American Mineralogist, Volume 63, pages 143–149, 1978

Plagioclase compositions from metabasalts, southeastern Llano Uplift: plagioclase unmixing during amphibolite-grade metamorphism

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Abstract

The Precambrian metamorphic rocks of the southeastern Llano Uplift include syntectonic basalt dikes intruded throughout the orogeny and metamorphosed under high temperatures and low pressures. Plagioclase phenocrysts from basalt dikes intruded early in the orogeny recrystallized and reacted to uniform compositions ($An_{32.0}Ab_{67.5}Or_{0.5}$ to $An_{44.4}Ab_{55.0}Or_{0.6}$) in equilibrium with amphibole. Zoned plagioclase phenocrysts in basalt dikes intruded during the closing stages of metamorphism reequilibrated to metamorphic compositions only to a depth of 30 microns into the grains. Compositions in the interiors of such phenocrysts fall within ranges of high-temperature unmixing. These crystal interiors did not equilibrate with grain exteriors, and they contain compositional domains 6–30 microns in width ranging from $An_{42.8}Ab_{57.0}Or_{0.2}$ to $An_{91.2}Ab_{7.1}Or_{1.7}$. Such compositional domains appear to reflect an approach to metastable equilibrium by unmixing into Bøggild and Huttenlocher intergrowths.

Introduction

The Precambrian metamorphic rocks of the southeastern Llano Uplift, central Texas, include the Packsaddle schist, a geosynclinal pile which is intruded by syntectonic igneous rocks. The syntectonic igneous suite consists of dikes and sills of basalt and gabbro, a Na-rich granodiorite (Big Branch gneiss) (Garrison, unpublished data), a sill-like granite body (Red Mountain gneiss), aplites, and a large serpentinite mass (Coal Creek serpentinite) (Burnitt, 1961; McGehee, 1963).

The rocks of the southeastern Llano Uplift underwent low-pressure metamorphism similar to the conditions described as Andalusite–Sillimanite Type by Miyashiro (1961) for the central Abukuma Plateau in Japan. The stable Al_2SiO_5 polymorphs are andalusite and sillimanite, staurolite is absent, and cordierite is widespread. Almandine is absent in the metabasalts, but is present in some metamorphosed pelitic rocks. Metamorphic mineral assemblages place the maximum conditions of metamorphism near 3.5 kbar and 650°C (McGehee, 1963). Maximum metamorphism probably occurred 1200 m.y. ago, according to Rb–Sr whole-rock results (Richmann and Long, in preparation), and K–Ar dates of hornblendes from the metabasalts indicate waning temperatures near 1070 m.y. ago (Garrison and McDowell, unpublished data).

At least two volumetrically important basaltic intrusive events occurred, although intrusive activity may have been continuous throughout the orogeny. The earlier of these events is thought to have occurred before major structural deformation (pre-granodiorite), and the later occurred after emplacement of the Na-rich granodiorite and granite. The earlier mafic intrusives occur as sill-like masses that are concordant with the local N 85° W foliation of the Packsaddle schist and Big Branch gneiss. The younger intrusions have two trends, one following weaknesses along the older intrusive trend and a second discordant trend in a band N 5° W to N 25° W.

All metabasalts have similar metamorphic mineral assemblages but differing degrees of foliation. The metabasalts of the later intrusive period commonly contain relict igneous plagioclases with twinning preserved, but the older metabasalts have either recrystallized groundmass mosaics or only retain outlines of relict phenocrysts.

This chemical and electron microprobe study was undertaken to explore the variations in compositions and degree of equilibration of recrystallized metamorphic plagioclases and relict igneous plagioclases, as a function of age and/or metamorphism.

