

CLINOPYROXENES FROM ACIDIC, INTERMEDIATE,  
AND BASIC ROCKS, LITTLE BELT  
MOUNTAINS, MONTANA<sup>1</sup>

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ABSTRACT

Clinopyroxenes from acidic, intermediate, and basic rocks in the Little Belt Mountains, Montana, are similar in chemical and optical properties, and in cell dimensions. The major components average  $\text{Ca}_{44}\text{Mg}_{42}\text{Fe}_{14}$ ; pyroxenes from basic rocks differ from those in intermediate rocks in that they have less  $\text{SiO}_2$  but more  $\text{Al}_2\text{O}_3$ . Pyroxenes from the intermediate rocks have small proportions of  $\text{Al}^{3+}$  in tetrahedral coordination (*i.e.*, low  $\text{Al}_2$  percentages); those from basic rocks have high  $\text{Al}_2$  percentages. These  $\text{Al}_2$  percentages probably reflect the molecular concentration of  $\text{SiO}_2$  in the parent magma. Optically they have large axial angles ( $2V_x \sim 59^\circ$ ), and  $\beta$  refractive indices that average 1.692.

Optical property curves have been constructed that give good results in determining the composition of the pyroxenes in terms of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $(\text{Fe}^{2+} + \text{Fe}^{3+} + \text{Mn}^{2+})$ . Viswanathan's (1966) modification of Brown's (1960) correlation diagram based on the unit-cell dimensions  $b$  and  $a \sin \beta$  give good agreement for some pyroxenes from intermediate rocks, but uniformly poor agreement for all pyroxenes from basic rocks. The lack of agreement may be caused by large amounts of  $\text{Al}^{3+}$  in tetrahedral coordination in those pyroxenes from the basic rocks.

Magmatic differentiation at depth by crystal settling led to the formation of both a crystal-enriched fraction which gave rise to the parent magma of the basic rocks, and a crystal-poor differentiate, which after assimilation of much siliceous material, gave rise to a magma of intermediate composition that formed a stock and its related laccoliths.

INTRODUCTION

This paper presents some chemical, optical, and cell-parameter data for clinopyroxenes from igneous rocks exposed in the Barker quadrangle, Little Belt Mountains, central Montana (Fig. 1). These clinopyroxenes, from such widely disparate rock types as rhyolite porphyry and vogesite, are strikingly similar. This correspondence of pyroxenes from diverse rocks apparently is not an isolated occurrence, for Pirsson (1905, p. 38) noted more than half a century ago that clinopyroxenes from igneous bodies scattered through central Montana are similar, regardless of rock type.

The data submitted here represent 18 different intrusions. Pure clinopyroxene concentrates were prepared from nine of these representing samples of pyroxenes in two major igneous bodies (a stock and a discrete laccolith), and seven minor intrusions (one plug, three sills, and three dikes). The paucity of pyroxenes in the other intrusions made any concentration impracticable.

<sup>1</sup> Publication authorized by the Director, U. S. Geological Survey.

## GEOGRAPHIC AND GEOLOGIC SETTING

The Little Belt Mountains are one of several laccolithic complexes which dot the plains of central and north-central Montana (Fig. 1). The mountains form an irregular-shaped, forested mass which occupies about 2,000 square miles. Of this total area only about 200 square miles

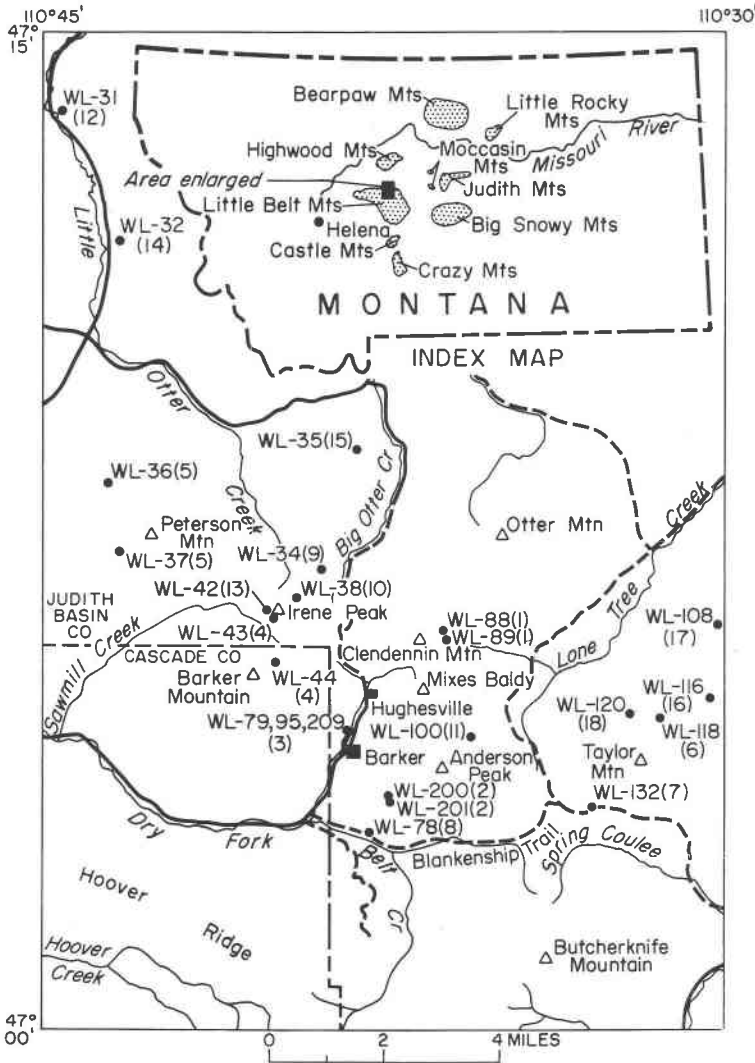


FIG. 1. Planimetric map of Barker quadrangle showing sample localities listed on Table 3. Insert locates major mountain masses near the Little Belt Mountains.

along the north flank of the mountains are included in the current investigation—a geologic study of the 15-minute Barker quadrangle (Fig. 1).

The basement rocks in the Barker quadrangle are a complex of metamorphosed Precambrian crystalline rocks overlain by about 4,500 feet of consolidated sedimentary strata which range in age from Middle Cambrian (Flathead Sandstone) to Early Cretaceous (Kootenai Formation). These sedimentary strata have been deformed by the intrusion of one stock and a host of hypabyssal bodies, mostly laccoliths, bysmaliths, sills, and dikes. The clinopyroxenes studied were collected from these post-Early Cretaceous igneous bodies.

