

**PHASE CHEMISTRY OF RECENT ANDESITE, DACITE, AND RHYODACITE
OF VOLCAN PICO DE ORIZABA, MEXICAN VOLCANIC BELT:
EVIDENCE FOR XENOLITIC CONTAMINATION**

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RESUMEN

El volcán Pico de Orizaba, el más alto del Cinturón Volcánico Mexicano, se desarrolló en tres diferentes etapas magmáticas iniciándose hace 1.5 Ma (Robin y Cantagrel, 1982). Las andesitas de dos piroxenos, dacitas y riódacitas de la tercera etapa (hace 13 000 años) han sido analizadas por fluorescencia de rayos-X y microsonda electrónica. Las muestras han sido recolectadas de flujos de lava, depósitos de caídas y flujos piroclásticos, en localidades situadas sobre 4 500 m.s.n.m.

Por lo menos ocurren dos tipos de andesita. Una andesita con presencia de olivino (60% SiO₂), con un volumen de 20 por ciento de plagioclasa y 15 por ciento de fenocristales de piroxeno, tiene una matriz vítrea con 61 por ciento en peso de SiO₂, 17.7% Al₂O₃, 4.8% Na₂O, y 2.5% K₂O; sorprendentemente, este tipo de andesita contiene algunos granos corroídos de olivino que son ricos en Fo (Fo 87-89) con inclusiones de espínela crómica. La composición del piroxeno es bimodal con distinto vacío composicional: los promedios de los ortopiroxenos son En₇₉Fs₁₉Wo₂ y En₅₇Fs₄₀Wo₃ y los promedios de los clinopiroxenos son En₅₀Fs₁₁Wo₃₉ y En₄₄Fs₁₈Wo₃₈. Las composiciones del margen de plagioclasa también son bimodales (An₇₀₋₇₈ y An₄₆₋₆₃). La geotermometría reproduce temperaturas superiores a 1050°C para las parejas de piroxenos ricos en magnesio y alrededor de 960°C para las parejas ricas en hierro. La andesita libre de olivino tiene las composiciones del interior de la plagioclasa, las cuales son bimodales. Las dacitas y riódacitas (63 a 68% de SiO₂, mayor que 16% de Al₂O₃) tienen de 20 a 40% de fenocristales de plagioclasa, de 3 a 20% de piroxeno, y de 0 a 15% de hornblenda. La matriz vítrea en estas rocas y la andesita libre de olivino son similares y tienen 74 a 75% de SiO₂, 11.8 a 12.6% de Al₂O₃, 2.5 a 4.0% de Na₂O y 2.5 a 4.4% de K₂O y caen cerca del mínimo en el sistema ternario del granito. Las fases máficas son ricas en magnesio; se obtienen temperaturas sobre 980°C para los dos tipos de piroxeno. Las composiciones de los dos tipos de piroxeno no parecen ser compatibles con el magma riolítico rico en sílice, el cual tiene una temperatura de saturación abajo de 800°C.

Por lo menos dos líquidos (una riolita rica en sílice y una andesita) han sido generados en la etapa más reciente de la evolución de Orizaba. La andesita ha sido contaminada en parte por el olivino y piroxeno ricos en magnesio, pero el líquido riolítico ha asimilado el material máfico de la corteza o del material de la chimenea, formándose así andesita, dacita y riódacita.

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ABSTRACT

Volcán Pico de Orizaba, the highest volcano of the Mexican Volcanic Belt, evolved through three distinct magmatic stages beginning about 1.5 Ma (Robin and Cantagrel, 1982). Two-pyroxene andesites, dacites, and rhyodacites from the third stage (<13 000 y. B.P.) have been analyzed by X-ray fluorescence and electron microprobe. Samples have been collected above 4 500 m from lava flows and pyroclastic fall and flow deposits.