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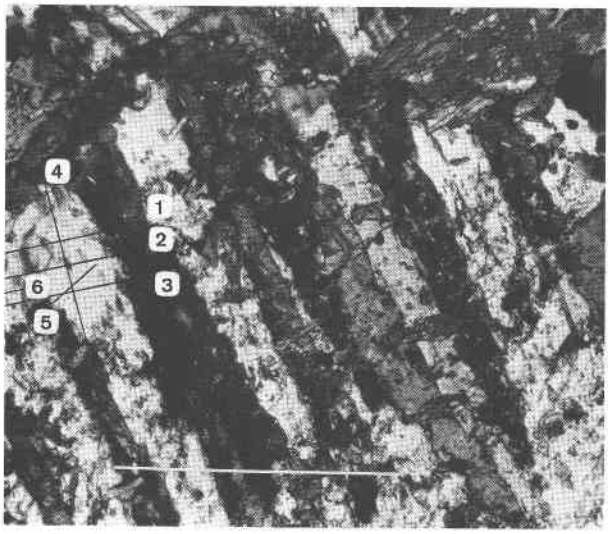

Fig. 1. Photomicrograph of relict igneous plagioclase from metabasalt A-4. Profiles 1, 2, 3, and 4 are 5-micron step traverses, and 5 and 6 are 1-micron step traverses. Scale bar is 0.5mm.

Petrology and mineralogy

Two of the metabasalts studied represent the earlier intrusive event (samples A-5 and A-6) and three represent the later intrusives (samples A-3, A-4, and A-12). Four of the metabasalts were analyzed, and have the major-element chemistry of low to medium-K tholeiites (Garrison, unpublished data). All are hypersthene-normative and all but A-6 contain normative olivine. Normative plagioclase compositions are $An_{67.0}$, $An_{57.9}$, $An_{54.1}$, and $An_{58.0}$ for metabasalts A-4, A-12, A-5, and A-6, respectively.

The metamorphic mineral assemblage is hornblende + plagioclase ± quartz ± biotite ± sphene ± ilmenite ± magnetite. The hornblende is a bluish-green variety that forms textures ranging from 0.1mm unoriented, idioblastic groundmass grains to 3mm nematoblasts, with decussate masses common. The plagioclase occurs in a variety of habits, ranging from relict igneous phenocrysts (Fig. 1) to recrystallized mosaic patches preserving relict phenocryst outlines to 0.1mm groundmass grains. Metabasalt A-12 contains a spectrum of plagioclase habits. Plagioclases occur as 3–5mm relict phenocrysts, as recrystallized mosaics preserving 0.5–0.7mm phenocryst outlines, and what appear to be recrystallized microlites in very fine trachytoid texture with groundmass hornblende.

Analytical results

The Ca, Na, and K analyses of plagioclase were made using an ARL EMX electron microprobe analyzer with a sample current of 2.0×10^{-8} amps at an accelerating potential of 15 kV. A 1-micron beam spot size was used, allowing a resolution of less than 3 microns. Plagioclase compositions were determined using the correction procedure of Albee and Ray (1970), presuming stoichiometric Al and Si. The presumption was checked by calculation of an analysis sum for each point, assuming plagioclase stoichiometry: all retained data yielded sums between 98 and 102. Repeated analysis of secondary standard $An_{50.0}Ab_{50.0}$ gave coefficients of variation of ±0.59 percent and ±1.41 percent (1 standard deviation) for weight percent CaO and Na_2O, respectively, with calculated compositions from $An_{49.3}Ab_{50.4}Or_{0.3}$ to $An_{49.9}Ab_{49.9}Or_{0.2}$.

Recrystallized grains

Recrystallized plagioclases from the older dikes (A-5 and A-6) were analyzed and found to have compositions ranging from $An_{32.0}Ab_{67.5}Or_{0.5}$ to $An_{44.4}Ab_{55.0}Or_{0.6}$. The uniformity of the hornblende compositions of A-5 and A-6 (Table 1) suggests equilibrium between coexisting hornblende and recrystallized plagioclase. The Ca content of the recrystallized plagioclase grains is less than that of a typical tholeiitic basalt plagioclase (*i.e.* $An_{55\pm}$), indicating partitioning of Ca between coexisting plagioclase and hornblende.

Metabasalt A-5 has recrystallized plagioclases occurring as mosaics preserving phenocryst outlines and as groundmass grains. Both occurrences were analyzed and found to have a relatively narrow range of compositions, ranging from $An_{38.3}Ab_{61.5}Or_{0.2}$ to $An_{43.2}Ab_{56.5}Or_{0.3}$ (Fig. 2a).