The geologic pattern of the Barker quadrangle has been described previously (Witkind, 1965). In brief, the central part of the quadrangle consists of laccoliths that radiate outward from the stock much like spokes from the hub of a wheel. The remainder of the mountainous part of the quadrangle is underlain by discrete laccoliths, bysmaliths, plugs, and other intrusions (mostly small) which seem to be unrelated to any exposed parental igneous body.

#### PETROLOGIC SETTING

The rocks that form the various intrusions belong to the Little Belt subprovince, one of Larsen's (1940) divisions of the central Montana petrographic province. In the Peacock (1931) classification, the Little Belt rocks have an alkali-lime index of 51.2 and are just within the alkali-calcic group. They range from rhyolite porphyry to vogesite, and fall into three groups: (1) acidic rocks, chiefly rhyolite and granite porphyries, (2) intermediate rocks, chiefly quartz latite porphyries, and (3) basic rocks, chiefly shonkinites, syenites, minette-vogesites, and vogesites. Chemical analyses, C.I.P.W. norms, and modes of the intermediate and basic rocks from which the clinopyroxenes were concentrated are shown in Table 1; several of these rocks (5, 10, 17, and 18) are characterized by fine-grained groundmasses, and these modes, therefore, are at best but approximations.

The acidic and intermediate rocks form the major intrusions, including the stock, the laccoliths, the bysmaliths, and their related sills, dikes, and apophyses. The basic rocks form only small local intrusions, mainly plugs, dikes, and sills. The volume of the acidic and intermediate rocks far exceeds that of the basic rocks.

The area has undergone a complex series of igneous events. Field relations suggest that the first igneous rocks emplaced were highly acidic; these are now represented by two partly denuded laccoliths. Subsequently the intermediate rocks intruded both these newly formed acidic rocks

as well as the sedimentary strata. At some time after this stage the area was once again deformed during the emplacement of a second group of acidic plutons. During or shortly after this episode some, if not all, of the basic rocks were emplaced.

Radiometric ages suggest that all this igneous activity occurred during the early Tertiary (R. F. Marvin, written commun., 1966).

#### SAMPLES

The clinopyroxenes make up a major part of the basic rocks, but only a minor part of the acidic ones. In the intermediate rocks they vary in distribution and abundance from intrusion to intrusion. They are common in the stock, in one laccolith, and in several sills and dikes, but are sparse or absent in other hypabyssal intrusions that are comparable in form and rock type. Of the nine pure mineral separates, three are from intermediate rocks and six are from basic rocks (Table 2).

The clinopyroxenes from two of the nine analyzed samples (5 and 10 of Table 1) are from porphyritic rocks in which the pyroxene phenocrysts are scattered irregularly through a dense fine-grained groundmass. Five of the other seven pyroxene concentrates (3, 12, 13, 14, and 15) are from granular rocks in which the pyroxenes are about the same size as the other component minerals. The remaining two samples (17 and 18) include two generations of pyroxenes, both as phenocrysts and in the groundmass.

Samples 12, and 13 contain either olivine phenocrysts or what are interpreted to be relicts of olivine phenocrysts. Samples 17 and 18 contain quartz xenocrysts encircled by reaction rinds.

The pyroxenes from the various intrusions differ chiefly in their color which ranges from light green to dark green. They form short stubby prisms marked by good prismatic cleavage. Twins are rare.

Optically they are much alike (Table 3). Invariably they are zoned, and all contain inclusions, chiefly of apatite(?) and ilmenite(?). All are free from exsolution lamellae.

The general distribution of the samples in relation to the area as a whole is shown in Figure 1.

Mineral separation procedures, optical techniques, and laboratory and analytical methods used are described in an attached appendix.

#### CHEMICAL COMPOSITION

Chemically all the pyroxenes are rich in calcium and magnesium, and poor in iron (Table 2); they differ somewhat in details of their composition.

A comparison of the major constituents  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $(\text{Fe}^{2+} + \text{Fe}^{3+} + \text{Mn}^{2+})$  indicates but slight variations. The pyroxenes from the intermediate rocks average  $\text{Ca}_{44}\text{Mg}_{41}\text{Fe}_{15}$ ; those from basic rocks average  $\text{Ca}_{45}\text{Mg}_{42}\text{Fe}_{13}$  (Table 2). They differ, however, in their contents of  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ . Those from the basic rocks on the whole contain less  $\text{SiO}_2$ , but more  $\text{Al}_2\text{O}_3$  than those from the intermediate rocks (A, Fig. 2). Only sample 13 deviates somewhat from this pattern, and this divergence is probably the result of the rock being rich in plagioclase. Apparently the plagioclase as it crystallized seized much of the available  $\text{Al}^{3+}$  ion, and

