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CRYPTIC TRACE-ELEMENT ALTERATION OF ANORTHOSITE, STILLWATER COMPLEX, MONTANA

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ABSTRACT

Evidence of cryptic alteration and correlations among K, Ba, and *LREE* concentrations indicate that a post-cumulus, low-density aqueous fluid phase significantly modified the trace-element contents of samples from Anorthosite zones I and II of the Stillwater Complex, Montana. Concentrations of Ba, Ca, Co, Cr, Cu, Fe, Hf, K, Li, Mg, Mn, Na, Ni, Sc, Sr, Th, Zn, and the rare-earth elements (*REE*) were measured in whole rocks and plagioclase separates from five traverses across the two main plagioclase cumulate (anorthosite) zones and the contiguous cumulates of the Stillwater Complex in an attempt to better understand the origin and solidification of the anorthosites. However, nearly the entire observed compositional range for many trace elements can be duplicated at a single locality by discriminating between samples rich in oikocrystic pyroxene and those which are composed almost entirely of plagioclase and show anhedral-granular texture. Plagioclase separates with high trace-element contents were obtained from the pyroxene-poor samples, for which maps of K concentration show plagioclase grains to contain numerous fractures hosting a fine-grained, K-rich phase, presumed to be sericite. Secondary processes in layered intrusions have the potential to cause cryptic disturbance, and the utmost care must be taken to ensure that samples provide information about primary processes. Although plagioclase from Anorthosite zones I and II shows significant compositional variation, there are no systematic changes in the major- or trace-element compositions of plagioclase over as much as 630 m of anorthosite thickness or 18 km of strike length. Plagioclase in the two major anorthosite zones shows little distinction in trace-element concentrations from plagioclase in the cumulates immediately below, between, and above these zones.

Keywords: Stillwater Complex, anorthosite, alteration, plagioclase, trace elements, Montana.

SOMMAIRE

Des signes d'une altération cryptique et des corrélations entre concentrations de K, Ba et les terres rares légères témoignent de la mobilisation, après la formation des cumulats, d'une phase aqueuse qui a sensiblement modifié la teneur en éléments traces d'échantillons d'anorthosite des zones I et II du complexe stratiforme igné de Stillwater, Montana. Nous avons mesuré les concentrations de Ba, Ca, Co, Cr, Cu, Fe, Hf, K, Li, Mg, Mn, Na, Ni, Sc, Sr, Th, Zn, et les terres rares dans des échantillons représentatifs de roche ainsi des concentrés de plagioclase prélevés le long de cinq coupes traversant la zone de cumulats à plagioclase (anorthosite) et les cumulats contigus du complexe de Stillwater, afin de mieux comprendre l'origine et la solidification de ces cumulats. Toutefois, on peut trouver l'intervalle de concentration presqu'en entier dans le cas de plusieurs éléments traces à un seul site de prélèvement en choisissant des échantillons riches en oïkocristaux de pyroxène ou d'autres qui contiennent presqu'uniquement du plagioclase en texture xénomorphe-granulaire. Les concentrés de plagioclase à teneur élevée en éléments traces proviennent d'échantillons à faible teneur en pyroxène. Des cartes illustrant la distribution de K démontrent la présence de multiples fissures tapissées d'un minéral potassique à granulométrie fine, qui serait de la séricite. Dans les complexes ignés stratiformes, les processus secondaires ont le potentiel de causer des anomalies cryptiques, de sorte qu'il est nécessaire d'exercer beaucoup de soin dans le prélèvement d'échantillons pour caractériser les processus primaires. Quoique le plagioclase de l'anorthosite des zones I et II fait preuve de variations importantes en composition, nous ne décelons aucun changement systématique dans la composition du plagioclase (éléments majeurs et éléments traces) sur une épaisseur atteignant 630 m et sur une distance de 18 km. Le plagioclase des deux zones les plus importantes d'anorthosite montre finalement très peu de différences dans sa teneur en élements traces avec le plagioclase des cumulats situés à des niveaux supérieurs ou inférieurs à ces deux zones d'anorthosite, ou entre les deux.

(Traduit par la Rédaction)

Mots-clés: complexe igné de Stillwater, anorthosite, altération, plagioclase, éléments traces, Montana.

INTRODUCTION

Major- and trace-element compositions are traditionally used to infer petrogenetic and crystallization processes for igneous rocks. In application to cumulates, such studies commonly have focussed on mineral separates in an attempt to deal with the fact that whole-rock samples do not represent melt compositions. As applied to the Stillwater Complex, recent examples of such studies include those of Lambert *et al.* (1994) and Loferski *et al.* (1994).

However, over the past 20 years, it has become increasingly evident that rocks of the Stillwater Complex have been subjected to a variety of post-cumulus processes. The best documented of these have not been those involving migration of interstitial melt in response to compaction and compositional convection, which seems almost a necessary part of the cumulus process (*e.g.*, Irvine 1980, Irvine *et al.* 1983, Sparks *et al.* 1985). Rather, they have involved magmatic and hydrothermal fluids that may have been active after consolidation of the pile of cumulates. Studies relevant to this post-cumulus history of the complex include those of pegmatoid development (Braun *et al.* 1994), apatite geochemistry (Boudreau *et al.* 1986, Boudreau & McCallum 1989, Meurer 1995, Meurer & Boudreau, in press), the sulfide enrichment of the Picket Pin zone (Boudreau & McCallum 1985), transport of Pt-group elements (Boudreau *et al.* 1986, Boudreau 1988), and formation of granophyres (Czamanske *et al.* 1991).

Here, we report on an investigation of the trace-element contents of a large suite of plagioclase separates from the Banded series, with emphasis on Anorthosite zones I and II (AN I and AN II). The study was designed to determine whether this suite of trace elements in Stillwater plagioclase could be used to distinguish products of crystallization from distinct, parental magmas and to investigate lateral geochemical variations within each anorthosite zone. Unexpectedly, we found that post-cumulus alteration by a fluid phase provides the best explanation for the dominant compositional patterns.

GEOLOGICAL BACKGROUND

The layered, mafic and ultramafic Stillwater Complex is exposed for a strike length of 43 km along the northern front of the Beartooth Mountains of south-central Montana (Fig. 1). It was intruded *ca.* 2700 Ma (*e.g.*, Premo *et al.* 1990) into Middle Archean metasedimentary rocks, is unconformably overlain by Paleozoic and Mesozoic sedimentary rocks, and was tilted during the Laramide orogeny, to give layering a steep northeasterly dip. Using the stratigraphic nomenclature of McCallum *et al.* (1980), as modified by Zientek *et al.* (1985), the complex (Figs. 1, 2) consists of: (1) a Basal series, which is as much as 240 m thick and consists of bronzite-rich cumulates, with minor segregations of non-cumulates, (2) an Ultramafic series, which averages about 1000 m thick, and consists of cumulates of olivine, chromite, and bronzite, and (3) a Banded series, which totals about 4500 m in thickness, and is composed of cumulates of plagioclase, augite, bronzite, and olivine. ("Bronzite" rather than the preferred "enstatite" has been retained here in deference to long-standing Stillwater tradition.) The Middle Banded series is anomalously rich in plagioclase, containing an estimated 82 vol.% plagioclase over its 1500-m thickness (McCallum *et al.* 1980). AN I and AN II occur at the base and top, respectively, of the Middle Banded series; both layers are of variable thickness along strike, with maximum thicknesses of about 370 m for AN I and 630 m for AN II.

Within AN I and AN II, plagioclase occurs as discrete grains, as glomerocrysts, and as domains of interlocking grains that may be tens of centimeters across. A significant proportion of the plagioclase is notably larger than is typical of plagioclase grains in multiphase cumulates of the Lower, Middle, and Upper Banded series. However, with the exception of a 5- to 15-m thick zone of finer-grained, pyroxene-poor anorthosite at the top of AN II, there is little discernable variation in grain size with stratigraphic position within AN I and AN II. Although the average normative An contents of AN I and AN II are each near 78 mol.% (Czamanske & Scheidle 1985), plagioclase grains throughout the Middle Banded series are zoned by as much as 20 mol.% An; this zoning is complex, and grains with variable, normal, reverse, and oscillatory zoning patterns occur in single thin sections (Scheidle 1983, Czamanske & Scheidle 1985, Meurer 1995, Meurer & Boudreau 1996). There is no evidence of systematic change in anorthite content with stratigraphic position in the Middle Banded series (Raedeke & McCallum 1980, Czamanske & Scheidle 1985, Meurer 1995, Meurer & Boudreau 1996), and the compositional range of average plagioclase for individual samples is comparable in AN I, AN II, and the contiguous cumulates (An_{72} to An_{80}). Using hundreds of electron-microprobe spot analyses, Scheidle (1983, Czamanske & Scheidle 1985) showed that: (1) plagioclase grains with symmetrical patterns of zoning are rare, (2) there is typically no grain-to-grain correspondence in zoning pattern within a given sample, but most samples contain grains in which An content varies by >10 mol.%, and (3) it is difficult to delineate those parts of grains that may or must represent post-cumulus overgrowth.