Metabasalt A-6 has plagioclases occurring as scattered mosaic patches. One grain was found to be zoned from $An_{32.0}Ab_{67.5}Or_{0.5}$ to $An_{36.8}Ab_{62.7}Or_{0.5}$. Two unzoned grains revealed compositions from $An_{44.2}Ab_{55.3}Or_{0.6}$ to $An_{44.4}Ab_{55.0}Or_{0.6}$ (Fig. 2b).

Mosaic grains of a 0.7mm recrystallized plagioclase phenocryst in young metabasalt A-12 have compositions from $An_{32.0}Ab_{67.5}Or_{0.5}$ to $An_{34.8}Ab_{64.8}Or_{0.4}$ (Fig. 2c). Several recrystallized plagioclase microphenocrysts have compositions from $An_{35.7}Ab_{63.9}Or_{0.4}$ to $An_{38.8}Ab_{60.8}Or_{0.4}$.

Relict igneous plagioclases

A relict igneous plagioclase from each of the three metabasalts of the later event was analyzed for compositional homogeneity and evidence of equilibrium. The relict plagioclase analyzed from A-4 is a 1.2mm, optically zoned, polysynthetically twinned grain cut

Table 1. Microprobe analyses of hornblendes

	A-4		A-6		A-5	
	center	rim	center	rim	center	rim
SiO_2	42.9	42.7	44.0	44.5	43.4	43.5
TiO_2	0.66	0.71	0.53	0.50	0.51	0.68
Al_2O_3	12.1	12.4	11.5	11.4	12.5	12.7
FeO^*	18.5	18.5	18.2	18.3	18.4	19.0
MnO	0.31	0.33	0.35	0.35	0.33	0.30
MgO	9.25	9.20	10.0	10.0	9.74	8.97
CaO	11.8	11.7	11.8	11.7	11.4	11.3
Na_2O	1.09	1.15	1.09	0.60	1.16	1.24
K_2O	0.57	0.64	0.47	0.42	0.42	0.46
	97.18	97.33	97.94	97.77	97.52	98.15
Cations (23 oxygens)						
Si	6.504	6.464	6.588	6.655	6.506	6.513
Al^{IV}	1.496	1.536	1.412	1.345	1.494	1.487
Al^{VI}	0.664	0.682	0.622	0.661	0.708	0.754
Ti	0.075	0.081	0.059	0.057	0.057	0.076
Fe^{+3}	---	---	---	---	---	---
Fe^{+2*}	2.343	2.346	2.281	2.289	2.310	2.381
Mn	0.042	0.041	0.044	0.044	0.042	0.038
Mg	2.092	2.075	2.237	2.233	2.173	2.004
Ca	1.914	1.890	1.889	1.880	1.837	1.812
Na	0.320	0.337	0.317	0.162	0.336	0.360
K	0.110	0.124	0.090	0.081	0.081	0.088

* Total Fe as Fe^{+2}.

perpendicular to (010) (Fig. 1). The plagioclase from A-12 is a 5mm, optically-zoned, Carlsbad-twinned phenocryst also cut perpendicular to (010). The grain from A-3 is a 2mm, unzoned, polysynthetically twinned grain cut perpendicular to (010). All three grains have seriticized centers and contain inclusions of amphibole. Petrographic examination reveals a mottled extinction pattern. The extinction discontinuities appear as diffuse, irregular patches (~0.03mm) and as mosaic patches (as in A-3) with differing extinction angles (Fig. 3a, b). The patches with the larger extinction angle show a higher index of refraction, suggesting compositional differences. The boundaries of patches appear sharp. No crystallographically controlled orientation was found.