TABLE 1. ANALYSES IN PERCENTAGES OF INTERMEDIATE AND BASIC ROCKS FROM WHICH CLINOPYROXENES WERE CONCENTRATED

| Ident. no. (See table 3)       | Intermediate rocks   |                        |          |              | Basic rocks              |          |          |                  |          |
|--------------------------------|----------------------|------------------------|----------|--------------|--------------------------|----------|----------|------------------|----------|
|                                | 3                    | 5                      | 10       | 12           | 13                       | 14       | 15       | 17               | 18       |
| Rock name                      | Syenite <sup>a</sup> | Quartz latite porphyry |          | Shonkinitite | Plagioclase shonkinitite | Syenite  |          | Minette-Vogesite | Vogesite |
| Laboratory no.                 | 163688               | 163678                 | W-169659 | 163677       | 163679                   | W-169661 | W-169662 | W-169663         | 163694   |
| Field no.                      | WL-79                | WL-37                  | WL-38    | WL-31        | WL-42                    | WL-32    | WL-35    | WL-108           | WL-120   |
| Chemical analyses <sup>b</sup> |                      |                        |          |              |                          |          |          |                  |          |
| SiO <sub>2</sub>               | 61.2                 | 62.4                   | 60.6     | 48.3         | 56.3                     | 55.0     | 54.5     | 52.2             | 49.2     |
| Al <sub>2</sub> O <sub>3</sub> | 16.4                 | 16.1                   | 15.8     | 10.4         | 14.1                     | 18.3     | 18.8     | 13.3             | 12.9     |
| Fe <sub>2</sub> O <sub>3</sub> | 3.2                  | 3.4                    | 3.0      | 2.0          | 2.3                      | 2.9      | 2.6      | 4.1              | 3.9      |
| FeO                            | 2.2                  | 1.5                    | 2.5      | 7.7          | 3.3                      | 2.8      | 3.4      | 3.3              | 3.1      |
| MgO                            | 1.9                  | 2.2                    | 2.9      | 16.0         | 7.6                      | 2.2      | 2.0      | 5.6              | 6.9      |
| CaO                            | 3.0                  | 3.0                    | 3.9      | 6.8          | 5.4                      | 3.3      | 3.9      | 6.7              | 9.4      |
| Na <sub>2</sub> O              | 4.6                  | 4.2                    | 3.9      | 1.4          | 5.0                      | 3.6      | 4.4      | 3.6              | 2.1      |
| K <sub>2</sub> O               | 4.5                  | 4.2                    | 4.3      | 3.6          | 3.2                      | 8.2      | 6.0      | 3.2              | 4.6      |
| H <sub>2</sub> O <sup>-</sup>  | 0.16                 | 0.59                   | 0.24     | 0.31         | 0.38                     | 0.00     | 0.18     | 0.93             | 1.6      |
| H <sub>2</sub> O <sup>+</sup>  | 0.36                 | 0.81                   | 1.2      | 1.7          | 1.0                      | 2.1      | 2.6      | 2.2              | 1.4      |
| TiO <sub>2</sub>               | 0.92                 | 0.47                   | 0.62     | 0.75         | 0.45                     | 0.51     | 0.62     | 0.78             | 1.3      |
| P <sub>2</sub> O <sub>5</sub>  | 0.44                 | 0.46                   | 0.52     | 0.65         | 0.57                     | 0.45     | 0.40     | 0.52             | 1.6      |
| MnO                            | 0.22                 | 0.07                   | 0.12     | 0.16         | 0.13                     | 0.12     | 0.14     | 0.12             | 0.10     |
| CO <sub>2</sub>                | 0.15                 | <0.05                  | <0.05    | 0.08         | 0.09                     | 0.36     | 0.06     | 3.4              | 1.3      |
| Sum                            | 99.25                | 99.45                  | 99.65    | 99.85        | 99.82                    | 99.84    | 99.60    | 99.95            | 99.40    |

<sup>a</sup> Correctly a quartz monzonite, but Weed's (1900, p. 353) original name "Hughesville syenite" retained here.

<sup>b</sup> Analysts: P. Elmore, L. Artis, J. Glenn, J. Kelsey, S. Bottis, H. Smith, and G. Chloe, U. S. Geol. Survey.

<sup>c</sup> Includes quartz xenocrysts.



TABLE 2. ANALYSES IN PERCENTAGES OF CLINOPYROXENES CONCENTRATED FROM INTERMEDIATE AND BASIC ROCKS, BARKER QUADRANGLE, LITTLE BELT MOUNTAINS, MONTANA

| Ident. no.<br>(See table 3)    | Clinopyroxenes from intermediate rocks |                        |          |         |                           | Clinopyroxenes from basic rocks |          |          |                      |                      |         |       |  | Average |
|--------------------------------|----------------------------------------|------------------------|----------|---------|---------------------------|---------------------------------|----------|----------|----------------------|----------------------|---------|-------|--|---------|
|                                | 3<br>S.C.A. <sup>a</sup>               | 5                      | 10       | Average | 12<br>S.C.A. <sup>a</sup> | 13<br>S.C.A. <sup>a</sup>       | 14       | 15       | 17                   | 18                   | Average |       |  |         |
| Source rock                    | Syenite                                | Quartz latite porphyry |          |         | Shonkinita                | Plagioclase-shonkinita          | Syenite  | Syenite  | Minette-vogesite     | Vogesite             |         |       |  |         |
| Laboratory no. <sup>b</sup>    | D-121080<br>D-101387                   | D-121074<br>D-129461   | D-121075 |         | D-121071<br>D-101385      | D-128910<br>D-101386            | D-127498 | D-121073 | D-121078<br>D-129463 | D-121079<br>D-129464 |         |       |  |         |
| Field no.                      | WL-79                                  | WL-37                  | WL-38    |         | WL-31                     | WL-42                           | WL-32    | WL-35    | WL-108               | WL-120               |         |       |  |         |
| Oxides                         |                                        |                        |          |         |                           |                                 |          |          |                      |                      |         |       |  |         |
| SiO <sub>2</sub>               | 50.76                                  | 51.06                  | 51.89    | 51.46   | 48.81                     | 50.7                            | 53.06    | 47.2     | 47.58                | 49.14                | 50.29   | 48.95 |  |         |
| Al <sub>2</sub> O <sub>3</sub> | 1.66                                   | 2.19                   | 2.38     | 2.02    | 4.10                      | 2.31                            | 1.89     | 4.18     | 4.46                 | 7.82                 | 3.17    | 4.34  |  |         |
| TiO <sub>2</sub>               | 0.78                                   | 0.83                   | 0.46     | 0.57    | 0.82                      | 0.22                            | 0.24     | 0.92     | 0.65                 | 0.44                 | 0.98    | 0.67  |  |         |
| Cr <sub>2</sub> O <sub>3</sub> | 0.04                                   | —                      | 0.04     | 0.04    | 0.31                      | —                               | —        | 0.04     | 0.04                 | 0.37                 | 0.45    | 0.22  |  |         |
| Fe <sub>2</sub> O <sub>3</sub> | 2.10                                   | 2.06                   | 1.86     | 2.32    | 1.79                      | 3.3                             | 2.95     | 3.63     | 4.39                 | 1.41                 | 1.45    | 2.66  |  |         |
| FeO                            | 7.31                                   | 7.14                   | 5.57     | 6.40    | 4.44                      | 4.6                             | 4.71     | 5.69     | 9.31                 | 4.02                 | 3.71    | 5.30  |  |         |
| MnO                            | 0.71                                   | —                      | 0.45     | 0.54    | 0.15                      | —                               | —        | 0.24     | 0.45                 | 0.18                 | 0.12    | 0.23  |  |         |
| MgO                            | 13.5                                   | 13.21                  | 13.5     | 13.5    | 14.3                      | 14.6                            | 14.18    | 13.5     | 10.40                | 15.8                 | 15.5    | 14.2  |  |         |
| CaO                            | 20.1                                   | 20.52                  | 20.6     | 20.47   | 21.3                      | 20.8                            | 21.62    | 21.6     | 20.60                | 20.6                 | 21.0    | 20.98 |  |         |
| Na <sub>2</sub> O              | 0.54                                   | 0.62                   | 0.55     | 0.55    | 0.38                      | 1.0                             | 1.06     | 0.36     | 0.49                 | 0.32                 | 0.44    | 0.50  |  |         |
| K <sub>2</sub> O               | 0.12                                   | 0.12                   | 0.11     | 0.11    | 0.10                      | 0.12                            | 0.08     | 0.10     | 0.12                 | 0.04                 | 0.07    | 0.09  |  |         |
| Sum                            | 97.62                                  | 97.75                  | 97.25    | 97.98   | 96.50                     | 98.00                           | 99.79    | 97.46    | 98.49                | 100.14               | 97.18   | 97.95 |  |         |