Clinopyroxene and inverted pigeonite are the principal mafic phases in the anorthosites; they occur predominantly as coarse-grained oikocrysts that compose from several to 25 modal % of the rock. Proportions of plagioclase and pyroxene may vary only modestly over large areas, but a notable textural variant

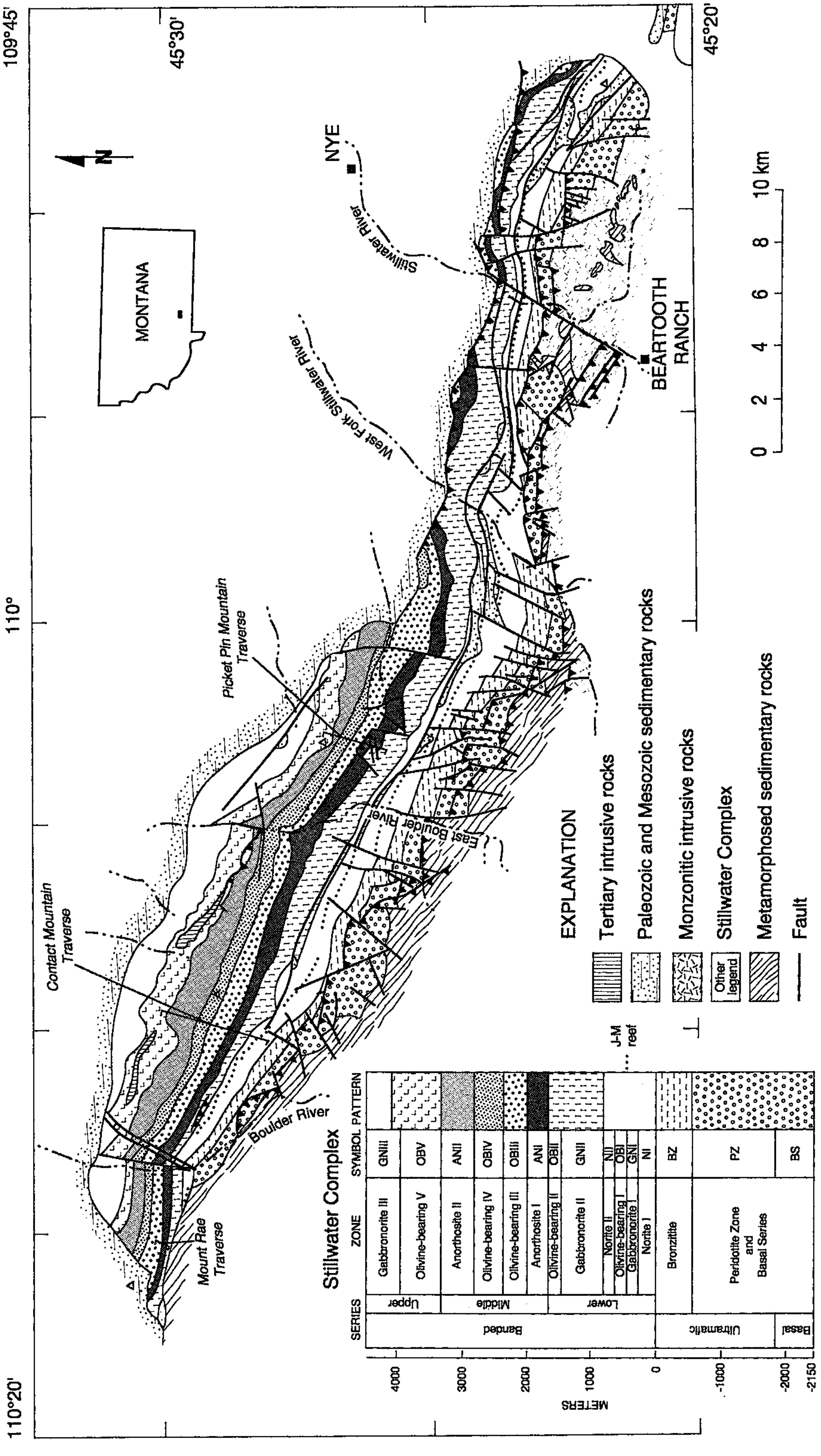


FIG. 1. Geological map of the Stillwater Complex, slightly modified from Zientek (1993), after revision from Segerstrom & Carlson (1982).

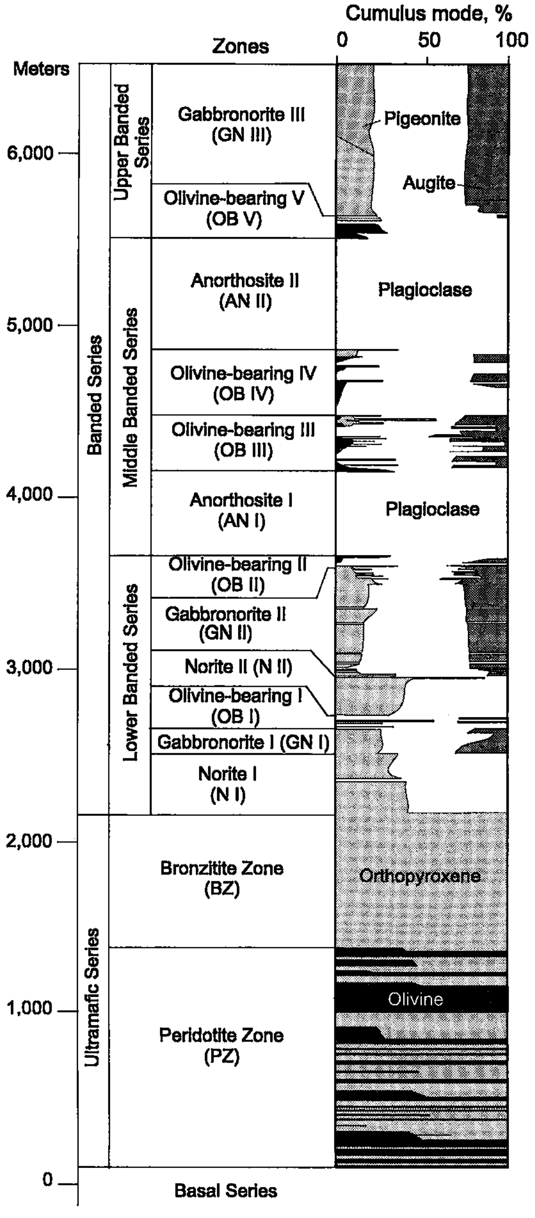


FIG. 2. Stratigraphic column for the Stillwater Complex. Courtesy of Alan Boudreau, modified from Boudreau & McCallum (1989).

is the development of a "mottled" aspect, with parts of the rock rich in oikocrystic pyroxene and others composed almost entirely of plagioclase. These distinctive domains range from hand-specimen scale (Fig. 3) to outcrop surfaces in which the pyroxene- and plagioclase-rich domains may be 20 cm across (*e.g.*, Czamanske & Scheidle 1985, their Fig. 5). Plagioclase textures within the pyroxene-rich and pyroxene-poor domains are generally quite different (*e.g.*, Fig. 4), but plagioclase aggregates with comparable intergrowth are common in each domain (*e.g.*, Figs. 4, 5, and 6). Minor, intercumulus phases, including quartz, apatite, titanite, monazite, ilmenite, and sulfide minerals, are more common in the pyroxene-poor domains. Olivine is a rare intercumulus phase at some locations in AN II.

Observations on the field relations, mineralogy, textures, and origin of AN I and AN II are presented by Hess (1960), McCallum *et al.* (1980), Salpas *et al.* (1983), Scheidle (1983), Boudreau & McCallum (1985), Czamanske & Scheidle (1985), Foose (1985), Czamanske & Bohlen (1990), Haskin & Salpas (1992), Loferski & Arculus (1993), and Loferski *et al.* (1994); Meurer (1995) and Meurer & Boudreau (1996) present comparable information for Olivine-bearing zones III and IV (OB III and OB IV), which lie between AN I and AN II (Fig. 2). These contributions are each more or less relevant to what may be considered the principal enigmas in the petrogenesis of the Stillwater anorthosites: (1) the locus of plagioclase precipitation and accumulation, with associated models for the "origin" of the anorthosite zones, and (2) the *in situ* evolution of the anorthosite zones subsequent to accumulation of cumulus plagioclase.

METHODS

Suites of large (typically ≥2 kg) samples were collected along traverses across AN I and AN II at Contact Mountain and Picket Pin Mountain, and across AN I near Mount Rae at the faulted, west end of the complex (Fig. 1). The true stratigraphic thicknesses represented by these traverses range from ~150 m for AN I at Mount Rae to ~630 m for AN II at Contact Mountain. Additional samples of cumulates above and below the anorthosite zones brought the total to 83 samples. Critical to our interpretation are samples 83CML10A and B and 83CML18A and B, collected 194.1 m and 16.1 m, respectively, above the base of AN I at Contact Mountain; they represent pyroxene-poor (A) and pyroxene-rich (B) domains in areas where it was possible to collect 2 kg samples of each domain.