All three relict igneous plagioclases analyzed show similar compositional variations: $An_{34.8}Ab_{64.5}Or_{0.7}$ to $An_{91.2}Ab_{7.1}Or_{1.7}$, $An_{40.9}Ab_{58.7}Or_{0.4}$ to $An_{79.9}Ab_{19.9}Or_{0.2}$, and $An_{38.7}Ab_{61.2}Or_{0.1}$ to $An_{60.7}Ab_{39.0}Or_{0.3}$, from metabasalts A-4, A-12, and A-3, respectively (Fig. 4). On the grain in A-4, three parallel 5-micron step traverses and one 5-micron step traverse perpendicular to the others (Fig. 1) reveal normal concentric zoning, upon which is superimposed extreme variations in weight percent CaO. The variations cannot be traced across the 50 micron distance between traverses. Two parallel 5-micron step traverses on the relict plagioclase in A-12 show similar variations. Inspection of the data suggests that the two grains were normally zoned from about An_{70} (core) to An_{50} (rim). The few data points more sodic than An_{44} are located within 30 microns of the grain boundaries, suggesting that Ca redistribution and equilibration to a metamorphic composition had begun along grain

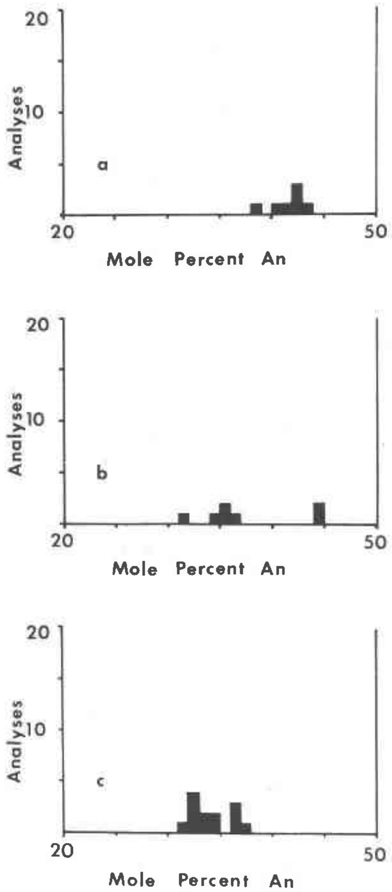

Fig. 2. Compositions of recrystallized plagioclase grains from (a) A-5, (b) A-6, and (c) A-12.

boundaries. These sodic compositions are consistent with metamorphic compositions of the recrystallized plagioclases in equilibrium with coexisting hornblende. The hornblende compositions of A-4 (Table 1) are identical to those of the older metabasalts A-5 and A-6. It appears that equilibration was only complete to a depth of 30 microns into the grains. The occurrence of the extremely calcic data points (An_{80} to An_{90}) suggests a process other than normal igneous crystallization.

Several 1-micron step traverses across selected areas of the three relict grains were made (Figs. 1 and 3). These traverses reveal variations in anorthite component indicating the presence of discrete compositional domains (Figs. 5 and 6). Within the 3-micron resolution of the electron microprobe, the domain boundaries are sharp. The widths of the domains traversed range from 6–30 microns. The domains themselves contain finer substructures, but with dimensions near microprobe resolution. These variations in all three grains can be correlated with the patches with differing extinction angles and indices of refraction (Figs. 3, 5 and 6). The areas of higher anorthite component correspond to the areas of higher extinction angle and index of refraction. Profile 5 (A-4) shows a series of domains with composi-