TABLE 2.—(Continued)

| Clinopyroxenes from intermediate rocks               |                     |                     |                     |                     |                     |                     |                     |                     |                     | Clinopyroxenes from basic rocks |                     |                     |                     |                     |                     |                     |                     |                     |                     |                     |
|------------------------------------------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|
| Number of ions on basis of six oxygens               |                     |                     |                     |                     |                     |                     |                     |                     |                     |                                 |                     |                     |                     |                     |                     |                     |                     |                     |                     |                     |
| Z                                                    | (Si <sup>4+</sup> ) | (Al <sup>3+</sup> ) | (Al <sup>3+</sup> ) | (Al <sup>3+</sup> ) | (Al <sup>3+</sup> ) | (Al <sup>3+</sup> ) | (Al <sup>3+</sup> ) | (Al <sup>3+</sup> ) | (Al <sup>3+</sup> ) | (Al <sup>3+</sup> )             | (Al <sup>3+</sup> ) | (Al <sup>3+</sup> ) | (Al <sup>3+</sup> ) | (Al <sup>3+</sup> ) | (Al <sup>3+</sup> ) | (Al <sup>3+</sup> ) | (Al <sup>3+</sup> ) | (Al <sup>3+</sup> ) | (Al <sup>3+</sup> ) | (Al <sup>3+</sup> ) |
|                                                      | 1.940               | 1.940               | 1.960               | 1.945               | 1.948               | 1.867               | 1.848               | 1.916               | 1.960               | 1.816                           | 1.838               | 1.795               | 1.897               | 1.854               |                     |                     |                     |                     |                     |                     |
|                                                      | >2.00               | >2.00               | >2.00               | >2.00               | >2.00               | >2.00               | >2.00               | >2.00               | >2.00               | >2.00                           | >2.00               | >2.00               | >2.00               | >2.00               |                     |                     |                     |                     |                     |                     |
|                                                      | 0.060               | 0.060               | 0.040               | 0.055               | 0.082               | 0.133               | 0.152               | 0.084               | 0.040               | 0.184                           | 0.162               | 0.205               | 0.103               | 0.146               |                     |                     |                     |                     |                     |                     |
|                                                      | .014                | .038                | .067                | .035                | .038                | .051                | .056                | .018                | .042                | .005                            | .041                | .132                | .037                | .048                |                     |                     |                     |                     |                     |                     |
|                                                      | .022                | .024                | .013                | .013                | .016                | .024                | .027                | .006                | .007                | .027                            | .019                | .028                | .028                | .019                |                     |                     |                     |                     |                     |                     |
| Y:                                                   | Cs <sup>+</sup>     | .001                | .001                | .001                | .001                | .009                | .003                | .003                | .001                | .001                            | .001                | .011                | .013                | .007                |                     |                     |                     |                     |                     |                     |
|                                                      | Fe <sup>2+</sup>    | .060                | .059                | .052                | .084                | .052                | .052                | .084                | .082                | .105                            | .128                | .039                | .041                | .076                |                     |                     |                     |                     |                     |                     |
|                                                      | Fe <sup>3+</sup>    | .234                | .199                | .177                | .198                | .142                | .143                | .145                | .146                | .183                            | .301                | .123                | .117                | .188                |                     |                     |                     |                     |                     |                     |
| X:                                                   | Mn <sup>2+</sup>    | .023                | .023                | .014                | .014                | .005                | .005                | .008                | .008                | .008                            | .015                | .006                | .004                | .007                |                     |                     |                     |                     |                     |                     |
|                                                      | Mg <sup>2+</sup>    | .769                | .748                | .763                | .754                | .815                | .811                | .822                | .781                | .774                            | .599                | .860                | .871                | .799                |                     |                     |                     |                     |                     |                     |
|                                                      | Ca <sup>2+</sup>    | .823                | .836                | .831                | .830                | .873                | .886                | .842                | .856                | .890                            | .853                | .806                | .849                | .852                |                     |                     |                     |                     |                     |                     |
| W:                                                   | Na <sup>+</sup>     | .040                | .046                | .040                | .040                | .028                | .037                | .073                | .076                | .027                            | .037                | .023                | .032                | .037                |                     |                     |                     |                     |                     |                     |
|                                                      | K <sup>+</sup>      | .006                | .006                | .005                | .005                | .005                | .005                | .006                | .034                | .005                            | .006                | .002                | .003                | .004                |                     |                     |                     |                     |                     |                     |
| Normalized constituents                              |                     |                     |                     |                     |                     |                     |                     |                     |                     |                                 |                     |                     |                     |                     |                     |                     |                     |                     |                     |                     |
| Ca <sup>2+</sup>                                     | 43.1                | 44.7                | 45.5                | 44.2                | 44.2                | 40.3                | 40.8                | 44.0                | 45.9                | 45.4                            | 45.0                | 44.0                | 45.1                | 45.0                |                     |                     |                     |                     |                     |                     |
| Mg <sup>2+</sup>                                     | 40.3                | 40.0                | 41.4                | 40.1                | 40.5                | 43.2                | 42.9                | 43.0                | 41.9                | 39.5                            | 31.6                | 46.9                | 46.3                | 41.8                |                     |                     |                     |                     |                     |                     |
| Fe <sup>2+</sup> +Fe <sup>3+</sup> +Mn <sup>2+</sup> | 16.6                | 15.3                | 13.2                | 15.7                | 15.3                | 10.5                | 10.3                | 13.0                | 12.2                | 15.1                            | 23.4                | 9.1                 | 8.6                 | 13.2                |                     |                     |                     |                     |                     |                     |
| Percent Al <sup>3+</sup> in Z                        | 3.0                 | 3.0                 | 2.0                 | 2.7                 | 2.6                 | 6.7                 | 7.6                 | 4.2                 | 2.0                 | 9.2                             | 8.1                 | 10.3                | 5.2                 | 7.3                 |                     |                     |                     |                     |                     |                     |

a S.C.A.=Standard chemical analysis; Analyst: George O. Riddle.

b The following pertains to all analyses except those labelled S.C.A.:

SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> percentages determined colorimetrically by G. T. Burrow.