At least two types of andesite occur. An olivine-bearing andesite (60% SiO₂) with over 20 volume percent plagioclase and 15 percent pyroxene phenocrysts has a glassy groundmass with 61 weight percent SiO₂, 17.7% Al₂O₃, 4.8% Na₂O, and 2.5% K₂O; surprisingly, these andesites contain a few grains of corroded olivine which are Fo-rich (Fo₈₇₋₈₉) with inclusions of chromian spinel. The pyroxene compositions are bimodal with distinct compositional gaps; two groups of orthopyroxene average En₇₉Fs₁₉Wo₂ and En₅₇Fs₄₀Wo₃ and those of the clinopyroxene average En₅₀Fs₁₁Wo₃₉ and En₄₄Fs₁₈Wo₃₈. Plagioclase rim compositions are bimodal also (An₇₀₋₇₈ and An₄₆₋₆₃). Geothermometry yields temperatures above 1050°C for Mg-rich pyroxene pairs and around 960°C for the Fe-rich pairs. The olivine-free andesite has plagioclase core compositions which are bimodal. The dacites and rhyodacites (63 to 68% SiO₂, over 16% Al₂O₃) have from 20 to 40% plagioclase phenocrysts, 3 to 20% pyroxene, and 0 to 15% hornblende. The glassy groundmasses in these rocks and the olivine-free andesite are similar with 74 to 75% SiO₂, 11.8 to 12.6% Al₂O₃, 2.5 to 4.0% Na₂O and 2.5 to 4.4% K₂O and plot near the minimum in the ternary granite system. The mafic phases are Mg-rich; two-pyroxene temperatures over 980°C are obtained. The compositions of the two pyroxenes do not appear to be compatible with the high-silica rhyolite liquid which has a liquidus temperature below 800°C.

At least two liquids (a high-silica rhyolite and an andesite) have been generated in the most recent stage of the evolution of Orizaba. The andesite has been contaminated in part by Mg-rich olivines and pyroxenes, but the rhyolitic liquids have picked up mafic crustal material or material from the vents resulting in the formation of andesite, dacite and rhyodacite.

INTRODUCTION

Volcán Pico de Orizaba is the third highest mountain in North America and the tallest of the Mexican Volcanic Belt. Robin and Cantagrel (1982) have made the most definitive study on the structure and evolution of this volcano. They proposed that the volcano was constructed during three distinct stages. After the primitive cone was built by andesitic lava flows, a caldera-forming stage followed with eruption of andesitic to dacitic lava flows and Plinian nuées ardentes which were associated with dacitic dome formation. The third stage which began about 13 000 y. B.P. produced the main peak above 4 000 m. Our paper concentrates on the phase chemistry of samples collected on this young peak at elevations above 4 500 m. We hope to show that xenolithic contamination of at least two magma types was responsible for the diversity of rocks erupted during the last stage of activity.

ANALYTICAL METHODS

All whole rock analyses were done on a Rigaku-3064 X-ray fluorescence unit. To

oxidize the iron, crushed samples were mixed with lithium tetraborate as flux and ammonium nitrate in the weight proportions 1:9:0.1 and fused into disks which were put into the unit with the standards. All major elements have a relative error of less than 0.5%; the minor elements such as MnO have a higher relative error closer to 1%.

Glass and mineral analyses were obtained using an ARL-EMX-SM fully automated electron microprobe and a JEOL Superprobe 733. Glass analysis was accomplished using a 20 micron beam, 15 keV, 0.02 microamps, with a Corning glass standard with 65% SiO₂. At least 20 spots in a section were analyzed; standard deviations determined indicated that the glasses were homogeneous with one standard deviation on silica being less than ± 1 percent. Mineral analyses were obtained using a 1 micron beam at 15 keV, 0.02 microamps. At least 10 "core" and rim analyses were done per section on each mineral phase.

