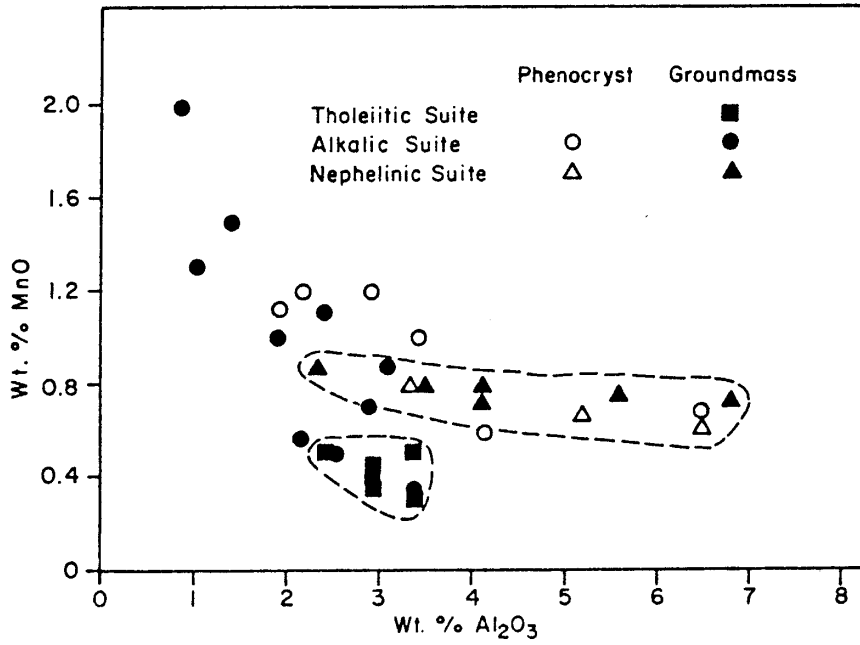


Figure 8. Contents of MnO and Al₂O₃ in titaniferous magnetite separate rocks of the tholeiitic from those of the nephelinic suites.

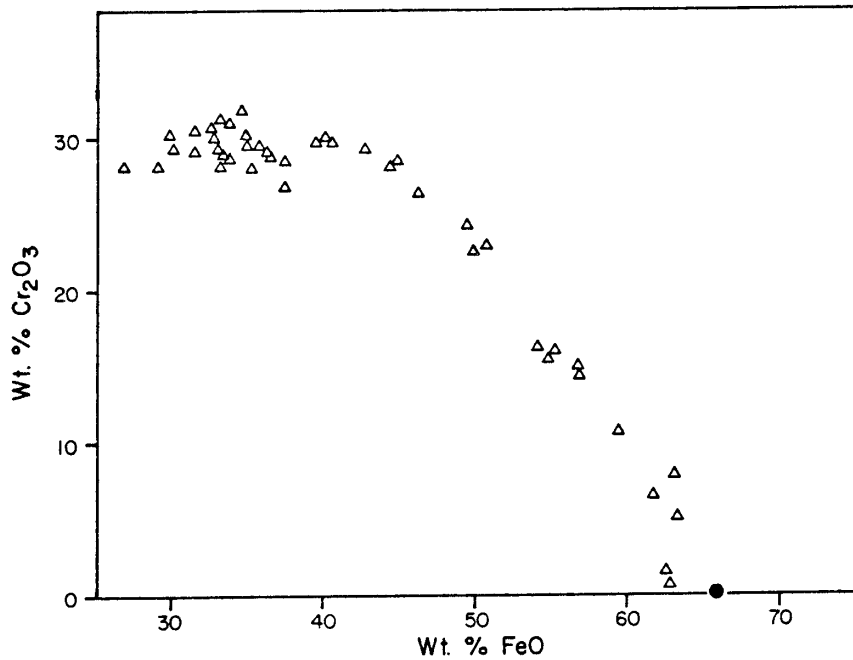


Figure 9. Compositional variations of Cr-spinel basanite C-130 of the nephelinic suite. The spinel is transitional to titaniferous magnetite of C-130, indicated by the filled circle.