Cr<sub>2</sub>O<sub>3</sub>, MnO, MgO, CaO, Na<sub>2</sub>O and K<sub>2</sub>O percentages determined by atomic absorption by J. D. Measik and Claude Huffman, Jr.

Total Fe as Fe<sub>2</sub>O<sub>3</sub> percentage determined by atomic absorption by Violet Merritt, and H. H. Lipp.

FeO percentages determined by dichromate titration by Elsie Rowe.

Fe<sub>2</sub>O<sub>3</sub> percentages calculated by Violet Merritt.

All analysts at U. S. Geological Survey laboratories, Denver, Colorado.



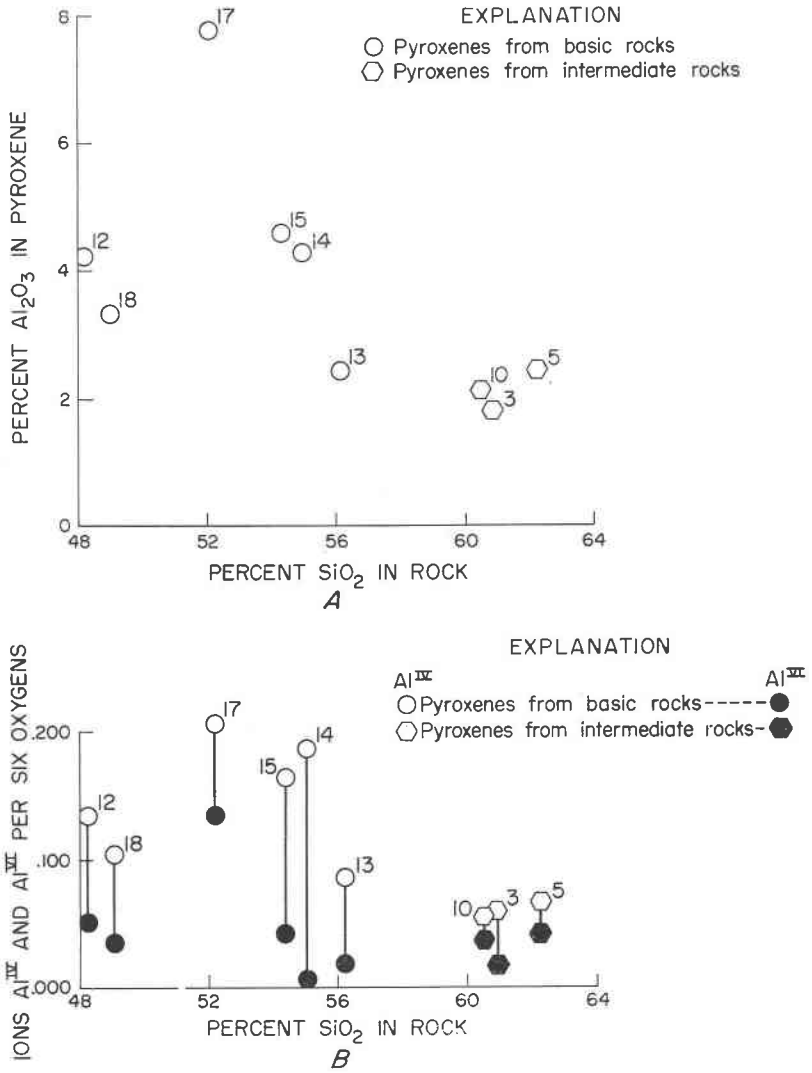


FIG. 2. Variation diagrams. A. Plot of percentage of  $\text{Al}_2\text{O}_3$  in pyroxenes versus percentage of  $\text{SiO}_2$  in rocks. B. Plot of  $\text{Al}^{\text{IV}}$  and  $\text{Al}^{\text{VI}}$  ions (on basis of six oxygens) versus percentage of  $\text{SiO}_2$  in rocks.

in so doing depleted the supply of  $\text{Al}^{3+}$  available to the crystallizing pyroxenes.

#### ALUMINUM

Aluminum can be considered in three ways: as total aluminum oxide ( $\text{Al}_2\text{O}_3$ ), as that part of the aluminum ion in tetrahedral coordination ( $\text{Al}^{\text{IV}}$ ), and as that part in octahedral coordination ( $\text{Al}^{\text{VI}}$ ). In four-fold coordination, aluminum ( $\text{Al}^{3+}$ ) substitutes for the silicon ( $\text{Si}^{4+}$ ) ion, and in six-fold coordination it substitutes for various cations such as magnesium ( $\text{Mg}^{2+}$ ) and iron ( $\text{Fe}^{2+}$ ).

*Total  $\text{Al}_2\text{O}_3$ .* Although there is considerable variation in the  $\text{Al}_2\text{O}_3$  content, those pyroxenes from the intermediate rocks contain about 2 percent, whereas those (except sample 13) from the basic rocks contain about 4.3 percent (Table 2).

Because this very significant difference in total  $\text{Al}_2\text{O}_3$  content does not seem to be reflected by the optical properties of the Little Belt pyroxenes, I am unable to separate the  $\text{Al}_2\text{O}_3$ -rich from  $\text{Al}_2\text{O}_3$ -poor pyroxenes on the basis of any specific optical property. This failure of total  $\text{Al}_2\text{O}_3$  to influence the optical properties was noted by Segnit (1953, p. 221) for synthetic diopside.

*Aluminum ion in tetrahedral coordination ( $\text{Al}^{\text{IV}}$ ).* It has been suggested by Hori (1954) that the position of the  $\text{Al}^{3+}$  ion in the structural framework of the pyroxene is much more meaningful than total  $\text{Al}_2\text{O}_3$  in influencing the optical properties. He (1954, p. 81-82) notes that if such minor cations as  $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Ti}^{4+}$ , and  $\text{Cr}^{3+}$  enter the tetrahedral position, the refractive indices decrease and the optic angle increases. If they enter octahedral coordination the reverse is true.

For the Little Belt clinopyroxenes,<sup>1</sup> the sum of  $\text{Si}^{4+}$  and  $\text{Al}^{3+}$  satisfies the numerical requirements of the Z group, and so none of the available  $\text{Ti}^{4+}$ ,  $\text{Fe}^{3+}$ , or  $\text{Cr}^{3+}$  are needed (Table 2). The range of substitution of  $\text{Al}^{3+}$  for  $\text{Si}^{4+}$  (*i.e.*, the percent of  $\text{Al}^{3+}$  ion in the Z group) is extreme, from 2 to 10 percent. But this range is not evenly distributed; the pyroxenes from the intermediate rocks consistently contain less  $\text{Al}^{3+}$  ion in tetrahedral coordination than those from the basic rocks (B, Fig. 2). In the clinopyroxenes from the intermediate rocks,  $\text{Si}^{4+}$  (on the basis of six oxygens) approaches 2, and therefore  $\text{Al}_z$  is low. By contrast  $\text{Si}^{4+}$  is not as plentiful in those clinopyroxenes from the basic rocks and so  $\text{Al}_z$  is high (Table 2).