CHEMISTRY

The rocks collected range in composition from andesite to rhyodacite (Table 1). Similarities to other suites in the Mexican Volcanic Belt are strong (Pal *et al.*, 1978). Being further from the Middle America trench than Colima, which lies on the western end of the MVB, Orizaba reflects this tectonic position by having higher K₂O values at 60% SiO₂ than Colima (Luhr and Carmichael, 1980). Although it is

Table 1. Chemical composition of selected whole rocks (wr) and some matrix glass (gl). X-ray fluorescence analysis was done on the whole rock and electron microprobe analysis on the glass.

	Or1		Or3		Or4		Or5		Or6
	wr	gl	wr	gl	wr	gl	wr	gl	wr
SiO ₂	63.6	75.0	60.0	61.0	68.5	73.9	59.8	74.8	62.9
TiO ₂	0.65	0.53	0.74	0.77	0.42	0.35	0.74	0.69	0.66
Al ₂ O ₃	17.1	12.1	17.0	16.6	16.1	12.6	16.9	11.8	17.0
Fe ₂ O ₃ *	4.47	1.03	5.78	5.78	3.05	1.78	6.00	2.53	5.02
MnO	0.08		0.10		0.07		0.10		0.09
MgO	2.49	0.11	4.12	2.66	1.14	0.33	4.11	0.25	2.64
CaO	5.23	0.95	6.21	5.38	3.33	1.29	6.19	1.33	5.16
Na ₂ O	4.44	2.50	4.06	4.53	4.56	3.86	4.04	3.99	4.24
K ₂ O	1.68	4.37	1.93	2.43	2.45	3.28	1.92	3.48	2.10
P ₂ O ₅	0.22		0.22		0.13		0.22		0.17

*Total Fe as Fe₂O₃

adjacent to the eastern alkaline province of Robin (1976) and Robin and Tourmon (1978), Orizaba's K_2O value is lower than those of the alkaline rocks. Typical calc-alkaline affinities are observed in the AMF, the $MgO-FeO-Al_2O_3$, and other diagrams. The five rocks on silica variation diagrams do not have linear trends for Al_2O_3 , TiO_2 , MgO , K_2O , and Na_2O (Fig. 1).