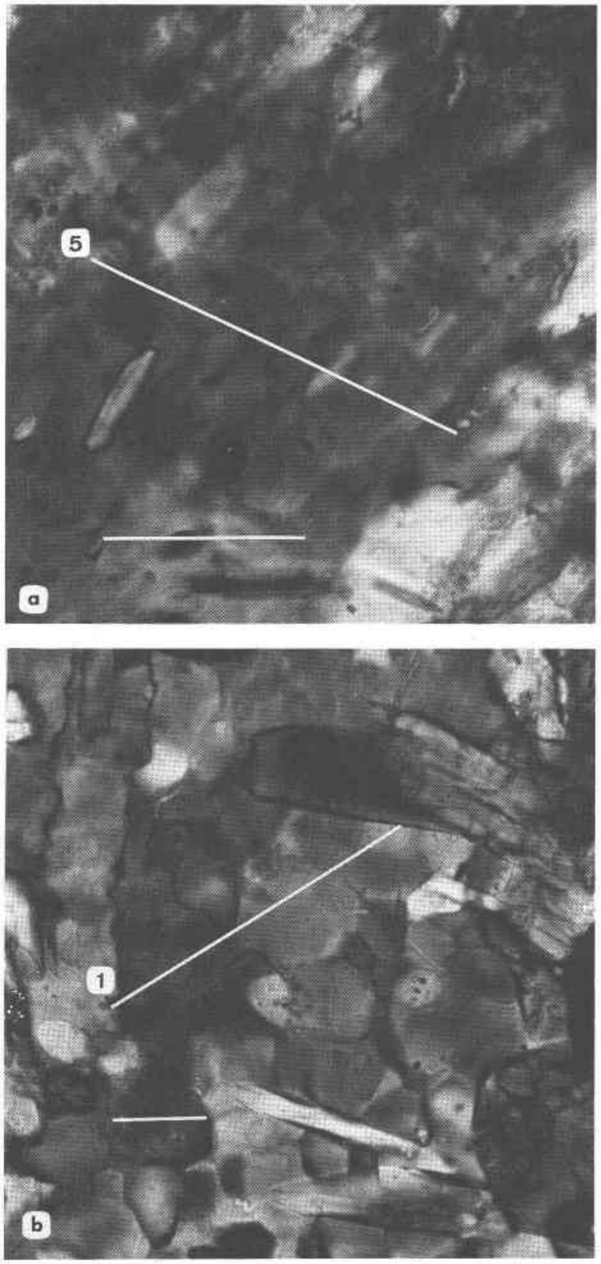

Fig. 3. Photomicrographs of mottled extinction patterns of plagioclases in (a) A-4 and (b) A-3. The numbered line in (a) shows the path of profile 5, and the corresponding traverse data are shown in Figure 5. The path of profile 1 (or A-3) is shown as the numbered line in (b) and its corresponding traverse data are shown in Fig. 6. Scale bars are 50 microns.

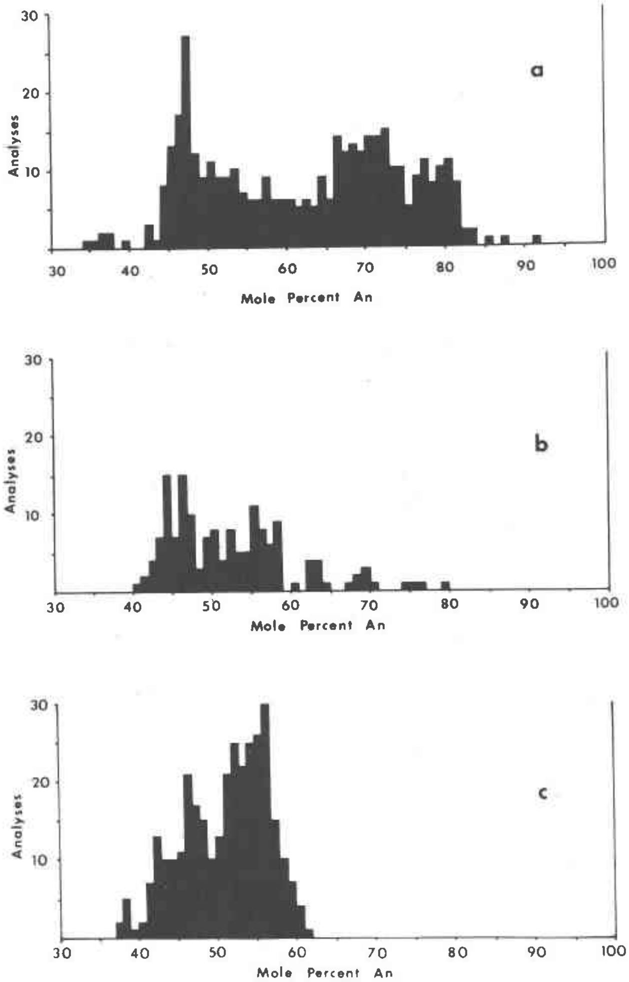

Fig. 4. Compositions of relict igneous phenocrysts of (a) A-4, (b) A-12, and (c) A-3. Histograms in (a) and (b) contain both 5-micron and 1-micron traverse data.

tions near An_{65}, An_{70}, and An_{80} (Fig. 5). Profile 6 (A-4) reveals domains with compositions near An_{45}, An_{55}, An_{60}, and An_{80} (Fig. 1). A-12 has domains with compositions near An_{45}, An_{55-58}, and An_{70}. In A-4 and A-12, it appears that the domain compositions vary along the compositional gradient of normal zoning, suggesting the original igneous compositions at least partially controlled the final chemical variations. Two traverses on the relict igneous plagioclase in A-3 reveal domains with compositions of An_{38}, An_{42-46}, and An_{55-58} (Fig. 6).