A reference slab was cut from each sample, weathered surfaces were removed, and the remainder crushed and carefully split for whole-rock analysis and plagioclase separation. The latter split was ground and then sized by wet sieving to obtain the 150–200-mesh fraction. Plagioclase separates presumed to be free of other phases and alteration were obtained by using heavy liquids (specific gravity 2.67 and 2.77), slow passage through a Frantz magnetic separator set at 7° forward and 5° side tilts, and hand picking. Whole-rock samples were analyzed for their major-element contents by X-ray-fluorescence

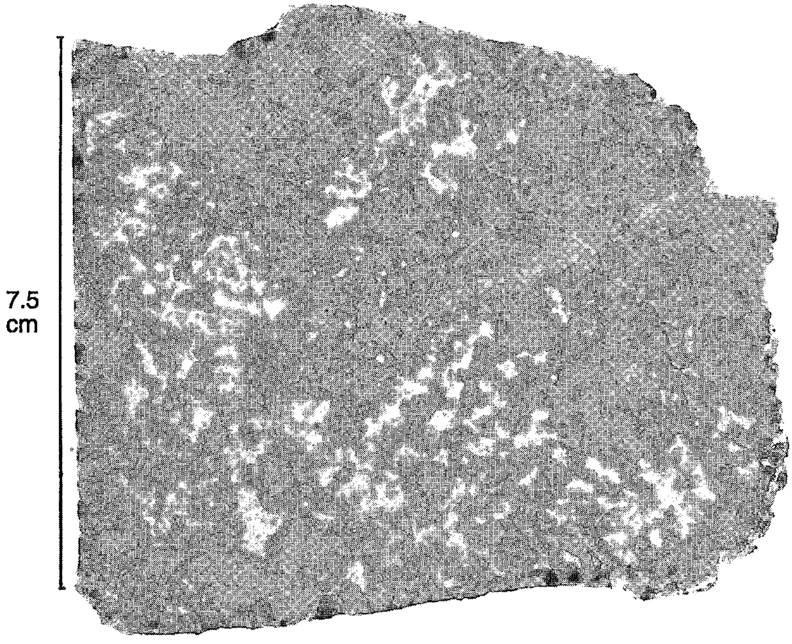


FIG. 3. Polished surface of sample 81CMC7 from AN II at Contact Mountain showing mottled aspect created by domains composed of nearly monomineralic plagioclase and those enriched in oikocrystic pyroxene. The composition of this sample is given in Table 1.

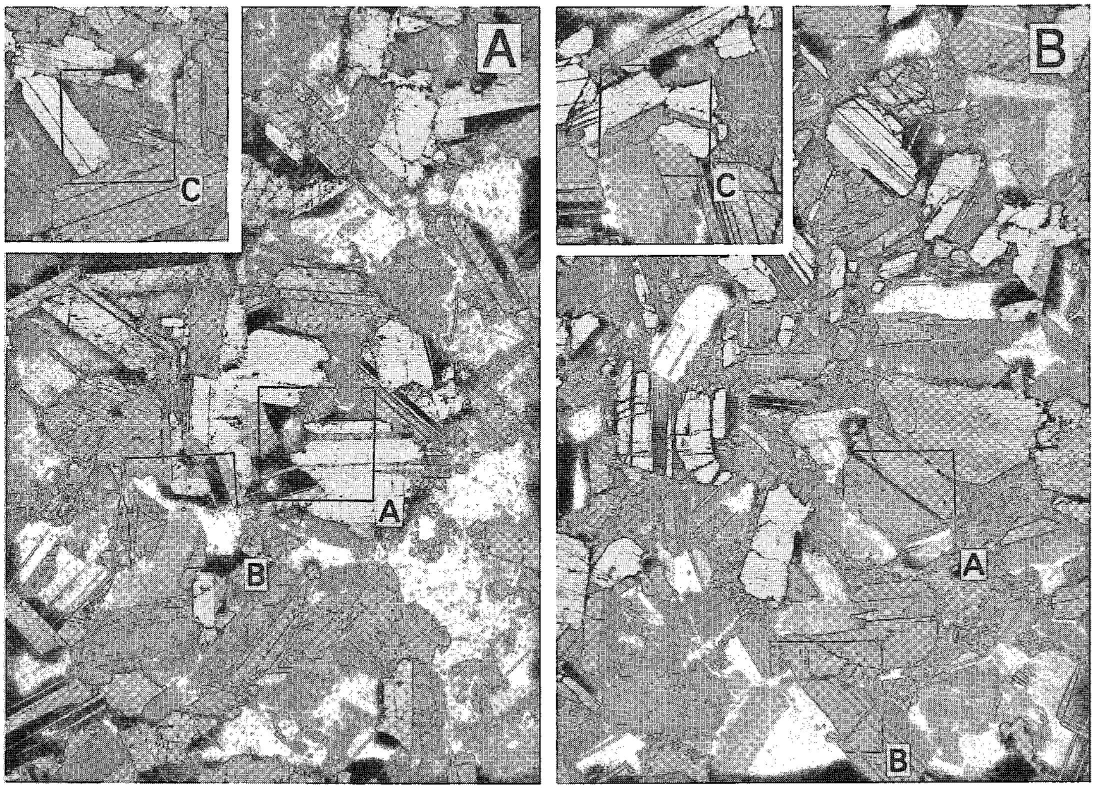
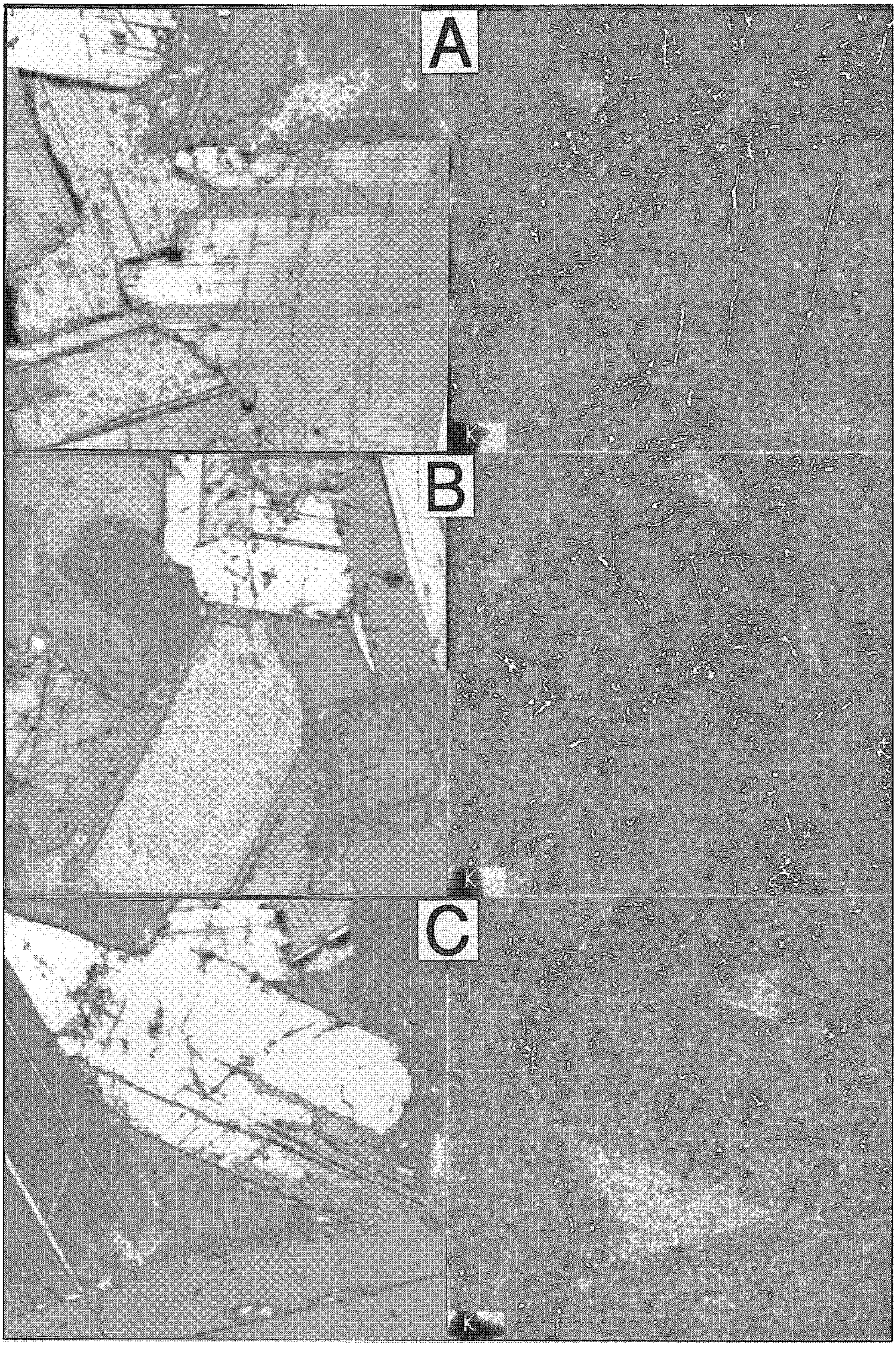
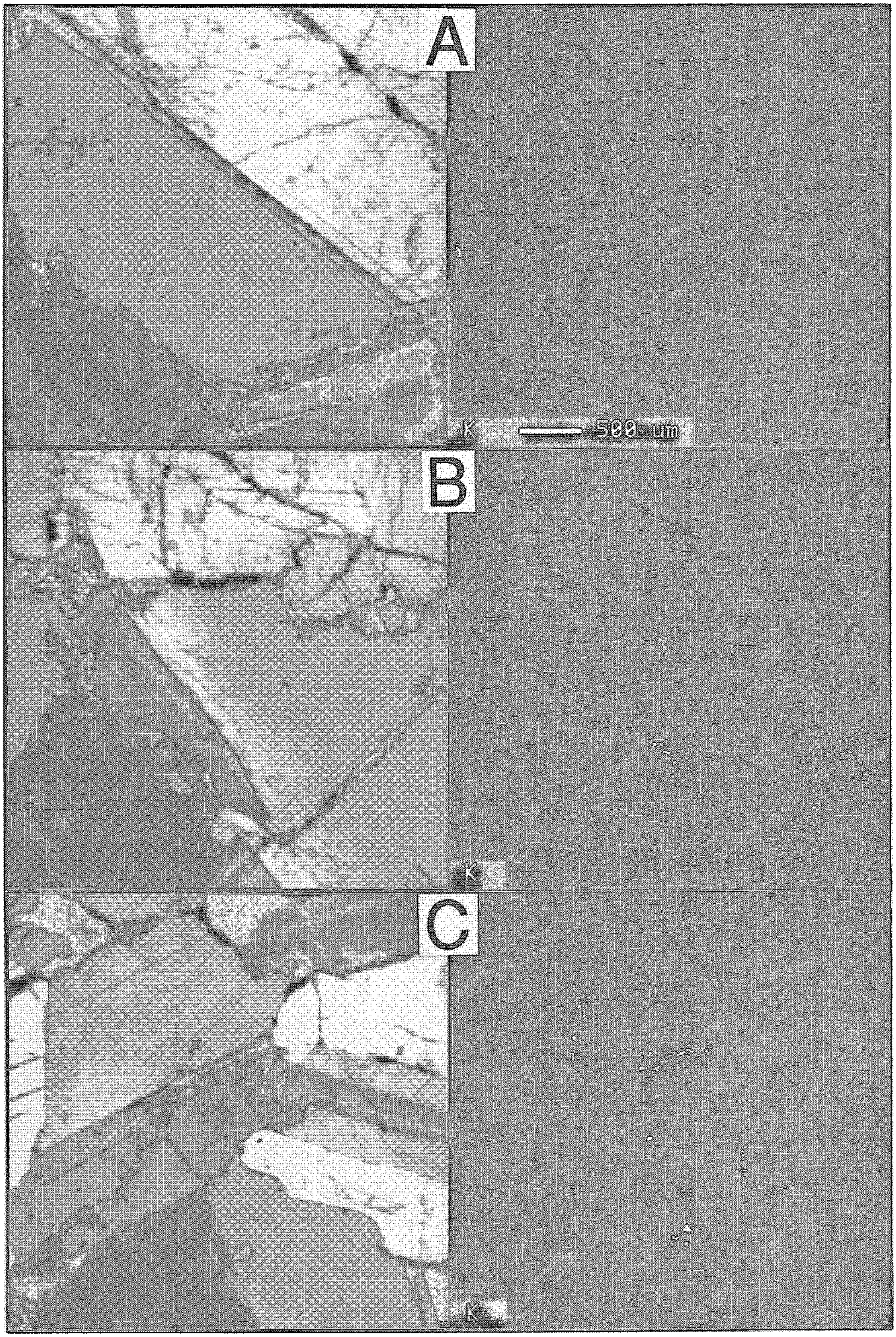