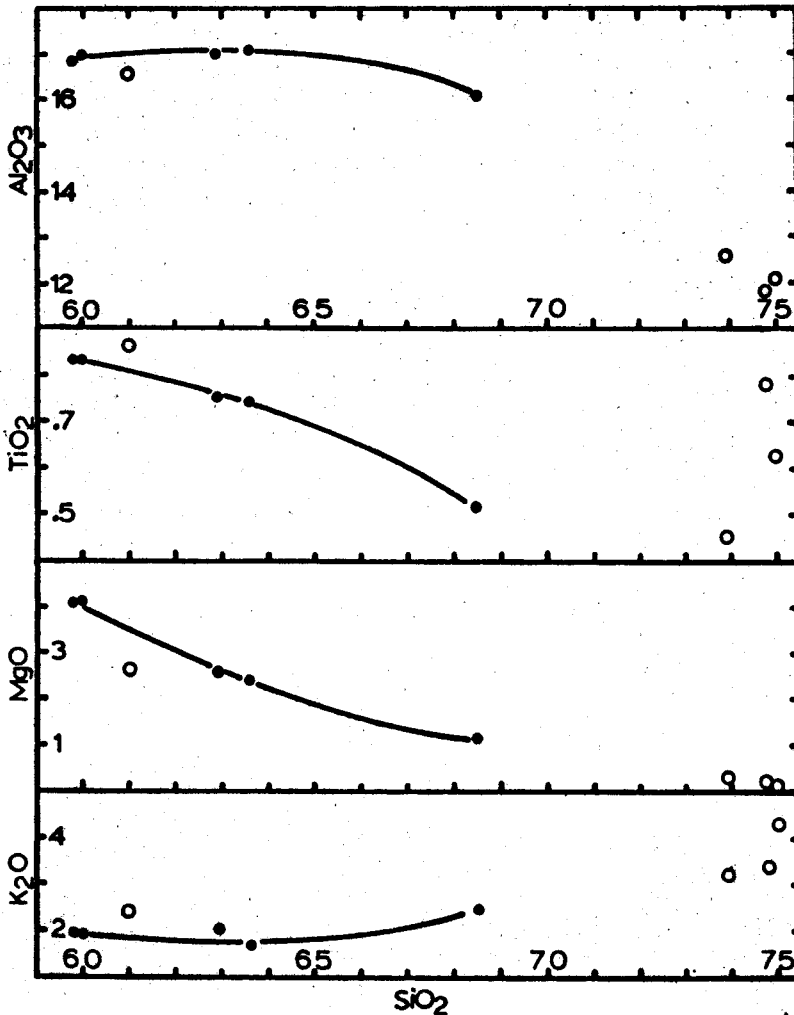


Fig. 1. Silica variation diagrams for whole rocks (solid circles) and glasses (open circles). All values are in weight percent. Solid curved line is drawn to illustrate the curvature in the whole rock trend with increasing silica.

Four glass compositions were determined on the electron microprobe (Table 1). All were remarkably homogeneous. The low silica glass with 61.0% SiO_2 has higher Na_2O , K_2O and lower CaO and MgO than the host andesite. The other three glasses are all high silica (from 73.9 to 75.0%), with low alumina and high alkalis, and plot near the granite minimum (Fig. 2). Two of these are from dacite/rhyodacite, but another (Or5) is from an andesite with less than 60% SiO_2 . Except for CaO and total Fe and Fe_2O_3 , the glasses all plot off the trend for the four analyzed rocks on silica variation diagrams; alumina and soda are lower than the projected trends but titanium dioxide is higher.

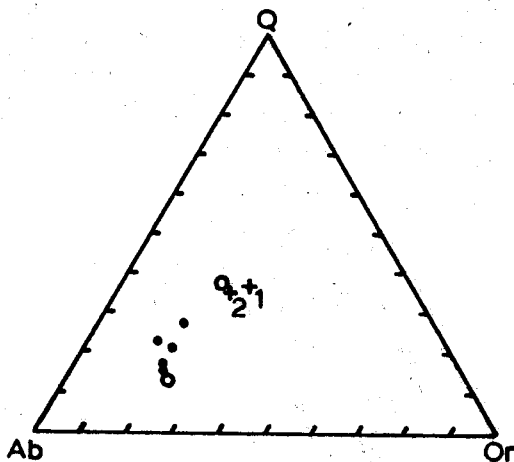


Fig. 2. Q-Ab-Or normative plot of glasses (open circles) and whole rocks (dots). The ternary minima for 1 and 2 kb PH_2O (crosses) come from Tuttle and Bowen (1958). More than one sample is shown for the high-silica glasses. Most of the calculations were done assuming a specific $\text{FeO}/\text{Fe}_2\text{O}_3$ ratio = 0.9.

PETROGRAPHY AND MINERAL CHEMISTRY

All samples collected are highly porphyritic ranging in phenocryst content from about 35 to 60 percent. The most abundant phenocrysts are euhedral to subhedral plagioclase many of which have corroded rims or cores and are strongly zoned. Two pyroxenes occur consistently even in the most siliceous samples; they range from 3 to 25 vol. percent with hypersthene being more abundant than augite. Augites commonly have rims of hypersthene. Hornblende is present in some of the dacite samples and can compose up to 15 percent of the rock. Reaction rims of opaque minerals and some augite occur around the hornblende. In a few andesite and dacite samples olivine phenocrysts occur, but in many cases the olivine is rimmed by opaque

minerals. The groundmass in most samples is glassy to microcrystalline. Some samples of large blocks/bombs taken from pyroclastic flows or falls are vesicular.

