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Clouded Plagioclase in Metadolerite Dikes, Southeastern Bighorn Mountains, Wyoming

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Abstract

Exsolution of iron oxides appears to account for the clouding of plagioclase in metadolerite dikes in the Bighorn Mountains, Wyoming. An intra- rather than extra-plagioclase source of the iron is indicated by its accumulation along crystallographic planes and by comparative chemical, electron microprobe, oxygen isotopic, and X-ray diffraction studies of the clouded plagioclase and compositionally and mineralogically similar clear plagioclase in younger quartz dolerite dikes of the same area. The emplacement of the metadolerite into a terrane heated by metamorphic processes and the resulting slow subsolidus cooling of the plagioclase are thought to explain the exsolution. Electron microprobe studies indicate that the concentration of iron in clear plagioclase increases with decreasing An content and with proximity to crystal edges. This is interpreted to mean that the incorporation of iron by plagioclase is responsive to the availability of iron to the plagioclase.

Introduction

Plagioclase clouded by microscopic to submicroscopic inclusions of iron oxide occurs in Precambrian metadolerite dikes in the Bighorn Mountains, Wyoming, whereas unclouded plagioclase occurs in younger but compositionally and mineralogically similar quartz dolerite dikes. X-ray diffraction and oxygen isotopic data and analyses for major and trace elements by electron microprobe and conventional chemical techniques indicate that both plagioclases are virtually identical and formed under essentially the same conditions, except that iron occurs in oriented oxide inclusions in the metadolerite plagioclase and in structural sites in the quartz dolerite plagioclase. This distribution suggests that the clouding in the metadolerite plagioclase formed by subsolidus exsolution of the iron.

At least three distinct types of clouding occur in mafic rocks of other terranes: (1) extremely dense clouding in plagioclase of coronitic metagabbroic rocks attributed to introduction of some components or to exsolution during metamorphism (Whitney, 1972; Carstens, 1955; Poldervaart and Gilkey, 1954); (2) relatively less dense clouding in plagioclase from metadolerites (Prinz, 1964; Pichamuthu, 1959; Burns, 1966; Armbrustmacher, 1972) here attributed to subsolidus exsolution of iron; and (3) clouding in plagioclase from certain volcanic rocks consisting of silicate minerals found in the parent rock (Bentor, 1951; Bottinga, Kudo, and Weill, 1966). Type 3 clouding is probably produced by entrapment of liquid in a rapidly growing crystal and subsequent crystallization of silicates from that liquid or entrapment of minerals nucleated adjacent to plagioclase. The inclusions causing the clouding in types 1 and 2 have been identified by different workers as magnetite, hematite, spinel, rutile, and various silicates.

Geologic Setting

Dikes of tholeiitic composition were emplaced during two different episodes into Precambrian gneisses and migmatites in the southeastern Bighorn Mountains (Armbrustmacher, 1966, 1972). The older metadolerite dikes, dated at about 2.5 b.y. (Condie, Leech, and Baadsgaard, 1969), contain two different pyroxene assemblages—hypersthene-augite and pigeonite-augite—and intrude almandine-amphibolite facies rocks (Hoppin, 1961). The dikes were not intruded before or during the main metamorphic event because they cut across the host rock foliation (Armbrustmacher, 1966) and are not plastically deformed (see Rowan and Mueller, 1971). On the other hand, flexing and granulation of mineral grains, amphibolitization of the dike margins, and clouding of plagioclase and clinopyroxene (see MacGregor, 1931; Poldervaart, 1953; Poldervaart and Gilkey, 1954) suggest the possibility that the dikes may have been intruded during the waning stages of the metamorphic event. Additional mineralogic and petrologic data are presented by Armbrustmacher (1972) and Heimlich, Nelson, and Gallagher (1973).

The younger quartz dolerite dikes, emplaced approximately 2 b.y. ago (Condie, Leech, and Baadsgaard, 1969), do not exhibit the metamorphic features of the metadolerite. In the southeastern Bighorn Mountains, they contain only the pigeonite-augite pyroxene assemblage, and the plagioclase is characteristically unclouded, although locally saussuritized and kaolinized. We assume that this clear plagioclase and the clouded plagioclase from metadolerites were originally very similar in composition and structure and that the origin of clouding can be evaluated by comparing the present physical and chemical parameters of the clear and clouded plagioclase.

Clouding of plagioclase in anorthosite from a small layered mafic-ultramafic intrusion mentioned by Hoppin (1961, p. 359) was also studied. The intrusion, which contains harzburgite, bronzitite, and serpentinized dunite with sparse intercumulus plagioclase, and gabbro, norite, and anorthosite with cumulus plagioclase, crops out adjacent to U.S. Highway 16 in the southeastern Bighorn Mountains. The cumulus plagioclase typically contains oriented rodlike inclusions similar to those found in the Carr Boyd Rocks Complex (Purvis, Nesbitt, and Hallberg, 1972, p. 1102), in the Stillwater Igneous Complex (N. J Page, personal communication, 1973), and at other localities. We suggest that the rodlike inclusions formed in a manner similar to the inclusions in plagioclase of the metadolerites.