FIG. 4. Photomicrographs of thin sections representing pyroxene-poor sample 83CML10A (A) and pyroxene-rich sample 83CML10B (B). Note that textures of the plagioclase intergrowth are comparable in the two photos, but that in (B), many subhedral grains of plagioclase are partly or totally surrounded by oikocrystic pyroxene. Fields of photos: approximately 15.5 × 22 mm.


A
K
B
K
C
K


A
K
500 um
B
K
C
K

(from page 564)

FIG. 5. Photomicrographs and comparably scaled K-concentration maps (electron microprobe) for three areas of identical size in a thin section of sample 83CML10A. See Figure 4A for perspectives of areas A, B, and C; area C is out of field of view and shown as inset. Note in the K-concentration maps that the darker, triangular areas in (C) represent interstitial quartz, as does the thin sliver in the right center of (B). Areas are approximately 3.5 × 3.5 mm.

(from page 565)

FIG. 6. Photomicrographs and comparably scaled K-concentration maps (electron microprobe) for three areas of identical size in a thin section of sample 83CML10B. See Figure 4B for perspectives of areas A, B, and C; area C is out of field of view and shown as inset. In comparison with Figure 5, note the small extent of K-enrichment (bright areas) shown in the three K-concentration maps. Areas are approximately 3.5 × 3.5 mm.

spectrometry. The plagioclase separates and selected whole-rock samples were analyzed for Ba, Ca, Cu, Fe, K, Mg, Mn, Na, Ni, Sr, Ti, and Zn by inductively coupled plasma – atomic emission spectroscopy (ICP–AES) and for Co, Cr, Hf, Sc, Th, and the rare-earth elements (*REE*) by instrumental neutron activation. Instrument calibration was verified using the international standard reference materials AN–G,

TABLE 1. ANALYTICAL DATA FOR WHOLE-ROCKS AND PLAGIOCLASE SEPARATES FROM AN I, AN II, AND CONTIGUOUS CUMULATES, STILLWATER COMPLEX

		Ca, wt %	Na	Fe	Mg	Ca/(Ca+Na)	Mg/(Mg+Fe)	Ba, ppm	Co	Cr	K
Concentrations in whole rock											
81CMC7	AN II	10.9	1.66	2.34	1.65	0.79	0.62	34.5	16.4	59	640
83CML10A	AN I	11.5	1.79	0.93	0.13	0.79	0.24	72	1.90	0.6	1970
83CML10B	AN I	11.0	1.38	2.24	1.83	0.82	0.65	28.3	16.4	39.7	540
83CML17	AN I	11.0	1.80	1.93	1.10	0.78	0.57	38.8	11.9	12.3	760
83CML18A	AN I	11.1	2.04	1.15	0.38	0.76	0.43	50.2	4.08	2.4	1290
83CML18B	AN I	10.4	1.48	2.42	1.98	0.80	0.65	29.2	17.1	22.9	620
Concentrations in plagioclase											
81CMC7	AN II	11.3	2.07	0.362	0.052	0.76	0.25	41.3	0.92	0.6	730
83CML10A	AN I	10.8	1.93	0.38	0.042	0.76	0.20	60.7	0.51	0.7	1560
83CML10B	AN I	11.4	1.66	0.364	0.059	0.80	0.27	33.7	1.04	0.9	580
83CML17	AN I	11.2	2.00	0.353	0.039	0.76	0.20	39.8	0.65	0.5	1480
83CML18A	AN I	11.2	1.97	0.391	0.038	0.77	0.18	49.5	0.59	<1	1160
83CML18B	AN I	11.5	1.82	0.395	0.060	0.78	0.26	35.2	1.03	0.6	750
Concentrations in whole rock											
82DCM15	OB V pC	10.9	1.89	1.22	0.70	0.77	0.57	54.3	-	-	1950
82DCM10	OB V pC	11.4	1.81	1.24	0.75	0.78	0.58	40.7	10.5	1.5	970
82DCM20	OB III paC	10.8	1.80	1.96	1.43	0.77	0.63	40.1	12.8	63.7	830
81CMC25	OB III poC	10.4	1.46	2.37	2.12	0.80	0.67	37.6	21.5	12.5	730
Concentrations in plagioclase											
82DCM15	OB V pC	10.5	2.13	0.364	0.056	0.74	0.26	51	-	-	1350
82DCM10	OB V pC	10.7	2.06	0.369	0.055	0.75	0.26	39.2	0.86	<0.4	780
82DCM20	OB III paC	11.1	2.04	0.396	0.048	0.76	0.22	43.3	0.60	0.3	940
81CMC25	OB III poC	11.3	2.16	0.376	0.069	0.75	0.30	47	1.79	0.4	950

Sample locations relative to base of AN I at Contact Mountain (corrected for dip): 83CML18, 16.1 m above; 83CML17, 121.2 m above; 83CML10, 194.1 m above; 81CMC25, 379.5 m above (~14 m above upper contact); 82DCM20, 480.8 m above (~115 m above upper contact).

Sample locations relative to base of AN II at Contact Mountain (corrected for dip): 81CMC7, 239 m above; 82DCM10, 651.1 m above (~22 m above upper contact); 82DCM15, 710 m above (~81 m above upper contact).

BHVO, DNC–1, GSD–2, GSD–4, BCR–1, and AVG–1; all measured values were found to be within 5% of recommended values. All analyses were done at the U.S. Geological Survey (Reston, Virginia and Menlo Park, California), and electron-microprobe maps of elemental distribution were produced on the JEOL 8900 at Menlo Park. These maps of ~3.5 × 3.5 mm areas of polished thin sections were each made in 7 3/4 hours with a 5-μm beam diameter for the elements K, Na, Ca, and Al.

Note that the effect of multiphase inclusions in Stillwater plagioclase (Loferski & Arculus 1993) on measured trace-element contents has been calculated to be insignificant and is confirmed negligible by the elemental correlations documented.

Results

Major-element composition of plagioclase

Tables 1 and 2 show that Ca/(Ca + Na) values for the plagioclase separates from AN I, AN II, and the contiguous cumulates range between 0.67 and 0.80. Table 1 shows that plagioclase separates from the pyroxene-poor, "A" domains are slightly less calcic and more sodic and potassic than those from the pyroxene-rich domains of mottled anorthosite. [Because Scheidle (1983) concluded that plagioclase spot analyses yielding values of Ca/(Ca + Na) less than ~0.72 probably reflect albitization, the few plagioclase separates having Ca/(Ca + Na) < 0.72 were excluded in calculating the average Ca/(Ca + Na) values reported in Table 2.]