Plagioclase

Two andesites have been sectioned for the electron microprobe; one sample contained olivine phenocrysts. Plagioclase core compositions in the olivine andesite (Or3) are between $An_{76}Ab_{23}Or_1$ and $An_{59}Ab_{39}Or_2$ (average = $An_{68}Ab_{31}Or_1$); many display reverse zoning (Fig. 3). Rim compositions are bimodal with calcic rim compositions between $An_{78}Ab_{21}Or_1$ and $An_{70}Ab_{29}Or_1$ and sodic rims between $An_{63}Ab_{35}Or_2$ and $An_{47}Ab_{49}Or_4$. The cores in the olivine-free andesite (Or5) have a broad compositional range which is bimodal; one group lies between An_{70} and An_{52} and the other between An_{47} and An_{42} . Rim compositions range from An_{59} to An_{42} . The sodic cores are reversely zoned (Fig. 3).

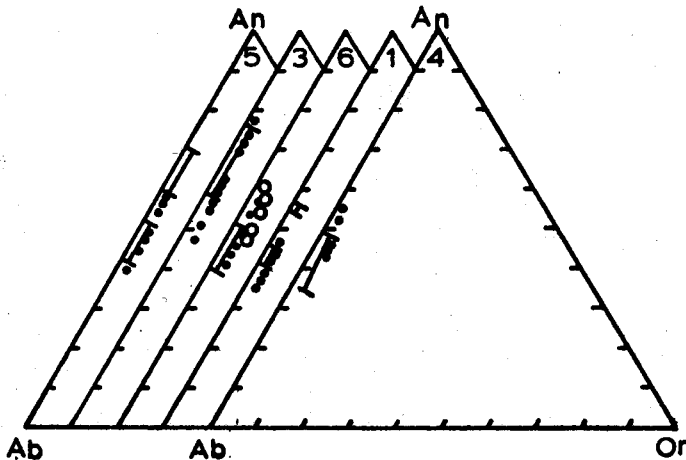


Fig. 3. Compositions of plagioclase grains on the ternary feldspar diagram. The numbers for each diagram refer (in order from left to right) to OR-5, OR-3, OR-6, OR-1 and OR-4, respectively. More than 15 phenocrysts have been analyzed for both core (within the brackets) and rim compositions (dots). Open circles are for groundmass compositions. Some dots and circles represent more than one analysis.

The plagioclase core compositions in the two dacites (Or1 and 6) range from An_{54} to An_{39} ; rim compositions span about the same range. Groundmass compositions in Or6 range from An_{57} to An_{48} with an average composition of An_{52} which is more calcic than the rims or cores. Sanidine compositions averaging about $Or_{45}Ab_{45}An_{10}$ occur in the groundmass of Or6 also.

The lone rhyodacite (Or4) analyzed yielded core compositions in the range from An₄₉ to An₃₄ with rims from An₅₅ to An₄₃.

Pyroxenes, hornblendes, and olivines

The olivine andesite (Or3) has corroded olivines measuring Fo₈₉ to Fo₈₆; one rim analysis yielded Fo₅₆ (Fig. 4). One of the measured olivine grains came from within an orthopyroxene phenocryst. Chromite was found as an inclusion in one grain of olivine. Mg-rich olivines with Cr-spinel inclusions have been found in basalts erupted from Volcán Colima (see Luhr and Carmichael, 1981). A striking bimodal distribution is apparent in both pyroxene compositions (Fig. 4). One group in the hyper-