Description of Plagioclase

The clouded plagioclase (av. 48 modal percent) is typically anhedral (Fig. 1). Local deformation has resulted in slight flexing, minor cataclasis especially along grain boundaries and internal fractures, and development of glide twin lamellae (Vance, 1961) in the plagioclase. Albite and Carlsbad twins are present but tend to be partly masked by the clouding, glide twinning, and weak-to-moderate compositional zoning. Saussuritization and kaolinitization are rarely observed.

The intensity of clouding in the metadolerite plagioclase varies between different rock specimens from the same dike, between different grains in the same thin section, and within individual crystals. The clouding is caused by mineral inclusions that show a large intrasample variation in grain size at the thin-section scale but a relatively small intragrain variation. Commonly, the inclusions appear to be equidimensional. Their sizes vary from near 1 μm to below the limit of resolution of a microscope at 1,000 × magnification. The inclusions are generally so small and numerous that at low magnification they appear to cloud the host crystal. Under high magnification, at least some of the smaller inclusions and thin edges of some of the larger inclusions are faintly red with substage illumination. Others are opaque even on thin edges. The inclusions tend to concentrate in bands parallel and perpendicular to (010) of plagioclase (Fig. 2), but the plagioclase margins are virtually devoid of inclusions whether the plagioclase is in contact with another plagioclase crystal or a different mineral species (Fig. 1). Associated clinopyroxene also commonly exhibits clouding, but the inclusions are clustered along the periphery of a relatively clear core.

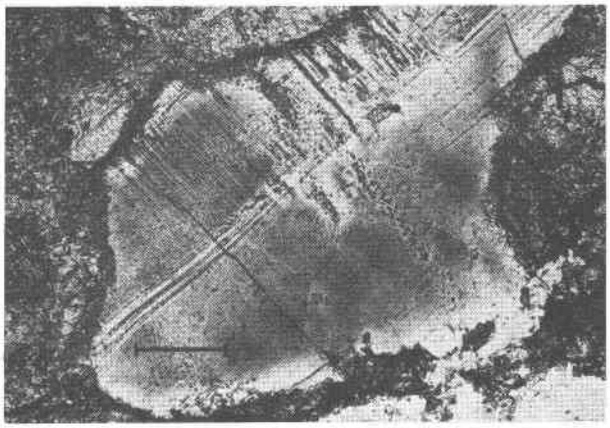

FIG. 1. Photomicrograph of anhedral clouded plagioclase in metadolerite. The distribution of the clouding is irregular, and crystal rims and areas around fractures with associated alteration tend to be unclouded. Plane polarized light. Sample A114. The bar scale measures 0.1 mm.

In plagioclase from anorthosite in the small ultramafic intrusion in the area (sample[1] T24A), larger rodlike inclusions up to 0.2 mm long (Fig. 3) occur with the equidimensional inclusions and appear to lie principally along the (010) and (001) crystallographic planes. In reflected light, the rods have moderate reflectivity, an off-white color, and are isotropic.

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[1] Sample locations are available from the authors.

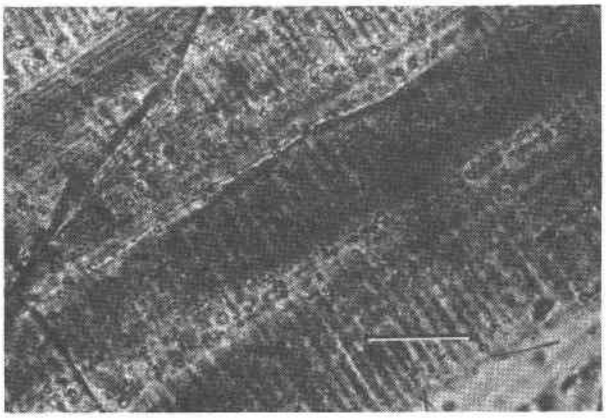

FIG. 2. Photomicrograph of iron oxide inclusions oriented parallel to twin lamellae in clouded plagioclase of metadolerite. The trace of the (010) twin plane crosses the photomicrograph from upper right to lower left. Plane polarized light. Sample A114. Bar scale measures 0.02 mm.

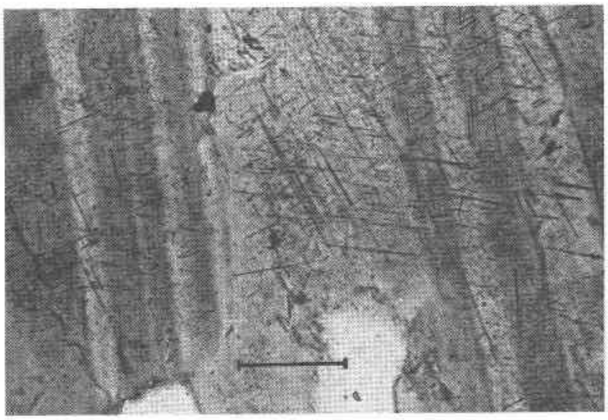

FIG. 3. Photomicrograph of crystallographically oriented rodlike inclusions of iron oxide in plagioclase from anorthosite. Partly crossed nicols. Sample T24A. Bar scale measures 0.2 mm.