There was no indication from Scheidle's work of extensive, regular overgrowth by Na- and K-rich plagioclase, and no indication that bulk plagioclase from pyroxene-poor domains of mottled anorthosite may contain more than two times as much K as plagioclase from pyroxene-rich domains (*e.g.*, 1560 *versus* 580 ppm, Table 1). Her data show a tendency for Or content to follow Ab content, but in the range An_{72} to An_{78}, An and Or contents are poorly correlated; *e.g.*, Or contents in An_{75} plagioclase range from 0.38 to 1.76 mol.% (~550 to 2500 ppm K). In general, Or

TABLE 1 (continued). ANALYTICAL DATA FOR WHOLE-ROCKS AND PLAGIOCLASE SEPARATES FROM AN I, AN II, AND CONTIGUOUS CUMULATES, STILLWATER COMPLEX

	Mn	Ni	Sc	Sr	Th	Ti	Zn	La	Ce	Sm	Eu	Yb	(La/Sm)N
Concentrations in whole rock													
81CMC7	396	32	10.7	163	0.09	680	22.9	0.94	1.89	0.272	0.322	0.35	1.90
83CML10A	144	5	1.52	163	0.46	530	8.7	2.28	4.33	0.658	0.377	0.46	1.90
83CML10B	347	56	10.1	148	0.12	500	22.0	0.66	1.25	0.224	0.255	0.26	1.62
83CML17	296	38	6.94	155	0.15	790	21.5	1.12	2.15	0.357	0.300	0.33	1.72
83CML18A	197	15	3.61	182	0.29	520	15.0	1.70	3.01	0.478	0.350	0.36	1.95
83CML18B	385	65	9.45	150	0.08	530	24.8	0.71	1.34	0.231	0.260	0.27	1.69
Concentrations in plagioclase													
81CMC7	31.8	-	0.264	186	0.049	190	12.0	0.95	1.67	0.120	0.390	<0.10	4.34
83CML10A	42.5	-	0.148	165	0.073	150	10.2	1.67	2.60	0.300	0.376	0.086	3.05
83CML10B	31.7	-	0.194	172	<0.08	160	7.0	0.76	1.14	0.097	0.302	<0.07	4.30
83CML17	31.3	-	0.163	176	0.071	150	6.2	1.18	1.90	0.165	0.320	0.033	3.92
83CML18A	44.7	-	0.184	181	0.067	170	8.9	1.35	2.46	0.242	0.361	0.07	3.06
83CML18B	34.8	-	0.214	174	<0.08	160	8.3	0.75	1.17	0.113	0.295	<0.07	3.64
Concentrations in whole rock													
82DCM15	180	-	-	219	-	540	14.2	-	-	-	-	-	-
82DCM10	163	175	2.01	197	0.13	430	14.4	1.03	1.50	0.233	0.284	0.16	2.42
82DCM20	302	54	9.62	156	0.17	990	19.5	0.75	3.30	0.480	0.320	0.46	0.86
81CMC25	341	125	6.78	153	0.16	780	24.1	1.37	2.50	0.344	0.320	0.41	2.18
Concentrations in plagioclase													
82DCM15	30.4	-	-	198	-	220	11.4	-	-	-	-	-	-
82DCM10	27.5	-	0.086	188	<0.03	220	11.2	1.03	1.54	0.128	0.271	<0.2	4.41
82DCM20	33.9	-	0.184	174	0.06	200	9.9	1.21	2.05	0.161	0.316	<0.1	4.12
81CMC25	32.8	-	0.173	184	<0.06	220	13.6	1.34	2.20	0.210	0.357	<0.1	3.50

TABLE 2. AVERAGES AND RANGES IN THE TRACE-ELEMENT CONTENTS OF PLAGIOCLASE IN SPECIFIC ZONES FROM AN I, AN II, AND CONTIGUOUS CUMULATES, STILLWATER COMPLEX

	OB II (7)*	AN I, CM** (20)	AN I, PP (11)	AN I, MR (6)	OB III+IV (10)	AN II, CM (15)	AN II, PP (8)	OB V (3)
Ca/(Ca+Na)$^+$	0.769 (0.72-0.80)	0.763 (0.67-0.80)	0.758 (0.67-0.78)	0.732 (0.69-0.74)	0.765 (0.75-0.79)	0.748 (0.72-0.77)	0.761 (0.74-0.78)	0.750 (0.74-0.76)
Mg/(Mg+Fe)	0.45 (0.30-0.60)	0.30 (0.18-0.47)	0.41 (0.31-0.51)	0.35 (0.26-0.43)	0.37 (0.22-0.46)	0.34 (0.23-0.47)	0.24 (0.16-0.37)	0.26 (0.26-0.27)
Ba, ppm	35.7 (31.9-47.4)	42.4^{++} (31.0-60.7)	42.8 (30.9-60.2)	44.9 (37.9-53.6)	45.8 (39.7-59.3)	43.9 (32.7-64.6)	39.5 (28.3-48.9)	40.2 (30.4-51.0)
Co	1.67^{++} (0.84-5.13)	1.00 (0.51-1.47)	1.27 (0.81-2.27)	1.28 (0.65-1.66)	1.37 (0.60-2.41)	1.27^{++} (0.76-9.34)	0.83 (0.55-1.33)	0.66 (0.45-0.86)
Fe	3900 (3240-4530)	3800^{++} (3400-4310)	3790 (3430-4180)	3760 (3530-3930)	4150 (3600-5100)	4010 (3480-4780)	3900 (3720-4120)	3680 (3640-3700)
K	950 (530-2220)	820^{++} (530-1560)	1890^{++} (690-5260)	710 (570-920)	860 (710-990)	820 (630-1320)	770 (540-1050)	910 (600-1350)
Mg	1480 (770-2310)	740 (380-1500)	1150 (750-1600)	920 (540-1270)	1090 (480-1890)	920 (440-1380)	560 (310-1030)	570 (550-610)
Mn	35.8 (27.9-43.2)	36.6^{++} (30.4-47.3)	36.7 (29.8-43.9)	40.9 (34.0-59.6)	36.5 (30.7-43.6)	39.8 (31.6-47.5)	34.0 (30.5-36.8)	30.0 (27.5-32.0)
Sc	0.194^{++} (0.133-0.239)	0.240 (0.148-0.378)	0.214 (0.174-0.244)	0.398 (0.255-0.469)	0.196 (0.149-0.262)	0.304^{++} (0.213-0.409)	0.182 (0.086-0.233)	0.094 (0.086-0.101)
Sr	171 (160-191)	171 (158-181)	183 (169-203)	181 (178-184)	182 (172-196)	185 (173-194)	183 (176-189)	194 (188-198)
Ti	166 (140-220)	164 (150-180)	165 (150-180)	177 (170-180)	203 (180-230)	188 (180-200)	179 (150-200)	213 (200-220)
Zn	8.0 (5.9-12)	12.7 (6.2-31.5)	10.3 (6.4-15.6)	9.6 (7.4-11.8)	9.0 (5.2-13.6)	16.4 (9.7-23.2)	9.0 (5.5-14.2)	9.4 (5.7-11.4)
La	0.853 (0.63-1.11)	0.911 (0.52-1.67)	0.845 (0.50-1.21)	0.975 (0.66-1.39)	1.147 (0.91-1.61)	0.929 (0.62-1.42)	0.960 (0.52-1.44)	0.835 (0.64-1.03)
Ce	1.189 (0.87-1.85)	1.524 (0.82-2.60)	1.335 (0.71-1.80)	1.522 (1.07-2.25)	1.777 (1.27-2.70)	1.489 (0.98-2.45)	1.608 (0.79-2.42)	1.335 (1.13-1.54)
Sm	0.089 (0.060-0.130)	0.139 (0.069-0.300)	0.126 (0.068-0.187)	0.138 (0.089-0.228)	0.132 (0.080-0.210)	0.124 (0.084-0.200)	0.132 (0.067-0.210)	0.112 (0.096-0.128)
Eu	0.254 (0.212-0.320)	0.308 (0.246-0.378)	0.276 (0.199-0.326)	0.304 (0.267-0.349)	0.306 (0.255-0.357)	0.357 (0.292-0.463)	0.323 (0.241-0.392)	0.264 (0.256-0.271)
$(La/Sm)_N$	5.25	3.59	3.68	3.87	4.77	4.12	3.99	4.09

*Number of values in average. For the elements Co, Sc, La, Ce, Sm, and Eu (determined by INAA) only 9 values are averaged for OB III + IV and only 2 values for OB II.

**To be concise: CM, Contact Mountain; PP, Picket Pin Mountain; MR, Mount Rae.

$^+$Averages exclude values < 0.72. Ratios in atomic proportions, except $(La/Sm)_N$.

$^{++}$Average and range excludes high values from one, common sample.

contents approaching 1 mol.% correlate with plagioclase compositions in the range An_{71-74}. She did find that euhedral grains trapped in pyroxene commonly are of more restricted composition, and contain 0.39 to 0.60 mol.% Or.

In search of an explanation for the unanticipated variation in the K contents of bulk plagioclase, we made automated, step traverses of four of the grains examined earlier by Scheidle. On the basis of these traverses, which included more than 560 analyses across grains at ~15 μm steps, we confirmed that Or content may vary by a factor of two as An content varies between 70 and 80 mol.%, but concluded that there is no possibility that Scheidle's study failed to recognize zones of significant K-enrichment within plagioclase grains. Moreover, diffusion of K in calcic plagioclase is presumed to be slow, and no mechanism of crystal fractionation, melt migration, or late-stage alteration could be envisioned whereby the *bulk* plagioclase separates from pyroxene-poor samples 83CML10A and 83CML18A could be enriched in K by factors of 2.7 and 1.5, respectively, relative to plagioclase from adjacent pyroxene-rich samples 83CML10B and 83CML18B (Table 1).

Ultimately, we made maps of K concentration for polished thin sections of closely spaced samples 83PPL4 and 83PPL5 from the Picket Pin Mountain traverse of AN I, for which the plagioclase separates exhibited nearly the extremes of K content (690 and 3650 ppm K, respectively). Sample 83PPL5 appears notably more altered in thin section, and K-concentration maps clearly show this cloudy, pervasive alteration to be associated with development of a fine-grained, K-rich phase (sericite?) along fractures and grain margins.