Discussion of data

The metamorphic conditions during intrusion and metamorphism of the younger basalts were insufficient for complete Ca partitioning between the large plagioclase phenocrysts and coexisting hornblende. Diffusion and exchange of Ca and Na were only complete to a depth of 30 microns into these large phenocrysts. The grain interiors are composed of irregular compositional domains perhaps formed in metastable equilibrium. Some of the smaller grains appear to have reached metamorphic compositions in equilibrium with hornblende (as in A-12).

Between An_{50} and An_{90} the plagioclase solid-solution is non-ideal (Orville, 1972) and undergoes a metastable spinodal unmixing in two regions (Smith, 1975). The Bøggild miscibility gap occurs between An_{45} and An_{55-60}. The Huttenlocher miscibility gap occurs between An_{65} and An_{90-95}. Nissen (1974) described exsolution in metamorphic bytownite in which the lamellae have compositions of An_{67} and An_{95}. These lamellae are on the order of 0.1 micron in width. Labradorites have been reported with lamellae with compositions of An_{69} and An_{88} (Cliff *et al*, 1976). Wenk (1977) reports metamorphic plagioclases with compositions of An_{35-45}, An_{65-70}, and An_{85-92} coexisting as crystallographic intergrowths. Crystallographic intergrowths of An_{34} andesine and An_{66} labradorite have been reported in Alpine calc-silicate rocks (Wenk *et al.*, 1975). These intergrowths are apparently the result of equilibrium growth. Wieland

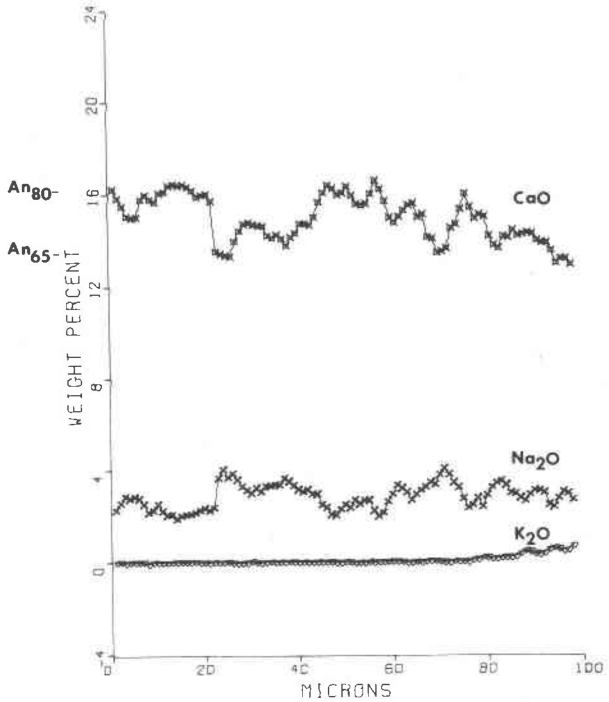

Fig. 5. 1-micron step traverse (profile 5) across relict grain from metabasalt A-4. The path of this traverse is shown in Fig. 3a.