Composition of the Plagioclase

The clouded plagioclase in metadolerites and the clear plagioclase in quartz dolerites (Table 1) would be chemically similar to the average of 19 intermediate plagioclase compositions published by Deer, Howie, and Zussman (1963), Wager and Mitchell (1951), and Moore (1971), except that both are relatively depleted in barium, strontium, and perhaps lithium, by an order of magnitude, and both are enriched in iron by two to three times these average concentrations. However, the total iron concentrations, although higher than average (0.5 wt percent), are within the range of published analyses.

Differences in concentrations of total iron, magnesum, titanium, manganese, cobalt, chromium, and nickel between samples A70P (clear) and A114P (clouded) could be attributed to the mineral inclusions causing the clouding in sample A114P, but in thin section a very fine grained, light-green mineral resembling amphibole is present along fractures and grain margins of the clouded plagioclase. Powder X-ray diffraction analysis of sample A114P reveals non-plagioclase reflections at *d*-spacings 8.26, 2.70, and 2.58 Å (Cu*K*α radiation); additional reflections are probably masked by those of plagioclase. These few reflections are insufficient for identification of the mineral but correspond to those

TABLE 1. Chemical Analyses of Clear Plagioclase (A70P) and Clouded Plagioclase (A114P) Separates

X-ray Fluorescence Analyses (weight percent)*	A70P	A114P
SiO_2	53.89	53.25
Al_2O_3	28.45	27.85
Total Fe as Fe_2O_3	1.06	1.62
CaO	12.63	12.86
Na_2O	3.70	3.06
K_2O	.29	.13
Total	100.02	98.77

Spectrographic Analyses (parts per million) Quantitative**	A70P	A114P
Mg	1,300	10,000
Ti	280	480
Mn	90	160
Ba	60	60
Co	N(4)	11
Cr	N(2)	26
Cu	34	26
Ni	6	36
Sr	200	150
V	N(20)	24
Ga	24	16

Semiquantitative†	A70P	A114P
Ag	1	7
Pb	N(7)	7
Sc	N(2)	7
Zr	15	10
Rare Alkali Metals††		
Li	3	4
Cs	<5	<5
Rb	4	2

*B. P. Fabbi, analyst.

**R. E. Mays, analyst; N, not detected above values in parentheses.

†Chris Heropoulos, analyst; looked for but not detected: As, Au, B, Be, Bi, Cd, Ce, Eu, Ge, Hf, In, La, Li, Mo, Nb, Pd, Pt, Re, Sb, Sn, Ta, Te, Th, Tl, U, W, Y, Yb, Zn.

††Harry Bastron, analyst.

of aluminian ferroanthophyllite, a metamorphic ortho-amphibole (Seki and Yamasaki, 1957). However, the reflections do not correspond to those of the minerals (iron oxides) that cause the clouding. Thus at least part if not all of the magnesium, titanium, manganese, cobalt, chromium, and nickel and some of the iron in clouded plagioclase A114P may be contained in silicate impurities.

To avoid problems of contamination inherent in bulk analysis of mineral separates and to determine compositional differences between the clouded cores and clear rims of the same crystal of clouded plagioclase, quantitative analyses (Table 2) were obtained with an A.R.L. Model EMX-SM electron microprobe. The following conditions were used: an ADP crystal for silicon, aluminum, calcium, and potassium, an LiF crystal for iron, and an RAP crystal for sodium; standards, labradorite and biotite; excitation voltage, 15 kV; sample current, 2.5×10^{-8} amp on brass; beam diameter, approximately 3 to 5 μm; and accumulation of X-ray intensity data terminated on a fixed beam current at about 20 seconds for calcium, silicon, and aluminum and at about 30 seconds for potassium, iron, and sodium. The site of the beam was moved a few microns once during accumulation of the potassium, iron, and sodium counts to minimize the effects of sodium volatilization. In a given analyzed area, eight to ten observation points were counted and averaged. Drift, background, and matrix corrections (mass absorption, secondary fluorescence, and atomic number effects) were made by computer (Beeson, 1967; Beaman and Isasi, 1970). The beam was large enough and data were gathered at enough points that the values for iron for the clouded cores represent the average present, not the actual amount in the plagioclase structure.

The values in parentheses after the weight percent oxide in Table 2 represent one standard deviation of the counts in the area analyzed, converted to oxide. They include both instrumental precision and homogeneity of the oxide in the analyzed area.