The apparent influence of modal mineralogy

Study of thin sections and comparable maps of K distribution for plagioclase aggregates in samples 83CML10A and B and 83CML18A and B (Figs. 4, 5, and 6) show that plagioclase in the pyroxene-poor samples or domains has undergone more fracturing and alteration, with attendant bulk-enrichment in K, than has plagioclase in pyroxene-rich samples or domains, although textures of much plagioclase within the two samples appear quite comparable (*e.g.*, Figs. 4A, 5A, B, C *versus* 4B, 6A, B, C). The three areas in Figures 4A and B chosen for "mapping" were selected at random for comparison of K distribution in plagioclase aggregates of comparable textural intergrowth. Because Table 1 shows that, along with K, plagioclase separates from the pyroxene-poor domains are significantly enriched in Ba and the light rare-earth elements (*LREE*), the conclusion seems inescapable that these elements also were concentrated in fractured plagioclase during the alteration event.

The data of Table 1 clearly indicate plagioclase to be the principal host of Ba, K, and Sr, and a major host of the *LREE*. Table 1 and Figure 7 reveal that La and Ce concentrations average slightly more than twice as high in plagioclase from pyroxene-poor samples as in that from the pyroxene-rich samples; the disparity in La and Ce concentrations is even greater for the whole-rock sample pairs. The ratio $(La/Sm)_N$ is in many cases more than twice as high in the plagioclase separates as in the whole-rock samples, but is lower in plagioclase from the pyroxene-poor samples than that from the pyroxene-rich samples. The fact that the positive Eu anomaly is distinctly smaller in the pyroxene-poor samples and bulk plagioclase separates prepared from them supports a thesis of *LREE* enrichment during alteration, as the Eu^{2+}/Eu^{3+} ratio would be expected to be lower in a hydrothermal fluid than during plagioclase crystallization. The alteration appears to have increased Mn and Zn contents in "A" plagioclase, despite the fact that contents of these elements are lower in the "A" whole-rock samples. The pyroxene-poor, "A" samples are also substantially enriched in Hf and Th, most of which clearly is not contained in plagioclase. Contents of Mg, Co, and Sc are lower in "A" than in "B" plagioclase, but not by nearly so much as for the "A" and "B" whole-rock samples.

Whereas the main purpose of Table 1 is to highlight the whole-rock and plagioclase-separate data for samples 83CML10A and B and 83CML18A and B, limited other data are shown for comparison. Note that sample 81CMC7, shown in Figure 3, is compositionally most similar to 83CML10B and 83CML18B, even though it contains pyroxene-poor domains of

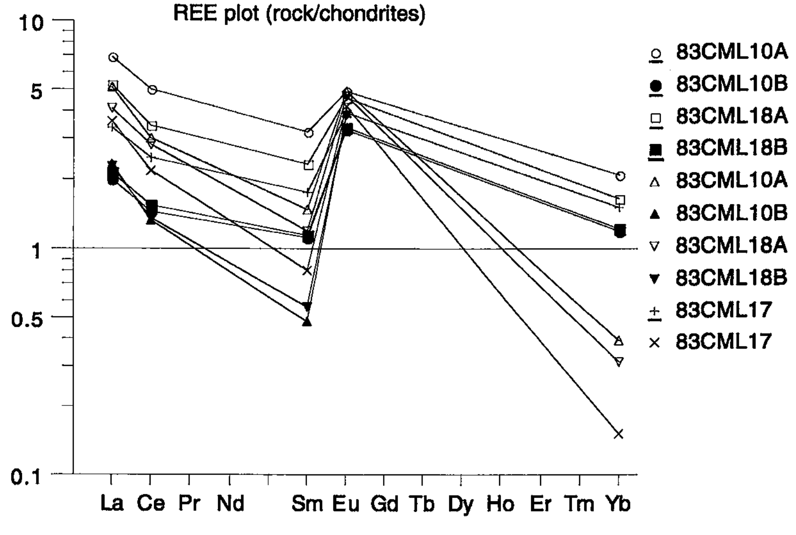


FIG. 7. Plot of chondrite-normalized concentrations of the *REE* for whole-rock samples and plagioclase separates. Symbols underlined in the legend represent whole-rock data. Note that the positive Eu anomaly is significantly less marked for the plagioclase separates from the trace-element enriched, pyroxene-poor samples, and that there is substantial overall *REE* enrichment in these samples. For comparison, data for a sample of relatively homogeneous Contact Mountain anorthosite (83CML17) are plotted, along with data for samples 83CML10A and B and 83CML18A and B.

small scale. Data for Cu and Hf are not shown in Table 1 because their contents in plagioclase separates are commonly below limits of detection. For the whole-rock sample pairs, these elements follow Ni and Th, respectively (all ppm): 83CML10A: Cu, 6, Hf, 0.51, 83CML18A: Cu, 17, Hf, 0.32, 83CML10B: Cu, 24, Hf, 0.11; and 83CML18B: Cu, 36, Hf, 0.09. Consideration of the entire suite of elements shows much compositional similarity between the whole-rock splits and plagioclase separates prepared from the pyroxene-rich samples, 83CML10B and 83CML10B; however, sample 83CML10A contains significantly less pyroxene than sample 83CML18A.

Nature of the alteration

The alteration we document has been termed "cryptic" to emphasize that it is neither conspicuous nor revealed by LOI determinations for whole-rock samples. For our entire suite of anorthosite samples, values of LOI range from 0.22 to 2.69 wt%. For our two whole-rock sample pairs, determinations of LOI (wt.%) and K (ppm) are, respectively: 83CML10A, 0.72 and 1970; 83CML10B, 0.92 and 540; 83CML18A, 1.26 and 1290; and 83CML18B, 1.28 and 620.

The alteration assemblage in the samples of Stillwater anorthosite includes sericite(?), blue-birefringent chlorite, and minor epidote. Alteration of the lesser amounts of pyroxene in the pyroxene-poor "A" samples is more advanced than that in the "B" samples, in which pyroxene is more abundant. Data for the sample pairs show whole-rock values of LOI to have no correlation with the greater sericite(?) and trace-element contents found in more fractured plagioclase of the "A" samples. Rather, the marginally higher values of LOI measured for the "B" samples would appear to relate to lesser alteration of more abundant pyroxene.

Correlations among trace elements

Correlations among trace-element concentrations in plagioclase are shown in Figure 8. Particularly striking are the main correlation trends among Ba, K, La, and Eu (Figs. 8A, B, C, D) and the unique relations among these elements in plagioclase from AN I at Picket Pin Mountain. The data of Table 1 show that the plagioclase separates from samples 83CML10A and B and 83CML18A and B fall within each main correlation trend. Several pairs of elements, including Zn–Ba and Zn–Co, show a broad positive correlation with extensive overlap for the various traverses, such as that displayed by Mn–Ba (Fig. 8E). Figure 8F clearly shows the Sc-rich composition of plagioclase from AN II at Contact Mountain; reference to Table 2 shows that this plagioclase is also substantially enriched in Co, Mg, and Zn, relative to plagioclase from AN II at Picket Pin. Figure 8F reveals a good correlation between Mg and Sc for plagioclase from AN I and AN II along the Contact Mountain traverse, which does not exist for plagioclase from the Picket Pin traverse of AN I or for plagioclase separated from samples of OB II, III, IV, and V. We strongly suspect that the aberrant Mg–Sc correlation revealed for AN I at Picket Pin Mountain in Figure 8F is not a magmatic feature, but is due to the same process of alteration responsible for the aberrant correlations among K, Ba, and La for samples from this traverse.

Lateral and vertical variation in composition

Table 2 summarizes data for all plagioclase separates and shows that, for many elements, the total observed ranges in concentration for entire traverses of the anorthosite zones are not significantly larger than the differences between the concentrations found in the plagioclase separate from 83CML10A and those in plagioclase separates from samples 83CML10B and 83CML18B.

Plagioclase An contents presented by Raedeke & McCallum (1980), Czamanske & Scheidle (1985), Meurer (1995) and Meurer & Boudreau (1996), and trace-element data for whole rocks and plagioclase separates presented by Steele & Smith (1982) and Salpas *et al.* (1983), have indicated little compositional variation with stratigraphic height in the Middle Banded series. Steele & Smith (1982) analyzed plagioclase from a traverse of the entire Banded series by electron microprobe for Fe, K, Mg, and Na and by ion microprobe for Ba, K, Li, Mg, Na, Sr, and Ti. They found that Na contents increase rather regularly with stratigraphic position in the Lower and Upper Banded series, but are essentially constant in the Middle Banded series, as first noted by Raedeke & McCallum (1980). Similarly, they found that there are no discernible trends in Ba, K, Sr, and Ti contents in the Middle Banded series, in contrast to overall enrichment trends for these elements in plagioclase from the Lower and Upper Banded series. If the data of Table 2 are plotted against stratigraphic height (Fig. 9), they largely support these earlier studies. However, because our data represent three traverses of AN I and two traverses of AN II, such plots are more revealing about possible subtle, lateral variation in the anorthosite zones. To enhance the utility and clarity of Figure 9, (1) data from the Mount Rae traverse of AN I are omitted, (2) the bases of AN I and AN II at Picket Pin Mountain were brought to coincidence with the complete Contact Mountain traverse (McCallum *et al.* 1980), (3) data for OB II, OB III+IV, and OB V were averaged for all five traverses, and (4) because of the stratigraphic hiatus, data for both anorthosite zones are represented by triangles for the Contact Mountain traverse and circles for the Picket Pin Mountain traverse. (Note that because AN I is thinner at Picket