SUMMARY

This study of Hawaiian volcanic rocks demonstrates the strong dependency of mineral composition on the composition of magmas, as represented by bulk rock analyses. Certain aspects of mineral composition, such as the amounts of Ca in pyroxene and feldspar, and Mn and Al in titaniferous magnetite, are diagnostic to actually allow discrimination between the major rock suites. Most other elements are less distinguishing, but are nevertheless present in minerals in amounts that were directly influenced by overall magma composition, such as is the case with Na and Fe in pyroxene, or Na and Si in feldspar. Mineral composition also reflects the transitional nature of rocks, such as those in a differentiated suite. The gradual changes in abundances of Fe, Mg, Al, Ca, Na, K, and Mn during magmatic fractionation are excellently displayed throughout a differentiated suite of rocks. Some of the transitions noted in this study of mineral composition also lend support for a genetic relationship between suites, as in the case of pyroxene or interstitial feldspar implying alkalic characteristics in rocks otherwise classified as tholeiitic. Finally, because the volcanic rocks of Maui represent the entire spectrum of basaltic rock types and several of their differentiates, and because they are uncontaminated by continental rock, the classification made on the basis of mineral composition have wide applications to volcanic rocks elsewhere.

REFERENCES

- Brown, G. M., and Vincent, E. A., 1963. Pyroxenes from the late stages of fractionation of the Skaergaard intrusion, East Greenland. *J. Petrol.* 4, 175-197.
- Carmichael, I. S. E., 1967. The mineralogy of Thingmuli, a Tertiary volcano in eastern Iceland. *Am. Mineralogist* 52, 1815-1841.
- Fodor, R. V., Keil, K., and Bunch, T. E., 1972. Mineral chemistry of volcanic rocks from Maui, Hawaii: Fe-Ti oxides. *Geol. Soc. Amer. Abs. with Program.*, 4, 507.
- Fodor, R. V., Keil, K., and Bunch, T. E., 1975. Contribution to the mineral chemistry of Hawaiian rocks IV. Pyroxenes in rocks from Haleakala and West Maui volcanoes, Maui, Hawaii. *Contr. Mineral. Petrol.* 50, 173-195.
- Fodor, R. V., Keil, K., and Bunch, T. E., 1977. Contribution to the mineral chemistry of Hawaiian rocks VI. Olivines in rocks from Haleakala and West Maui volcanoes, Maui, Hawaii. *Pacific Science* 31, 299-308.

- Huckenholz, H. G., 1965. Der petrographische Werdegänge der Klinopyroxene in den tertiären Vulkaniten der Hocheifel. I. Die Klinopyroxene der Alkaliolivinbasalt-Trachyt-Assoziation. *Beitr. Mineral. Petrog.* 11, 138-195.
- Keil, K., Fodor, R. V., and Bunch, T. E., 1972. Contributions to the mineral chemistry of Hawaiian rocks. II. Feldspars in rocks from Haleakala and West Maui volcanoes, Maui, Hawaii. *Contr. Mineral. Petrol.* 37, 253-276.
- Macdonald, G. A., 1968. Composition and origin of Hawaiian lavas. *Geol. Soc. Am. Mem.* 116, 477-521.
- Macdonald, G. A., and Katsura, T., 1962. Relationship of petrographic suites in Hawaii. *Amer. Geophys. Un., Monograph* 6, 187-195,
- Macdonald, G. A., and Katsura, T., 1964. Chemical composition of Hawaiian lavas. *J. Petrol.* 5, 82-133.
- Macdonald, G. A., and Powers, H. A., 1968. A further contribution to the petrology of Haleakala volcano, Hawaii. *Bull. Geol. Soc. Am.* 79, 877-888, 1968.
- McDougall, I., 1962. Differentiation of the Tasmanian dolerites: Red Hill dolerite-granophyre association. *Geol. Soc. Am. Bull.* 73, 279-316.
- Muir, I. D., and Tilley, C. E., 1963. Contributions to the petrology of Hawaiian basalts, 2. Tholeiitic basalts of Mauna Loa and Kilauea. *Am. J. Science*, 261, 111-128.
- Muir, I. D., and Tilley, C. E., 1964. Iron enrichment and pyroxene fractionation in tholeiites. *Geol. Jour.*, 4, 143-156.