TABLE 2. Quantitative Electron Microprobe Analyses of Clouded Plagioclase

	A114		A60			A122	T24A	
	Clouded core	Clear rim	Clouded core I	Clouded core II	Clear rim	Clouded core	Clear core*	Clear rim
SiO_2	52.8 (2)**	54.0 (4)	52.7 (2)	51.9 (4)	53.8 (4)	53.9 (3)	54.2 (4)	54.2 (4)
Al_2O_3	29.5 (2)	29.2 (2)	29.9 (2)	30.3 (3)	29.6 (3)	29.2 (3)	28.7 (1)	28.9 (2)
Fe_2O_3†	.79 (14)	.18 (1)	.77 (10)	.82 (4)	.29 (8)	.38(10)	.12(1)	.12 (1)
CaO	12.0 (1)	11.4 (1)	12.3 (1)	12.8 (1)	11.7 (2)	11.6 (1)	10.8 (1)	11.1 (2)
Na_2O	5.0 (1)	5.40 (4)	4.70 (14)	4.60 (8)	5.10 (8)	5.10 (4)	5.60(4)	5.50 (4)
K_2O	.060 (1)	.050(3)	.060 (2)	.080(3)	.070(4)	.150(2)	.26(7)	.190(1)
Total	100.15	100.23	100.43	100.50	100.56	100.33	99.68	100.01
			Number of ions on the basis of 32(O)					
Si	9.58	9.75	9.53	9.40	9.68	9.73	9.83	9.80
Al	6.32	6.20	6.37	6.48	6.28	6.21	6.14	6.17
Fe^{3+}	.11	.02	.10	.11	.04	.05	.02	.02
Ca	2.33	2.20	2.39	2.49	2.25	2.24	2.09	2.14
Na	1.74	1.88	1.65	1.62	1.78	1.79	1.97	1.93
K	.01	.01	.01	.02	.02	.03	.06	.04
Z††	16.01	15.97	16.00	15.99	16.00	15.99	15.99	15.98
X	4.08	4.09	4.05	4.13	4.05	4.05	4.12	4.11
Ab	42.6	45.9	40.7	39.3	44.0	44.0	47.8	46.9
An	57.1	53.8	59.0	60.3	55.6	55.1	50.8	52.1
Or	.3	.3	.3	.4	.4	.9	1.4	1.0

**Between rodlike inclusions.*

***Parenthesized figures represent the estimated standard deviation in terms of least units cited for the value to their immediate left, thus 52.8(2) indicates an estimated standard deviation of 0.2.*

†Total iron calculated as Fe_2O_3.

††Z equals the sum of Si, Al, and Fe^{3+}; X equals the sum of Ca, Na, and K.

The limits do not imply accuracy of measurement with respect to the absolute amount of the oxide present, but are useful in comparing or evaluating differences in the amount of oxide present in each area or grain analyzed. The Z group includes Si, Al, and Fe^{3+}, and the X group includes Ca, Na, and K (Deer, Howie, and Zussman, 1963).

Inclusion-rich cores are enriched in calcium relative to inclusion-free rims (Table 2), which is consistent with normal continuous igneous zoning (Brown, 1967). Total iron is greater in clouded crystal cores relative to clear rims in samples A114 and A60 (Table 2) because the analyzed area of the core was a composite of both plagioclase and the inclusions causing the clouding. However, in sample T24A, from anorthosite in the small ultramafic intrusion, the iron content is the same in both the plagioclase core and the rim. In this plagioclase, enough area exists between inclusions so that analysis of the plagioclase could be made without interference from the inclusions. Thus it is possible, but not mandatory, that the iron content of the plagioclase in samples A114 and A60, like sample T24A, is not significantly different between rim and core.

Structural State and Oxygen Isotopic Composition of Plagioclase

The structural states of clouded plagioclase (A114P) in metadolerite and clear plagioclase (A70P) in quartz dolerite (Table 3) were determined by plotting Γ versus An composition for each on curves of similar data for Lower Bushveld plagioclase (Desborough and Cameron, 1968), Stillwater plagioclases (Jackson, 1961), and the general curves of Smith and Gay (1958, p. 749). These plots show that both clear and clouded plagioclases have nearly identical structural states that are somewhat more disordered than Bushveld and Stillwater plagioclases and typical of those from hypabyssal intrusions. Although Γ values give a more reliable indication of structural change in the composition range An 0-70 (Smith and Gay, 1958, p. 752), measurements of β (Smith and Gay, 1958, p. 754) result in a similar interpretation. Similar conclusions are also reached by plotting 2θ (131)-2θ ($1\bar{3}1$) against An content (Smith, 1972, p. 515).

TABLE 3. X-ray Powder Diffraction Data for Clear Plagioclase (A70P) and Clouded Plagioclase (A114P)

	A70P	A114P
	$Ab_{33\cdot7}An_{64\cdot6}Or_{1\cdot7}$	$Ab_{34\cdot1}An_{65\cdot3}Or_{0\cdot6}$
Unit Cell Parameters*		
a	8.170(2)Å**	8.171(2)Å**
b	12.862(1)Å	12.863(2)Å
c	7.099(1)Å	7.105(1)Å
α	98°33(1)'	98°31(1)'
β	116°09(1)'	116°09(1)'
γ	90°15(1)'	90°19(1)'.
V	668.0(1)$Å^3$	668.6(2)$Å^3$
Functions for Determining Structural State†		
Γ $(2\theta(131)+2\theta(220)-4\theta(1\bar{3}1))$	.898	.932
β $(2\theta(1\bar{1}1)-2\theta(\bar{2}01))$	.825	.825
$2\theta(131)-2\theta(1\bar{3}1)$	1.998	2.015

*These parameters are calculated from least-squares analysis of X-ray powder diffraction data using the computer program of Appleman and Evans (1973). X-ray diffractometer conditions are: Cu/Ni radiation, λ CuK_{α} = 1.5418Å, Si internal standard, scanned at 1/4°2θ per minute.