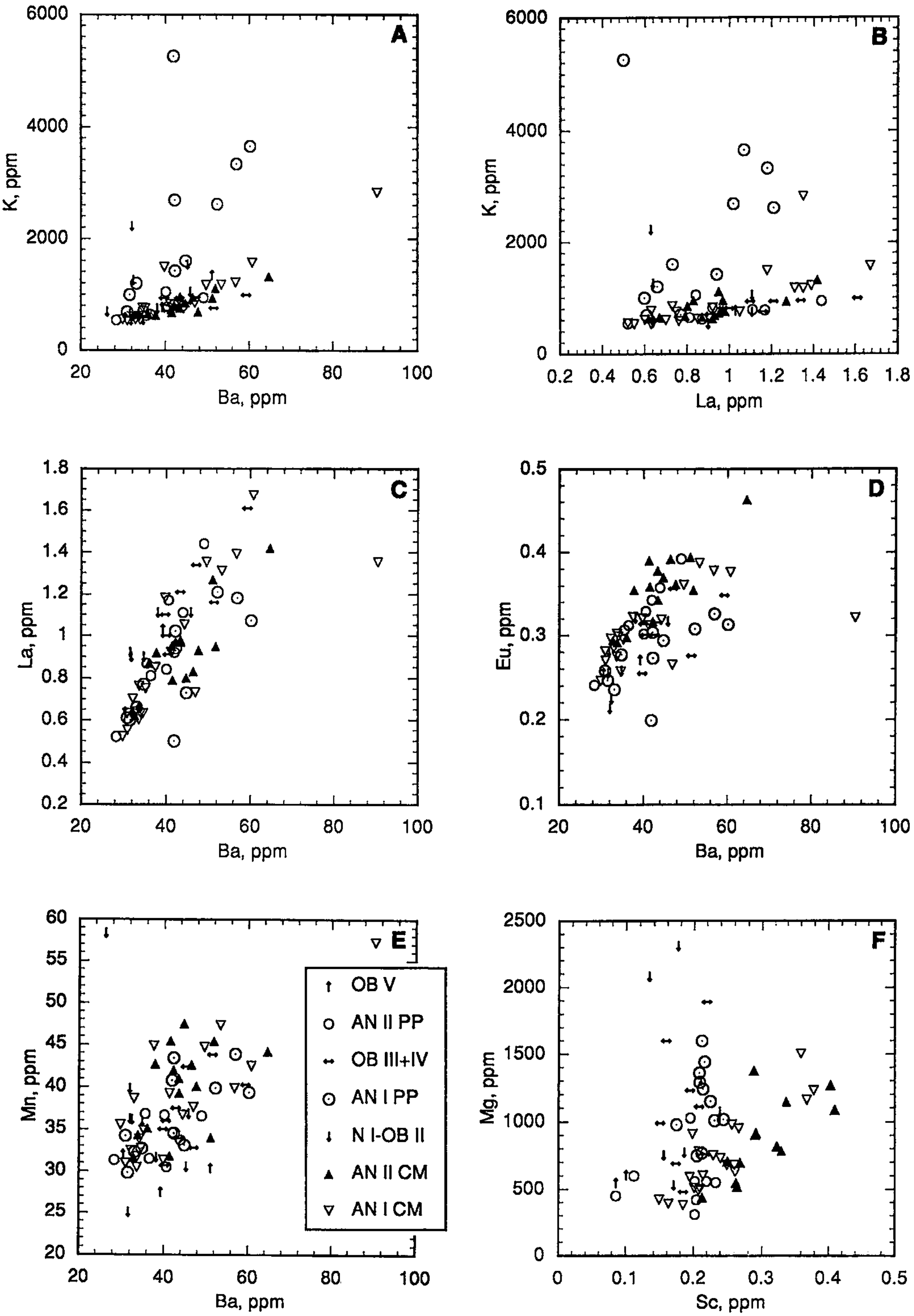


FIG. 8. Correlation plots for selected pairs of elements in plagioclase separates from ANI, ANII, and contiguous cumulates. Abbreviations in the legend box: for stratigraphic units, as in Figure 2; for traverses, CM, Contact Mountain and PP, Picket Pin Mountain.

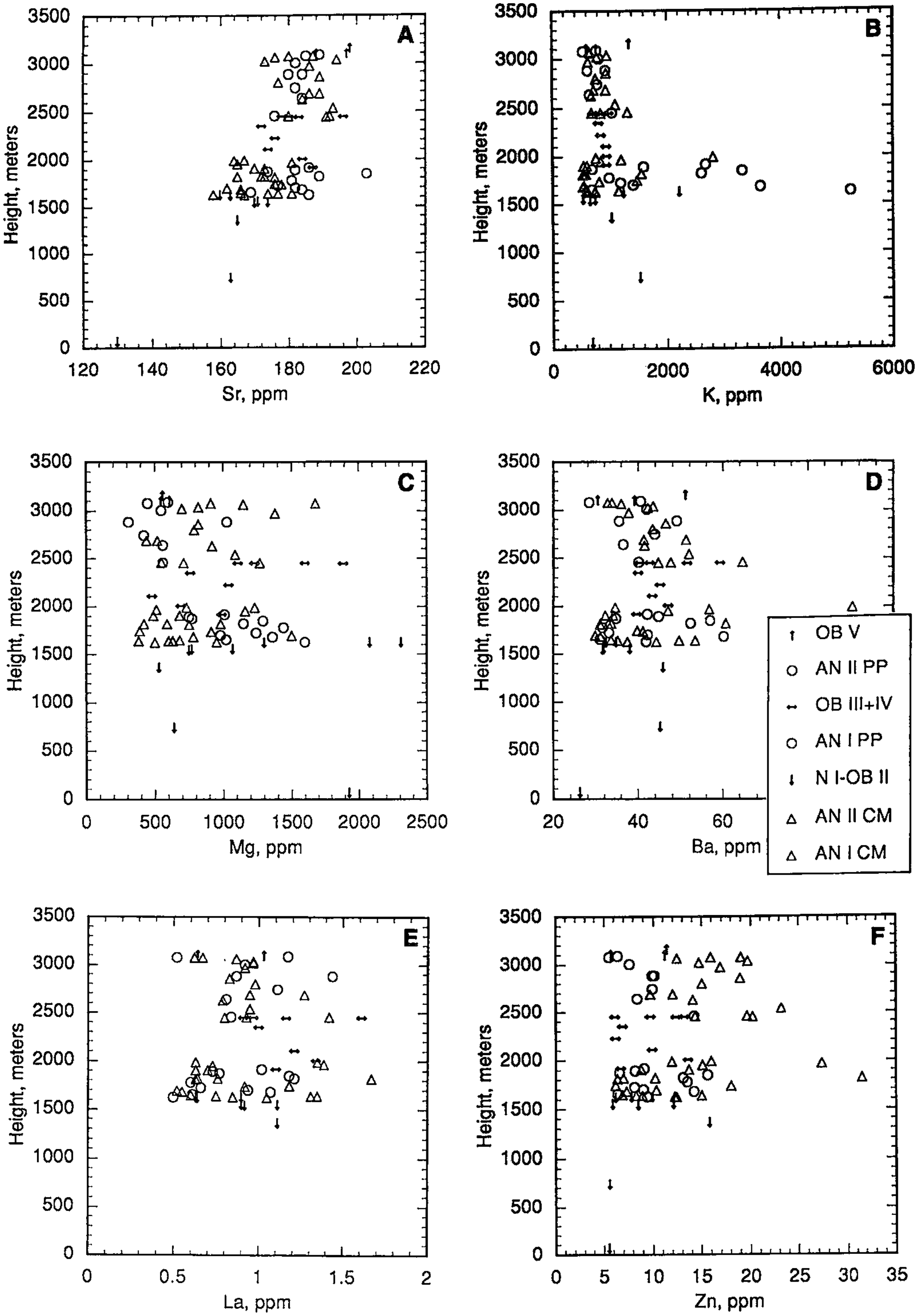


FIG. 9. Concentrations of individual elements in plagioclase separates from ANI, ANII, and contiguous cumulates plotted against stratigraphic height measured from the base of the Banded series on the Contact Mountain traverse (see Fig. 2). Note minor change in symbols from Figure 8.

Pin Mountain, there is one symbol for OB III data that appears to lie within the stratigraphic range of AN I.) Table 2 shows that most trace-element concentrations in plagioclase from AN I at Mount Rae are similar to those for AN I at Contact Mountain.

Strontium contents are atypically low in plagioclase from AN I at Contact Mountain (Fig. 9A, Table 2). With the notable exception of the traverse of AN I at Picket Pin Mountain, K content (Fig. 9B) shows little variation with stratigraphic or lateral position. Iron content (Table 2) is comparably restricted (0.34–0.44 wt.% Fe for all except four plagioclase separates), with the result that a plot of Fe/(Fe + Mg) in plagioclase is virtually indistinguishable in aspect from Figure 9C, in which Mg content is plotted. There is a modest cross-over in average Mg content, with AN II being relatively enriched with respect to AN I on the Contact Mountain traverse and relatively depleted on the Picket Pin traverse. For numerous elements, minimum concentrations appear to increase with stratigraphic position in AN I and decrease in AN II, *e.g.*, Mg, Ba, La, and Zn (Figs. 9C, D, E, F), as well as Co, Mn, and Sc (not shown). For the Contact Mountain traverse of AN II, Ba content appears to decrease with stratigraphic height, as does Zn content for AN II on the Picket Pin traverse. It is curious that none of the 20 plagioclase separates from OB II, III, IV, and V contains as much Mn or Zn as much of the plagioclase from AN I and AN II at Contact Mountain. Of all the elements sought, only Ti may be enriched in plagioclase from OB III, IV, and V, as compared to plagioclase from the anorthosite zones.