<sup>1</sup> In the following discussion only those analyses completed chiefly by atomic absorption spectroscopy are considered.

Regrettably this very striking difference in content of  $\text{Al}^{3+}$  ion in tetrahedral coordination is not markedly shown by their optical properties. Although the refractive indices of all the pyroxenes decrease when plotted against  $\text{Al}^{\text{IV}}$ , the optic angles fail to show any meaningful variation or pattern.

Kushiro (1960) and LeBas (1962) have called attention to the significance of the proportion of aluminum ion in tetrahedral coordination in clinopyroxenes as a guide to the silica content of their parent magma. In essence, if much  $\text{Si}^{4+}$  ion is available—as in a magma oversaturated with  $\text{SiO}_2$ —the ionic requirements of the *Z* group are almost completely satisfied by the  $\text{Si}^{4+}$  ion; little space is available for the  $\text{Al}^{3+}$  ion. By contrast, if the parent magma contains only small amounts of  $\text{SiO}_2$ , little  $\text{Si}^{4+}$  ion is available to the crystallizing pyroxenes, and the unoccupied sites in the *Z* group are then filled by available  $\text{Al}^{3+}$  ion.

This explanation is favored for the Little Belt clinopyroxenes. The pyroxenes from the basic rocks, characterized by high  $\text{Al}_z$  ratios ( $\sim 7\%$ ), probably faithfully reflect the low  $\text{SiO}_2$  concentration of their parent magma. Pyroxenes from the intermediate rocks contain only  $\sim 2.5$  per cent  $\text{Al}_z$ , and they reflect the higher  $\text{SiO}_2$  content of their parent rocks.

*Aluminum ion in octahedral coordination ( $\text{Al}^{\text{VI}}$ ).* Not all of the available  $\text{Al}^{3+}$  ion has been needed to fill the *Z* group, and some has been assigned to the octahedral position (*Y* group) along with the other minor cations ( $\text{Fe}^{3+}$ ,  $\text{Ti}^{4+}$ ,  $\text{Cr}^{3+}$ ). In general the average proportion of  $\text{Al}^{3+}$  ion in octahedral coordination in pyroxenes from intermediate rocks (0.038) approximates the average  $\text{Al}^{\text{VI}}$  content in pyroxenes from basic rocks (0.048) (Table 2).

Octahedral  $\text{Al}^{3+}$  ion should cause an increase in the refractive indices, and a decrease in the optic angle (Hori, 1954, p. 81). The pyroxenes from the intermediate rocks do show an increase of refractive indices with increasing  $\text{Al}^{\text{VI}}$  content; those from the basic rocks do not. The optic angles seem unaffected by the amount of  $\text{Al}^{3+}$  ion in octahedral coordination.

#### OPTICAL PROPERTIES

It matters little whether the pyroxenes are from acidic, intermediate, or basic rocks, optically they are strikingly alike (Table 3).

The optic axes are about *Z*, and the optic angle for most grains is high, averaging  $59^\circ$ . The dispersion of the optic axes—more intense on one than on the other—is consistently weak to moderate, and  $r > v$  in all grains studied. Although there is considerable range of the refractive indices, in general  $\alpha$  averages 1.685,  $\beta$  averages 1.692, and  $\gamma$  averages

1.715. The birefringence averages 0.029. Pleochroism is weak, and ranges from yellow green to blue green. The extinction angle  $Z \wedge c$  averages  $43^\circ$ .

Several optical property diagrams were tested in an attempt to locate one that would show good coincidence between the predicted compositions (based on plots of the optic angle  $2V_z$ , and the  $\beta$  refractive index) and the determined chemical compositions of the nine analyzed pyroxenes (Fig. 3). Neither Hess' (1949) optical property curves, nor Muir's revision of these curves (Muir, 1951, Fig. 4) gave acceptable results. Using the determined mean values for  $2V_z$  and the  $\beta$  refractive index (Table 3), none of the nine analyzed samples plotted on Hess' diagram, and only eight of the nine could be plotted on Muir's revision. Of the total 18 samples studied only three plotted on Hess' diagram, although 15 plotted on Muir's revision of Hess' optical property curves.

When the predicted and determined compositions of the eight samples that could be plotted on Muir's revision were compared, it was apparent that the determined compositions consistently contained less calcium and more magnesium than the compositions predicted by the optical data. In an attempt to overcome this bias and to bring the predicted compositions closer to the actual compositions, I have, by inspection, drawn new optical property curves for the Little Belt pyroxene separates (Fig. 3) using the nine analyzed samples. If the optical data for all 18 samples (Table 3) are plotted on these revised curves, all fall on the diagram near the augite-salite boundary. Seven are in the augite field, and the remaining 11 are in the salite field. The predicted compositions, in terms of atomic percentages of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $(\text{Fe}^{2+} + \text{Fe}^{3+} + \text{Mn}^{2+})$ , are given in Table 4.

Whether these new curves apply to clinopyroxenes from other parts of the Little Belt Mountains, and from some of the adjacent mountain complexes in central Montana, which are reported to have similar clinopyroxenes, is as yet unknown.

#### UNIT-CELL PARAMETERS

The unit-cell parameters for both groups of pyroxenes are given in Table 5. Degrees of freedom range from 6 to 9 for eight of the nine samples. The uncertainties are larger for the unit-cell data for sample 5.