**Parenthesized figures represent the standard deviation in terms of least units cited for the value to their immediate left, thus 8.170(2)Å indicate a standard deviation of 0.002.

† calculated from d_{hkl} values in Table 4.

J. R. O'Neil of the U.S. Geological Survey determined δO^{18} (SMOW) for the same plagioclase separates. The resulting values, δO^{18} = 7.25 ± 0.04 per mil for clear plagioclase (A70P) and δO^{18} = 7.31 ± 0.02 per mil for clouded plagioclase (A114P), are nearly identical and are typical of δ values for plagioclase in mafic igneous rocks (Taylor and Epstein, 1963; Taylor, 1964; Epstein and Taylor, 1967). They indicate that neither the clear nor clouded plagioclase exchanged measurable amounts of oxygen with a postmagmatic fluid phase (see O'Neil and Taylor, 1967). This differs from the observations of Epstein and Taylor (1967) and Taylor (1964), who found that plagioclase with heavy concentrations of inclusions (type 1 clouding) in Adirondack metagabbro was isotopically reequilibrated by intercrystalline diffusion and solid state reaction (Whitney, 1972) in the presence of interstitial fluids of metamorphic origin.

Nature of the Inclusions

All inclusions observed, even the rod-shaped inclusions in anorthosite (sample T24A), are too small for quantitative analysis; moreover, most inclusions except those in the anorthosite are too small and too closely spaced to resolve with the electron microprobe. However, X-ray images of areas 1.6 by 2 μm displayed on a cathode ray tube (CRT) screen 8 × 10 cm indicate that plagioclase with relatively intense clouding contains more iron than intervening less clouded plagioclase. Concentrations of magnesium, titanium, chromium, and sulfur are below detection levels even in the most densely clouded areas. The presence of iron alone suggests that the inclusions are iron oxides and not ilmenite, chromite, rutile, spinel, or sulfide minerals.

As indicated earlier, some of the inclusions appear to be red, and thus may likely be hematite. However, many of the inclusions are not red and most of these are too small for quantitative analysis. Some of the rodlike inclusions in the anorthosite sample T24A (0.8 μm) and a few of the equidimensional inclusions in metadolerite sample A122 (0.4 μm) are large enough to analyze qualitatively. We cannot rule out the possibility that some of the larger inclusions in sample A122 are primary magmatic inclusions (type 3) rather than large secondary exsolved iron oxide inclusions. However, the rodlike inclusions in sample T24A are not primary inclusions. The largest grains in each sample contain a minimum of 66 (sample T24A) and 69 (sample A122) wt percent iron, whereas concentrations of titanium, chromium, and aluminum are too low to be detected. Therefore these larger inclusions may not be spinel, chromite, or titaniferous magnetite but are either specular hematite, magnetite, or maghemite, all of which contain 70 wt percent or more iron. Because of the optical properties of the larger inclusions in samples A122 and T24A, hematite is the least likely choice. Therefore, both types of inclusions, the fine dust in metadolerite plagioclase and the rodlike inclusions in anorthosite, appear to be iron oxides. The larger are most likely magnetite, but perhaps also maghemite; the smaller are partly hematite because of their red color and perhaps partly magnetite or maghemite because of their opacity.

Origin of the Inclusions

Source of the Iron

The preceding data on structural state and oxygen isotopic ratios are compatible with an exsolution origin for the clouding in plagioclase of metadolerites, provided the plagioclase contained appropriate amounts of structural iron prior to formation of the inclusions. The clear rims of the clouded plagioclase contain detectable amounts of iron (Table 2) that are not associated with exsolved phases observable with the microscope or electron microprobe. However, the amount present in the clear rims is much less than that required to form the inclusions, and the pervasive nature of the clouding precludes the possibility of finding plagioclase with unexsolved iron in the metadolerites. Thus direct evidence for original high content of iron in the plagioclase is not available. As an alternative, the iron and calcium content of the clear plagioclase from the younger, petrochemically similar (although not identical) quartz dolerites was determined semiquantitatively to see whether it was possible that iron was present in the plagioclase in appropriate amounts and distributed in the appropriate manner. Cores and rims of seven plagioclase grains from three samples of quartz dolerite range from 0.9 to 1.1 (av. 0.96) and 0.8 to 1.3 (av. 1.1)

TABLE 4. Indexed X-Ray Diffraction Data for Clear Plagioclase (A70P) from Quartz Dolerite and Clouded Plagioclase (A114P) from Metadolerite, Southeastern Bighorn Mountains, Wyoming