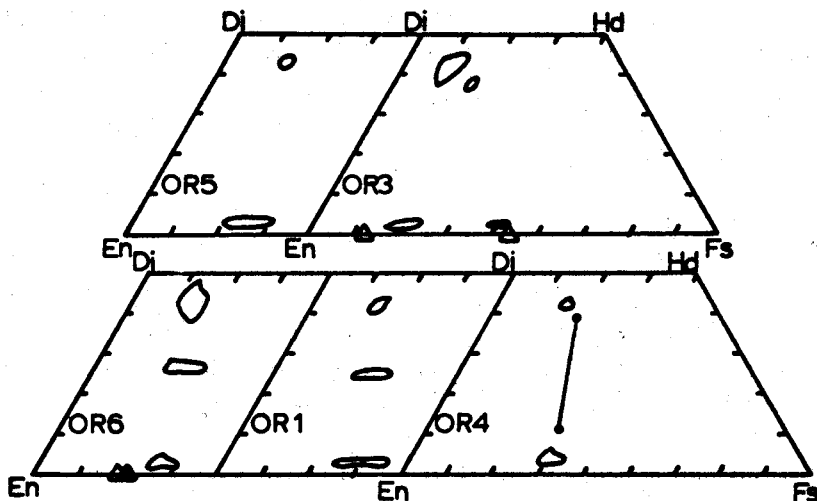


Fig. 4. Pyroxene, hornblende and olivine compositions plotted on pyroxene quadrilateral diagrams. The fields enclose at least 30 individual core and rim analyses for pyroxene and hornblende phenocrysts. The open triangles are for several grains of olivine; the dots with the tie line is an analysis of an adjacent pair of exsolved lamellae from a pyroxene.

sthene lies between En₈₂ and En₇₄ including both rim and core compositions; the other lies between En₆₁ and En₅₅. The Mg-rich group of augites plot between En₄₂ and En₅₂, Fs₈ and Fs₁₃, and Wo₃₆ and Wo₄₅. Both reverse and normal zoning occurs. Augites are aluminous and can contain up to 0.9% Cr₂O₃. The Fe-rich group clusters tightly around En₄₅Fs₁₇Wo₃₈. The olivine-free andesite (Or5) has a fairly homogeneous grouping of the pyroxenes with little difference between the cores and rims; the orthopyroxenes range from En₇₆ to En₆₆ and the clinopyroxenes group tightly around En₄₃Fs₁₅Wo₄₂. The dacites contain two pyroxenes and hornblende. One of

the dacites (Or6) has both core and rim compositions of the olivines which measure Fo_{82} to Fo_{79} . The orthopyroxene compositions in both dacites range from En_{73} to En_{63} for both core and rim; the clinopyroxenes range from En_{40} to En_{49} , Fs_{10} to Fs_{16} , and Wo_{38} to Wo_{48} . The hornblendes have Wo contents between 25 and 29 percent, and En contents from 57 to 47 percent. The hornblendes plot between the tie lines joining the most Mg-rich pyroxene pairs and the most Fe-rich. The silica contents of the hornblende range from 41 to 47 percent and alumina from 8 to 13 percent. The rhyodacite has orthopyroxene ranging from En_{69} to En_{62} with Wo contents between 2 and 11 percent. The clinopyroxene grains were rare in the slide but a few grains yielded compositions clustering around $En_{42}Fs_{15}Wo_{43}$.

Two-pyroxene geothermometers (after Wood and Banno, 1973; Wells, 1977; and Linsley and Anderson, 1983) yield for the Mg-rich pairs in the olivine andesite temperatures about 1050°C, and around 960°C for the Fe-rich group. Temperatures of about 990°C are obtained for the olivine-free andesites. Both dacite and rhyodacites have pyroxene temperatures of 980°C.

Opaques

The olivine-bearing andesite has a chromium-rich spinel included within the olivine phenocrysts. Approximately 25 percent chromium oxide occurs with over 47 percent FeO. The other opaques occurring in the groundmass are ilmenite with 52 to 58.5 percent Fe as FeO and 27.8-35.7 percent TiO_2 .