Brown (1960) has suggested that  $b$  and  $a \sin \beta$  are important diagnostic cell parameters in clinopyroxenes. A correlation diagram, prepared by Brown (1960, Fig. 5) and subsequently modified by Viswanathan (1966, Fig. 3), based on these cell parameters was proposed as a useful tool to determine the chemical compositions of clinopyroxenes in terms of atomic percentages of the major constituents  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{Fe}^{2+}$ . If  $b$  and  $a \sin \beta$  of the nine clinopyroxene samples from the Little Belt Mountains

TABLE 3. OPTICAL DATA OF CLINOPYROXENES FROM ACIDIC, INTERMEDIATE, AND BASIC ROCKS FROM THE BARKER QUADRANGLE, LITTLE BELT MOUNTAINS, MONTANA

| Rock name           | Clinopyroxenes from intermediate rocks |              |                |                        |              |              |              |             |              |              | Clinopyroxenes from basic rocks |              |                          |              |              |              |              |              |                       |  |  |                     |  |  |
|---------------------|----------------------------------------|--------------|----------------|------------------------|--------------|--------------|--------------|-------------|--------------|--------------|---------------------------------|--------------|--------------------------|--------------|--------------|--------------|--------------|--------------|-----------------------|--|--|---------------------|--|--|
|                     | 1                                      | 2            | 3              | 4                      | 5            | 6            | 7            | 8           | 9            | 10           | 11                              | 12           | 13                       | 14           | 15           | 16           | 17           | 18           |                       |  |  |                     |  |  |
| Field number        | Syenite                                |              |                | Quartz latite porphyry |              |              | Syenite      |             |              | Shon-kinite  |                                 |              | Phagio-clase shon-kinite |              |              | Syenite      |              |              | Mi-nette-ker-san-tite |  |  | Mi-nette-voege-site |  |  |
|                     | WL-88, 89                              | WL-200, 201  | WL-79, 85, 200 | WL-43, 44              | WL-36, 37    | WL-118       | WL-132       | WL-78       | WL-84        | WL-38        | WL-100                          | WL-31        | WL-42                    | WL-32        | WL-35        | WL-116       | WL-108       | WL-120       |                       |  |  |                     |  |  |
| $n_x^a$             | 1.6854 (20)                            | 1.6875 (10)  | 1.6841 (22)    | 1.6829 (79)            | 1.6863 (33)  | 1.6880 (55)  | 1.6870 (35)  | 1.6855 (21) | 1.6860 (—)   | 1.6852 (60)  | 1.6840 (71)                     | 1.6844 (18)  | 1.6850 (18)              | 1.6888 (40)  | 1.6956 (43)  | 1.6770 (71)  | 1.6806 (50)  | 1.6832 (30)  |                       |  |  |                     |  |  |
| $n_y$               | 1.6920 (37)                            | 1.6940 (16)  | 1.6903 (10)    | 1.6913 (32)            | 1.6948 (29)  | 1.6910 (71)  | 1.6927 (15)  | 1.6925 (07) | 1.6920 (14)  | 1.6916 (54)  | 1.6885 (64)                     | 1.6894 (34)  | 1.6906 (17)              | 1.6850 (40)  | 1.7036 (42)  | 1.6850 (42)  | 1.6874 (61)  | 1.6888 (30)  |                       |  |  |                     |  |  |
| $n_z$               | 1.7149 (96)                            | 1.7178 (05)  | 1.7123 (20)    | 1.7126 (40)            | 1.7158 (33)  | 1.7135 (21)  | 1.7163 (46)  | 1.7160 (14) | 1.7145 (07)  | 1.7154 (44)  | 1.7150 (71)                     | 1.7112 (38)  | 1.7148 (11)              | 1.7198 (43)  | 1.7254 (45)  | 1.7065 (50)  | 1.7086 (31)  | 1.7098 (86)  |                       |  |  |                     |  |  |
| Birefringence       | .0285                                  | .0303        | .0282          | .0287                  | .0295        | .0275        | .0263        | .0305       | .0285        | .0302        | .0310                           | .0268        | .0298                    | .0310        | .0298        | .0295        | .0280        | .0266        |                       |  |  |                     |  |  |
| $2V_z$              | 55.9° (3.1°)                           | 60.3° (1.3°) | 58.6° (0.9°)   | 59.7° (3.1°)           | 59.0° (1.2°) | 59.0° (2.8°) | 53.7° (1.5°) | 62.0° (—)   | 57.5° (2.1°) | 50.8° (1.6°) | 58.0° (1.4°)                    | 58.8° (1.3°) | 60.6° (0.9°)             | 56.3° (0.8°) | 58.8° (1.8°) | 59.0° (1.4°) | 57.8° (2.9°) | 59.6° (0.6°) |                       |  |  |                     |  |  |
| $Z \wedge c$ (mean) | 40°                                    | 43°          | 41°            | 44°                    | 43°          | 41°          | 43°          | 37°         | 45°          | 43°          | 41°                             | 43°          | 44°                      | 49°          | 43°          | 48°          | 44°          | 41°          |                       |  |  |                     |  |  |
| Dispersion          | r > v                                  | r > v        | r > v          | r > v                  | r > v        | r > v        | r > v        | r > v       | r > v        | r > v        | r > v                           | r > v        | r > v                    | r > v        | r > v        | r > v        | r > v        | r > v        |                       |  |  |                     |  |  |
| $\alpha$            | Yellow                                 | Light green  | Light green    | Yellow                 | Olive        | Light green  | Light green  | Light green | Light green  | Light green  | Yellow                          | Light green  | Light green              | Green        | Green        | Light green  | Light green  | Yellow       |                       |  |  |                     |  |  |
| $\beta$             | Yellow                                 | Green        | Green          | Light green            | Green        | Yellow       | Green        | Yellow      | Blue         | Green        | Yellow                          | Yellow       | Yellow                   | Green        | Olive        | Yellow       | Light green  | Green        |                       |  |  |                     |  |  |
| $\gamma$            | Blue                                   | Light green  | Light green    | Blue                   | Light green  | Blue         | Light blue   | Blue        | Light green  | Light green  | Blue                            | Green        | Light green              | Green        | Green        | Light green  | Light green  | Light green  |                       |  |  |                     |  |  |
| Abundance           | Rare                                   | Rare         | Common         | Rare                   | Common       | Rare         | Rare         | Rare        | Rare         | Common       | Rare                            | Common       | Common                   | Common       | Common       | Rare         | Common       | Common       |                       |  |  |                     |  |  |
| Suggested mineral   | Augite                                 | Salite       | Salite         | Salite                 | Augite       | Salite       | Augite       | Salite      | Augite       | Salite       | Augite                          | Salite       | Salite                   | Augite       | Augite       | Salite       | Salite       | Salite       |                       |  |  |                     |  |  |

<sup>a</sup> Mean refractive indices at 25°C; in parentheses, standard deviation of data derived from number of clinopyroxene grains studied as shown below.