	A70P(Ab$_{33.7}$An$_{64.6}$Or$_{1.7}$)		A114P(Ab$_{34.1}$An$_{65.3}$Or$_{0.6}$)	
hkl	d_{hkl}(Å)obs*	d_{hkl}(Å)calc**	d_{hkl}(Å)obs*	d_{hkl}(Å)calc**
$\bar{1}10$	6.462	6.463	6.476	6.466
020		6.415		6.415
001		6.356		6.361
110		6.269		6.267
$\bar{1}\bar{1}1$		5.824		5.825
$\bar{1}11$		5.638		5.642
$0\bar{2}1$	4.687	4.685	4.687	4.686
021		4.363		4.365
$\bar{2}01$	4.040	4.040	4.044	4.041
$1\bar{1}1$	3.895	3.895	3.899	3.897
111	3.756	3.755		3.756
$\bar{1}30$		3.752	3.756	3.754
200		3.665		3.665
130	3.638	3.638	3.636	3.637
$\bar{1}\bar{3}1$		3.625		3.624
$\bar{1}31$		3.491		3.493
$\bar{1}\bar{1}2$	3.471	3.471	3.473	3.473
$\bar{2}\bar{2}1$		3.428		3.427
$\bar{2}21$		3.409		3.411
$\bar{1}12$	3.362	3.362	3.362	3.365
$\bar{2}20$	3.231	3.231	3.232	3.233
040	3.206	3.207	3.207	3.207
$\bar{2}02$		3.201		3.203
002	3.179	3.178	3.180	3.181
220	3.135	3.135	3.135	3.134
$1\bar{3}1$	3.021	3.022	3.023	3.023
$0\bar{4}1$	2.948	2.949	2.948	2.949
$0\bar{2}2$	2.932	2.932	2.935	2.934
$\bar{2}\bar{2}2$		2.912		2.912
131	2.834	2.834	2.834	2.834
$\bar{2}22$		2.819		2.821
$\bar{1}\bar{3}2$		2.816	2.816	2.816
041		2.785		2.786
022		2.771		2.772
$\bar{1}32$	2.649	2.649	2.651	2.650
$\bar{2}40$		2.457	2.457	2.458
$\bar{3}10$		2.416	2.416	2.416
$\bar{3}\bar{3}1$		2.285	2.283	2.284
060	2.139	2.138	2.138	2.138
$2\bar{4}1$	2.126	2.125		
151	2.100	2.100	2.101	2.100
222	1.877	1.878	1.878	1.878
400		1.832	1.832	1.832
113	1.795	1.795		1.796
$\bar{2}04$	1.771	1.771		1.773

**X-ray diffractometer conditions are: Cu/Ni radiation, λCuK_{α} = 1.5418Å; silicon used as internal standard; scanned at ¼°2θ per minute.*

***All calculated spacings listed for $d_{hkl} \geq$ 2.770Å; calculated spacings less than 2.770Å are listed only when they correspond to an indexed observed reflection. Indices are from least-squares analysis of X-ray powder data using the computer program of Appleman, D. E., and H. T. Evans, Jr. (1973) Job 9214: indexing and least-squares refinement of powder diffraction data, U.S. Dept. of Commerce, Nat. Tech. Inf. Serv., PB 216188.*

****Parenthesized numbers are standard errors in terms of the least decimal place cited; e.g. (2) = ±0.002.*

percent Fe_2O_3, respectively, which is comparable to the amount in the clouded plagioclase in metadolerite (Tables 1 and 2) and the amount in the clear plagioclase of Table 1. Calcium is more abundant in the interior of clear plagioclase crystals than in the rims, indicating normal composition zoning similar to that in the clouded plagioclase (compare data in Fig. 4 with Table 2). Thus it appears that plagioclase in similar mafic rocks can incorporate a suitable amount of iron to explain the inclusions as exsolution products. However, we cannot entirely rule out an extra-plagioclase source for the iron in the inclusions. On the contrary, clouding accompanied by iron enrichment and hornblendization (the hornblende containing more iron than the clinopyroxene) occurs irregularly along the rims of coexisting clinopyroxene in the metadolerite. Thus, if part or all of this "excess" iron in the clinopyroxene was introduced during development of the plagioclase clouding, an obvious extra-plagioclase source was available in the intergranular fluids. We do not speculate on the source of this iron. However, iron enrichment in the clinopyroxene occurs along rims and fractures in grains, the cores remain unclouded, and the inclusions are not crystallographically oriented or localized. In plagioclase, the inclusions are oriented and localized along crystallographic directions and are pervasive through the grains while being depleted at the rims of the grains, along major grain discontinuities, and around fractures with associated hydroxyl-bearing alteration minerals (Fig. 1). Thus we feel that the process of enrichment of iron in the clinopyroxene and the development of iron oxide inclusions in the plagioclase are not necessarily attributable to the same process. Furthermore, the distribution and spacing of the inclusions (Fig. 2) require intimate contact of the presumed fluid with all parts of the plagioclase. If the presumed fluid was nonmagmatic, this should, but did not, result in observable cation exchange (see experimental data of Eskola, Vuoristo, and Rankama, 1937, and O'Neil and Taylor, 1967, for fluid-plagioclase cation exchange at relatively low temperatures), structural state alteration (see Smith and Gay, 1958; Vogel and Spence, 1969; Noble, 1966), and adjustment of the oxygen isotopic composition of the plagioclase (O'Neil and Taylor, 1967).