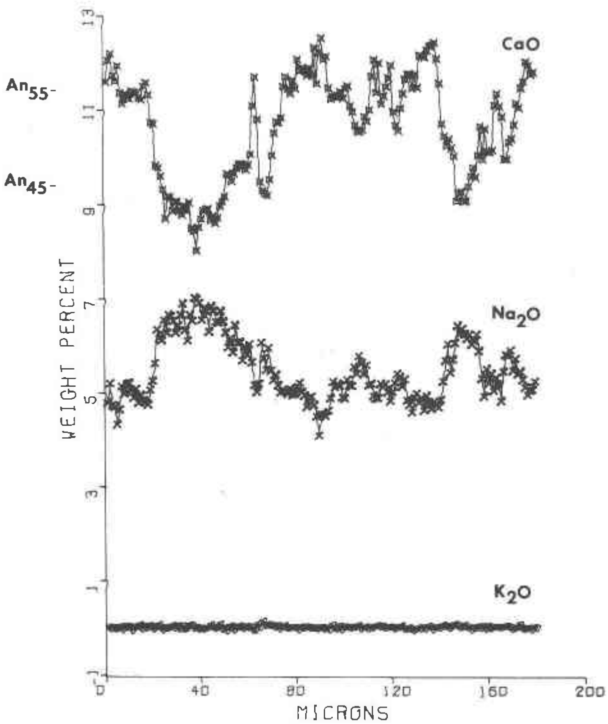

Fig. 6. 1-micron step traverse across relict grain from metabasalt A-3. The path of this traverse is shown in Fig. 3b.

(1966) reports plagioclases composed of irregularly arranged and shaped patches of An_{37} andesine and An_{67} labradorite. These "Fleckenplagioklase" contain optically distinct irregular zones with cloudy transition zones between. All intergrowths such as these appear to occur only in metamorphic rocks of sedimentary origin (Wenk *et al*, 1975).

Metamorphism allowed the igneous plagioclases of the younger Llano basalts to anneal within the temperature range of unmixing (600° to 850°C). The relict igneous plagioclases of A-4 and A-12 are zoned from An_{70} to An_{50}, so the compositional range spans both miscibility gaps. The irregular domains occurring in the plagioclases fall within the range of compositions of the Bøggild and Huttenlocher intervals. A composition near An_{90} occurs only twice ($An_{87.8}$ and $An_{91.2}$). I find eight discrete domains to exist within the compositional range of the miscibility gaps: An_{38}, An_{42-46}, An_{55-58}, An_{60}, An_{65}, An_{70}, An_{80}, and An_{88-91}. The existence of eight discrete domains suggests (1) both Bøggild and Huttenlocher intergrowths could be present in the same zoned grain, (2) the immiscibility region is extremely complex, allowing more than the four metastable endmember compositions to exist, or (3) a disequilibrium situation exists within the unmixing intervals due to unfavorable metamorphic conditions. The second appears to be the most probable, although domain compositions may depend on such factors as (1) cooling history, (2) original bulk composition, or (3) K_2O content.

The Llano plagioclases have irregular domains similar to the "Fleckenplagioklase" of Wieland (1966), although the domain boundaries are sharp in some cases. The crystallographic relationships described by Wenk *et al.* (1975) are not present in the Llano metabasalt plagioclases. In contrast to the previously reported occurrences of such intergrowths, these plagioclases are found in metamorphosed igneous rocks.

It appears that the relict igneous plagioclase interiors are in a metastable state, in which the structure is changing from high-albite solid solution and I-anorthite solid solution to a more ordered structure consisting of lower energy sodic and calcic members (Smith, 1975; Grove, 1976).

The degree of equilibration between plagioclase and coexisting hornblende can indicate relative durations of metamorphic events. The older basalts were intruded prior to 1200 m.y. ago. The plagioclases had at least 100 m.y. to anneal and recrystallize to uniform compositions in equilibrium with hornblende. The younger basalts were intruded some time after 1200 m.y. ago, probably near 1150 m.y. ago. The plagioclases had significantly less time to anneal than those of the earlier intrusions (*i.e.*, 50 m.y.). The occurrence of plagioclases in metastable equilibrium indicates the significance of this shorter annealing interval.

Acknowledgments

I thank Douglas S. Smith for his many hours of discussion, advice, and support during this research; D. S. Barker, S. E. Clabaugh, and F. W. McDowell for reviewing this manuscript; T. L. Grove and R. A. Yund for critical reviews of an earlier version; and Mike Roden and Calixto Ramirez for helpful discussions. The electron microprobe laboratory has been supported in part by the Geology Foundation of the University of Texas at Austin and by the NSF Earth Science Section, NSF Grants GA-41414, EAR76-12368, and EAR75-22201.

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Manuscript received, March 7, 1977; accepted for publication, August 12, 1977.