DISCUSSION

No information regarding parental magmas or stratigraphic evolution can be extracted from our data set because the total observed ranges in concentration for entire traverses of the two anorthosite zones are little different than the ranges of concentrations found in plagioclase separates from contiguous samples. There appear to be at least two, essentially independent causes of the compositional variability documented in this report.

(1) Some of the subtle, overall compositional distinctions observed for plagioclase from individual suites of samples taken from AN I or AN II at Contact Mountain, Picket Pin Mountain, and Mount Rae are thought to reflect real, local compositional heterogeneity in the two anorthosite zones. Regardless of whether they formed *in situ* or represent emplacement from a lower chamber, such subtle geochemical distinctions between different parts of these units are not surprising.

(2) Some trace-element contents in whole-rock samples and plagioclase separates from the pyroxene-poor domains of mottled anorthosite from AN I have been significantly elevated during fracturing and alteration of plagioclase grains. Correlations among K, Ba, and *LREE* concentrations for our entire set of samples suggest that, to varing degrees, this alteration may have affected much of the thick units of anorthosite. Alteration of plagioclase in AN I at Picket Pin Mountain has produced a discordant correlation trend, presumably because of a dissimilar fluid composition or alteration history.

We speculate that interconnected and relatively brittle, pyroxene-poor domains provided preferred channelways for fluid migration and that solutions were less able to migrate through domains rich in oikocrystic pyroxene. The correlation is not good, but samples containing 0.3 to 4.2 wt.% MgO may contain <1000 ppm K in the whole rock and plagioclase separate, whereas only samples containing <2.5 wt.% MgO may contain as much as 3600 ppm K in the whole rock and plagioclase separate. On the other hand, despite the strong compositional parallels between our two widely separated pairs of samples, we do not exclude the possibility that the modal proportions of pyroxene in samples 83CML10A and B and 83CML18A and B may be of less importance than we have assumed in controlling plagioclase fracturing and fluid access, and that degree of alteration alone is more responsible for our observations.

In contrast to earlier studies, based largely on whole-rock samples of rocks of variable mode from a single traverse or on relatively few electron- or ion-microprobe data points for zoned crystals, our data sets include major- and trace-element analyses for whole rocks and bulk separates of plagioclase from multiple traverses, with substantial electron-microprobe support. We doubt that our conclusions could have been reached on the basis of less information, because this study and those cited earlier indicate that whole-rock and bulk data on the plagioclase for the anorthosites reflect primary crystallization, interaction with magmatic or hydrothermal fluids, and varying degrees of alteration. Not amenable to resolution with this data set is an explanation for the marked enrichment of Hf and Th in the more altered, pyroxene-poor, whole-rock samples 83CML10A and 83 CML18A, although Meurer's (written comm., 1995) recognition of thorian monazite in widely scattered anorthositic rocks may be relevant.

The previous work most relevant to this study is that of Salpas *et al.* (1983) and Haskin & Salpas (1992). As in our case, their original intent was to determine elemental concentrations representative of stratigraphic height and parental magmas. However, Salpas *et al.* ultimately wrote, "Specifically, we have questioned whether such trace-element-poor, mafic-mineral-poor rocks can be produced by the classical concepts of cumulus plus adcumulus growth. If not, then the assumption that the plagioclases in these rocks are in equilibrium with the residue of the magma from which they crystallized is unwarranted...". They found that no whole-rock sample contained very high concentrations of any element incompatible in both plagioclase and pyroxene. On this basis, they concluded that the component of trapped residual liquid in the anorthosites is relatively insignificant, and that much poikilitic pyroxene formed at the front of crystallization, in communication with the bulk liquid. They determined that *REE* data do not support equilibration between pyroxene and plagioclase, and that whole-rock trace-element concentrations vary substantially and unsystematically. They suggested that interstitial liquids migrated away from crystallizing pyroxene, causing pyroxene oikocrysts and minor interstitial quartz to be virtually exclusive, and the highest concentrations of incompatible elements to reside in samples containing the least pyroxene. Finally, they noted that as whole-rock concentrations of incompatible elements rise, so do concentrations in plagioclase, suggesting that some of the plagioclase may have equilibrated with sources of higher concentrations of these elements. We agree with most of these observations and conclusions, but our data suggest that the processes involved may have had even less to do with the magmatic evolution of the rocks.

The contribution of Haskin & Salpas (1992) was designed to extend the earlier investigation, in particular with regard to the development of the pyroxene-rich domains of mottled Stillwater anorthosite. In our opinion, Haskin & Salpas (1992) failed to advance the work of Salpas *et al.* (1983) for two primary reasons. First, they chose not to incorporate study of the pyroxene-poor, plagioclase-rich domains or of plagioclase separates; these appear to be critical to understanding the limitations of trace-element analyses of the Stillwater anorthosites. Second, they became distracted by a number of questionable assumptions, including (1) that compositional trends in the anorthosites relate to mixing, (2) that adcumulus plagioclase has no distinction under the electron microprobe, (3) that diffusion is a viable process for significant growth of pyroxene, and (4) that perhaps, after all, both the adcumulus and intercumulus portions of the rocks might have been derived entirely from trapped liquid.

As part of their argument that pyroxene oikocrysts formed at the crystallization front, Salpas *et al.* (1983) emphasized that Stillwater anorthosite samples are "missing" the trace elements that should have been associated with a trapped melt phase. Table 1 shows that most Stillwater cumulates simply contain low concentrations of trace elements. Under those circumstances which led to formation of mottled anorthosite, pyroxene crystallized quite "efficiently" within a framework of relatively loose-packed cumulus plagioclase. A necessary corollary was precipitation elsewhere of cotectic plagioclase, and generation of residual melts and fluids enriched in incompatible elements. Evidences of the migration of such melts are by now myriad (*e.g.*, Irvine 1980, Tait *et al.* 1984, Tait & Jaupart 1992, McBirney & Hunter 1995). However, the contrast in the trace-element compositions of plagioclase separates from the pyroxene-poor and pyroxene-rich domains (more or less altered samples?) within the anorthosite zones probably resulted less from such cotectic precipitation than from movement of hydrothermal fluids.

Our work has not been definitive as to when or at what temperature the trace elements were redistributed, or whether the low-density aqueous fluids we envision as responsible for this mobilization were derived from Stillwater magma or an external source. Studies such as those of Norton & Taylor (1979) and Bird *et al.* (1988) provide ample documentation of hydrothermal alteration in layered mafic complexes; Bird *et al.* (1988) showed that, as a function of waning temperature, five distinct stages of alteration can be recognized in the layered gabbros of East Greenland. Because the Nd-isotopic studies of DePaolo & Wasserburg (1979) and Lambert *et al.* (1994) indicate that mobilization of the *LREE* did not significantly disrupt the Nd-isotopic systematics of some samples, it seems probable that the mobilization of K, Ba, and *LREE* took place during initial cooling of the complex. On the other hand, Sm and Nd undoubtedly would not be fractionated significantly, and the variability in Nd-isotopic composition (ε_{Nd} in the range −1.5 to +2) among the A-type samples of Lambert *et al.* (1994) is well beyond analytical error; the possibility that this is a reflection of alteration should now be considered. If the fluids involved had a crustal source, they were apparently not a source of *REE*, as larger variations in ε_{Nd} values would have been expected. Insofar as the study of Dunn (1986) indicates that rocks of the complex have retained near-magmatic oxygen-isotopic compositions, there is reason to believe that, over all, relatively small amounts of extraneous fluid were involved. It is quite possible that the alteration we document may represent more than one stage of alteration. Formation of chlorite and epidote, as well as the albitization that is evident in some samples, could represent a later event than that associated with trace-element mobilization, possibly associated with disturbance of the Sr-isotopic systematics approximately 1 b.y. after formation of the complex [see discussion in Wooden *et al.* (1991)] or even the Laramide orogeny.

Evidence for mobilization of *LREE* during rock alteration will be disturbing to students of petrogenesis and has not often been substantiated in crustal systems. However, Hickmott *et al.* (1987, 1992) present convincing evidence for open-system mobilization of the *REE* and Y during prograde metamorphism. Their ion-microprobe studies of zoned garnet in amphibolites from the Tauern Window, Austria and the Catalina Schist, California show that metamorphic fluids can selectively transport *REE* relative to some high-fieldstrength elements. Whereas the evidence presented here is not as direct, we can provide no better explanation that fits our observations.

Students of layered intrusions already face formidable obstacles in trying to reconstruct magmatic evolution and emplacement sequences from cumulates, and it is particularly troubling that the trace-element correlations seen in Table 1 and Figures 7 and 8 show that the *LREE* were as mobile during alteration as K and Ba. Potential problems are especially great for mafic rocks in which trace-element contents are typically low. Samples must be chosen extremely carefully, and in some cases it may be essential to use mineral, whole-rock isochrons to verify that samples represent closed systems that will be relevant to primary magmatic crystallization.

Pb-isotopic compositions (Wooden *et al.* 1991) suggest that the Stillwater Complex was not formed from parental magmas as distinct as those proposed for the Bushveld Complex (*e.g.*, Sharpe 1985). Most studies suggest intimate relations between the magmas parental to the anorthosite zones and the contiguous cumulates in the midsection of the complex. Unfortunately, our data provide no tangible insight into the mechanisms by which the massive anorthosites formed or by which "normal" trends of fractionation in mineral chemistry were suspended during evolution of the Middle Banded series. A speculative scenario to account for this lack of compositional evolution during formation of the Middle Banded series could build on the idea that the Stillwater Complex represents a subvolcanic magma chamber (*e.g.*, Helz 1995). Perhaps the Middle Banded series evolved during a period of abnormally intense volcanic activity, such that great quantities of complementary melt were erupted on Earth's surface?

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