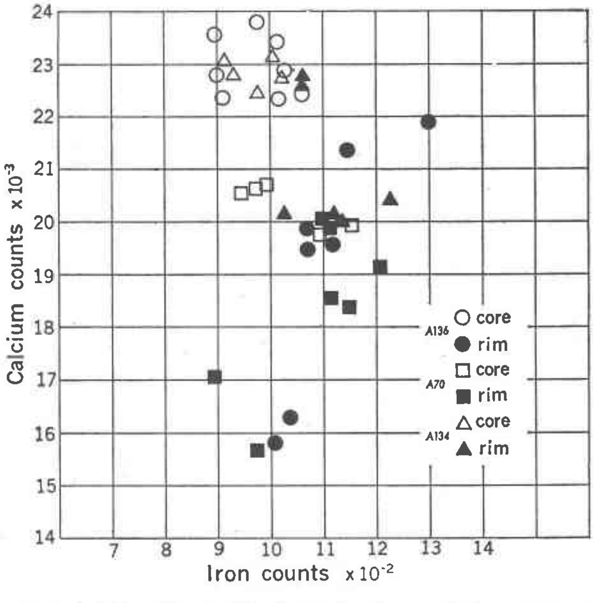

FIG. 4. X-ray intensities (counting interval about 20 seconds, terminated on fixed beam current) of calcium *vs* iron for 2 to 3 observations of both cores and rims of 2 to 3 grains per sample of clear plagioclase from quartz dolerites. The distribution of points reflects both machine counting error and real variations of calcium and iron within and between grains and samples. Average calcium counts of all observations are 22,200 ± 140 (± equals one standard deviation) for grain centers and 19,850 ± 170 for grain edges. Average iron counts are 995 ± 70 for grain centers and 1,100 ± 95 for grain edges.

In contrast to the iron distribution in the clouded plagioclase (Table 2), the rims of the clear plagioclase tend to contain slightly more iron than the interiors (Fig. 4). This suggested negative correlation between iron and calcium content is a reverse of observations by Ribbe and Smith (1966) based on analysis of plagioclases from a variety of lithologic types. They attribute the decrease in the iron content of plagioclase observed with decreasing An content to decreasing temperature and number of Al^{IV} (Fe^{3+}) and Ca^{2+} (Fe^{2+}) sites in the plagioclase (see also Sen, 1960). However, our observations, although based on limited data, suggest that the iron content of plagioclase may be responsive to changes in the iron available to the plagioclase. This observation is also reflected in the data of Bottinga, Kudo, and Weill (1966), which show that the iron content of plagioclase in basaltic glass increases with decreasing An content toward the crystal rim and that the concentration of iron in the glass is greater adjacent to the crystal than away from it. Presumably, this gradient in iron content in the glass occurs because the crystals incorporated smaller amounts of iron than the total amount available in the melt. The end result, however, is the same as that we observed—the plagioclase crystals apparently can react to an increasing iron content in the adjacent liquid by incorporating more iron. Thus Ribbe and Smith's (1966) data that show greater amounts of iron in calcic plagioclase from mafic rocks relative to more sodic plagioclase in acidic rocks may reflect the increasing availability of iron to the plagioclase instead of, or in addition to, an increase in the number of suitable sites and/or temperature.

Diffusion of the Iron

The simplest explanation of the origin of the iron oxide inclusions in plagioclase of metadolerites consistent with field, chemical, oxygen isotopic, and plagioclase structural data is that iron exsolved from the plagioclase structure and moved to more stable sites along crystallographic planes. The distance that the iron was required to move to form the inclusions was quite small in crystal interiors compared with the distance that iron is required to move to form clear rims of relatively low iron content in the clouded plagioclase, assuming that the iron distribution in the clouded plagioclase originally was similar to that in the clear plagioclase in the quartz dolerites. Comparatively, the iron is required to move only a few tenths or hundredths of a micron in the clouded areas but had to move several tens of microns either out of the plagioclase rim into adjacent minerals or toward clouded plagioclase interiors to form clear rims. We have no data supporting or refuting diffusion of iron toward crystal interiors. On the other hand, some of the iron in the clouded clinopyroxene rims in the metadolerite (Fig. 5) may have come from iron originally in the plagioclase rims. However, the volume and iron content of clear plagioclase rims are less than the volume and iron content of clouded clinopyroxene rims (see Fig. 5 for relative iron contents). Thus the amount of iron contributed (difference between iron contents of plagioclase cores and rims) to the clinopyroxene rims must have been small.