The other andesite has groundmass magnetite with total Fe as FeO between 76.7 and 81 percent and 8.2 and 13.6 percent TiO_2 . One sample (Or1) of dacite contains magnetite and ilmenite; the magnetite has a range of total Fe as FeO between 72.4 and 77.4 and TiO_2 between 6.0 and 15.1. The ilmenite has total Fe as FeO between 49 and 59 percent with TiO_2 ranging from 29.6 to 41.4. The other dacite sample has only magnetite similar to Or5. Magnetite in the rhyodacite (Or4) has total Fe as FeO from 77.1 to 82.4 percent and TiO_2 from 8.2 to 10.4. The values of coexisting Usp (25%) and Hem (66%) in the lone sample are outside of the limits of the model of Spencer and Linsley (1981) but project to a temperature of about 1050°C and oxygen fugacity of about 10^{-8} atm.

DISCUSSION

Compositional disequilibrium is most prominent in all the samples studied in detail.

Many of the minerals are obviously from a source separate from the magma; in many cases, the minerals appear normal for the whole-rock chemistry of the rock, but clearly the glassy matrix appears too enriched in silica to be in equilibrium with them.

The olivine-bearing andesite with a glass composition of about 61% SiO_2 has a Mg-number too low to be in equilibrium with the measured Mg-Fe of the olivine. Chromian spinel as a poikilitic inclusion in the olivine together with the high Mg content of the olivine support a separate origin from the andesite. The glass matrix is probably in "equilibrium" with the one corroded rim composition determined at a Fo content of 56 percent. The bimodal distribution of pyroxene compositions, the aluminous and chrome-bearing diopside/augite, and a high two-pyroxene temperature support a xenocrystic origin for the Mg-rich pyroxene. It may be possible that these xenocrysts have been derived from more basic portions of the Orizaba magma system or from crustal gabbros. The bimodal distribution of plagioclase rim compositions is unusual and puzzling. This may result from crystallizing plagioclase grains attempting in a local area to adjust to the contamination from the mafic minerals and in other areas to the normal response to the cooling magma.

The olivine-free andesite contains pyroxenes which appear normal to andesites of this bulk composition, but the surrounding groundmass is silica rich and plots near the minimum in the ternary granite system. Two-pyroxene temperatures of over 980°C suggest disequilibrium between the pyroxene pairs and the glass which should have a liquidus temperature below 800°C. The bimodal distribution of the plagioclase core compositions suggests two separate origins. One group possibly is the xenocrysts and the other the equilibrium crystallization phase. Perhaps the contaminant was a norite or gabbro.

The dacite and rhyodacite both contain Mg-rich pyroxenes which are unlikely to be in equilibrium with the high-silica glasses found in these rocks. The one rare grain of corroded olivine rimmed by opaques and pyroxene most likely is a xenocryst. In this same dacite, the plagioclase rim compositions are more sodic than the groundmass which is more calcic than even the most calcic cores. The core compositions may be xenocrystic.

A common interpretation for the disequilibrium textures and compositions involves magma mixing; however, no evidence exists for a silicic endmember. The silica variation diagrams are not linear but curved. Moreover the glass is fairly homo-

geneous throughout the slide; for example, the olivine-bearing andesite has an average glass composition of about 61% silica with a standard deviation of around 0.53. The dacite (Or1) has an average silica of 75% with a standard deviation of 0.93. Using a simple binary eutectic diagram, McBirney (1980) showed that two magmas, each of which are in equilibrium with a different phenocryst, will not mix until both phenocrysts are completely resorbed. Conversely, if one or more of the phenocrysts are unresorbed, two separate liquid compositions must be present. The existence of a homogeneous liquid with unresorbed phenocrysts which are not in equilibrium with the liquid argues against magma mixing.

Based only on the few samples examined in some detail here, we conclude that at least two "pristine" magmas, a high-silica and an andesitic one, have evolved. The andesite probably was generated in the upper mantle or lower crust. The high-silica magma may have originated by partial melting of the lower crust, possibly from the heat provided by the andesite. These magmas have been contaminated by xenocrystic olivines and pyroxenes to form the rocks analyzed here. More work is in progress at the present time; until this is completed the relative contributions of other differentiation processes cannot be determined.

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