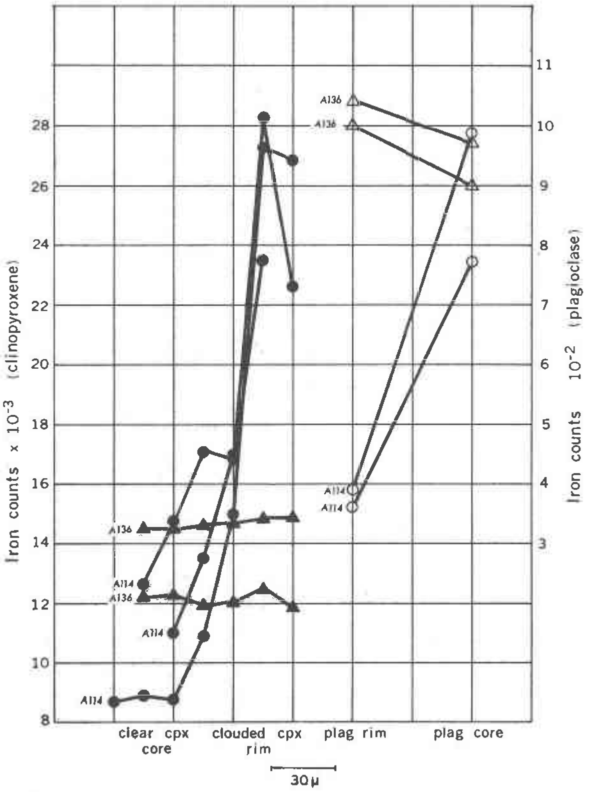

FIG. 5. X-ray intensity (counting interval about 20 seconds, terminated on fixed beam current) of iron in clinopyroxene (solid) and plagioclase (open) in metadolerite (circles) and quartz dolerite (triangles).

Conditions of Exsolution

The liquidus cooling rates of the metadolerite and quartz dolerite probably were not appreciably different because crystal sizes in dikes of similar width are nearly identical. In addition, because the plagioclase order-disorder structural states are nearly identical and because the order-disorder structural states of plagioclase are assumed to be frozen in before 475°C (Leavitt and Slemmons, 1962), the initial subsolidus cooling rates of the two dike types were probably similar. Finally, the oxygen isotopic data suggest that the exsolution either occurred in the presence of magmatic fluids, or was postmagmatic and occurred without appreciable transfer of the plagioclase components by metamorphic or other fluids. We attribute iron exsolution in the metadolerite plagioclase and the lack of iron exsolution in the quartz dolerite plagioclase to either (1) a paucity of magmatic fluid in the quartz dolerites or (2) slower subsolidus cooling rates of the metadolerites below about 475°C by virtue of their intrusion during the waning stages of a metamorphic event into rocks still at elevated temperatures (but below about 475°C). We tend to favor the latter. The exsolution of crystallographically oriented magnetite (or maghemite) rods from plagioclase in anorthosite (sample T24A) may have occurred over a greater period of time with a slower cooling rate or at a higher temperature than in the metadolerite because the host ultramafic intrusion is somewhat older and larger than the metadolerite dikes. Either condition might explain the larger size of the inclusions in sample T24A relative to those in metadolerite.

Clouding of plagioclase cannot be attributed to localized heating because clouded plagioclase occurs in mafic rocks throughout the metamorphic terrane of the Bighorn Mountains (Hoppin, 1961, 1970; Kiilsgaard *et al,* 1972; Heimlich, Nelson, and Gallagher, 1973). In the Beartooth Mountains, Montana-Wyoming, identical clouding of plagioclase in metadolerite occurs (Prinz, 1964; Simons *et al,* 1973) and the same relative sequence of events seems to prevail.

Conclusions

Clouding of plagioclase in metadolerites in the Bighorn Mountains appears to be best explained by exsolution of structural iron. Thermal energy and perhaps water required for the exsolution of iron are assumed to have been supplied by the country rocks, which were still in the waning stages of a metamorphic episode that changed gneissic and migmatitic country rock to almandine amphibolite facies (Hoppin, 1961, p. 360). Exsolution probably occurred below about 475°C in an environment impoverished in postmagmatic fluids. Diffusion of some of the iron from plagioclase rims into adjoining clinopyroxene rims might also have occurred during or perhaps after exsolution. The original ratio of Fe^{3+} to Fe^{2+} in the metadolerite plagioclase is not known. If we assume that the iron occupies structural sites, published analyses indicate that Fe^{3+} and Fe^{2+} occur in plagioclase in ratios appropriate to form both magnetite and hematite without requiring oxidation-reduction reactions. The source of the oxygen to form the magnetite and hematite is not known. If a small amount of water was involved, however, an oxygen source and the possibility of redox reactions through hydrogen diffusion require consideration.

Detailed experimental data on the solubility of Fe^{3+} and Fe^{2+} in the plagioclase structure have not been published. When compared with other accounts of electron microprobe analyses of iron in plagioclase of similar An content (Corlett and Ribbe, 1967; Brown and Carmichael, 1971; Quaide, 1972), clouded plagioclase from metadolerite and clear plagioclase from quartz dolerite in the Bighorn Mountains appear to contain close to maximum concentrations of iron reported. We suspect that such concentrations of iron in plagioclase must alter the temperature at which plagioclase separates from the melt and have some effect on the Ab–An solidus relative to iron-free plagioclase.

Finally, our data and the data of Bottinga, Kudo, and Weill (1966) suggest that increased iron content with decreased An content from plagioclase core to rim might reflect changes in the amount of iron available to the plagioclase rather than, or in addition to, changes in the number of Al^{IV} or Ca^{2+} sites into which iron can be substituted.

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