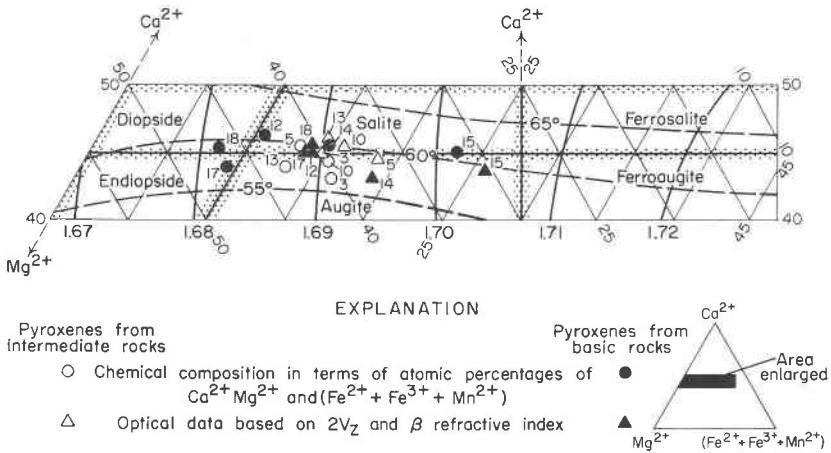


Fig. 3. Partial trapezium showing new optical property curves based on Little Belt pyroxenes. Determined chemical compositions (circles) compared with compositions estimated from optical data (triangles) (i.e., mean values of  $2V_z$  and  $\beta$  refractive indices) of nine analyzed clinopyroxenes listed in Table 3. Nomenclature from Poldervaart and Hess (1951).

are plotted on Viswanathan's modification of Brown's correlation diagram, two plots (3 and 5 of Table 5) are in close agreement with the de-

←

Description of Samples for Table 3

| No. | Number of clinopyroxene grains studied | From samples of same intrusion | Locality                                                                                              |
|-----|----------------------------------------|--------------------------------|-------------------------------------------------------------------------------------------------------|
| 1   | 7                                      | 2                              | Clendennin-Otter laccolith, T. 16 N., R. 9 E.                                                         |
| 2   | 4                                      | 2                              | Mixes Baldy-Anderson Peak laccolith, NW $\frac{1}{2}$ , T. 15 N., R. 9 E.                             |
| 3   | 9                                      | 3                              | Hughesville stock, sec. 7, T. 15 N., R. 9 E., (unsurveyed)                                            |
| 4   | 7                                      | 2                              | Barker laccolith, TS 15 and 16 N., R. 8 E.                                                            |
| 5   | 4                                      | 2                              | Peterson laccolith, sec. 28, T. 16 N., R. 8 E.                                                        |
| 6   | 2                                      | 1                              | Taylor Mountain laccolith, NE $\frac{1}{2}$ , T. 15 N., R. 9 E.                                       |
| 7   | 3                                      | 1                              | Lone Tree laccolith, NE $\frac{1}{2}$ , T. 15 N., R. 9 E.                                             |
| 8   | 2                                      | 1                              | Chocolate porphyry sill, W $\frac{1}{2}$ , T. 15 N., R. 9 E.                                          |
| 9   | 2                                      | 1                              | Sill, Big Otter Creek, sec. 25, T. 16 N., R. 8 E.                                                     |
| 10  | 5                                      | 1                              | Sill, west valley wall, Big Otter Creek, N $\frac{1}{2}$ sec. 36, T. 16 N., R. 8 E.                   |
| 11  | 2                                      | 1                              | Dike, Lone Tree Park, sec. 9, T. 15 N., R. 9 E.                                                       |
| 12  | 5                                      | 1                              | Plug, Little Otter Creek, SE $\frac{1}{2}$ , sec. 18, T. 17 N., R. 8 E.                               |
| 13  | 5                                      | 1                              | Dike (?) at Irene Peak, W $\frac{1}{2}$ , sec. 36, T. 16 N., R. 8 E.                                  |
| 14  | 5                                      | 1                              | Sill at Hansens Coulee, secs. 28 and 33, T. 17 N., R. 8 E.                                            |
| 15  | 5                                      | 1                              | Sill along west valley wall, Big Otter Creek, sec. 18, T. 16 N., R. 9 E.                              |
| 16  | 2                                      | 1                              | Dike along northwest flank, Granite Mountain, W $\frac{1}{2}$ sec. 6, T. 15 N., R. 10 E. (unsurveyed) |
| 17  | 5                                      | 1                              | Dike along northwest flank, Granite Mountain, S $\frac{1}{2}$ sec. 31, T. 16 N., R. 10 E.             |
| 18  | 5                                      | 1                              | Dike, Frenchies Coulee, NW $\frac{1}{2}$ sec. 12, T. 15 N., R. 9 E.                                   |

TABLE 4. COMPARISON OF PREDICTED AND DETERMINED COMPOSITIONS BASED ON OPTICAL PROPERTY CURVES SHOWN IN FIGURE 3 AND DATA IN TABLES 2 AND 3

| Sample number | Composition      |            |                  |            |                                                         |            |
|---------------|------------------|------------|------------------|------------|---------------------------------------------------------|------------|
|               | Ca <sup>2+</sup> |            | Mg <sup>2+</sup> |            | (Fe <sup>2+</sup> +Fe <sup>3+</sup> +Mn <sup>2+</sup> ) |            |
|               | Predicted        | Determined | Predicted        | Determined | Predicted                                               | Determined |
| 1             | 43               |            | 40               |            | 17                                                      |            |
| 2             | 46               |            | 37               |            | 17                                                      |            |
| 3             | 45               | 43         | 41               | 40         | 14                                                      | 17         |
| 4             | 46               |            | 39               |            | 15                                                      |            |
| 5             | 45               | 45         | 37               | 42         | 18                                                      | 13         |
| 6             | 45               |            | 39               |            | 16                                                      |            |
| 7             | 42               |            | 39               |            | 19                                                      |            |
| 8             | 47               |            | 37               |            | 16                                                      |            |
| 9             | 44               |            | 39               |            | 17                                                      |            |
| 10            | 46               | 44         | 39               | 40         | 15                                                      | 16         |
| 11            | 45               |            | 41               |            | 14                                                      |            |
| 12            | 45               | 46         | 41               | 43         | 14                                                      | 11         |
| 13            | 46               | 44         | 39               | 43         | 15                                                      | 13         |
| 14            | 43               | 45         | 38               | 40         | 19                                                      | 15         |
| 15            | 44               | 45         | 31               | 32         | 25                                                      | 23         |
| 16            | 46               |            | 43               |            | 11                                                      |            |
| 17            | 45               | 44         | 42               | 47         | 13                                                      | 9          |
| 18            | 46               | 45         | 41               | 46         | 13                                                      | 9          |

terminated Ca<sup>2+</sup>:Mg<sup>2+</sup>:Fe<sup>2+</sup> ratios; one (13) is in poor agreement; and six give widely disparate results.

Of these six samples, five (12, 14, 15, 17, and 18) are pyroxenes from the basic rocks characterized by high total Al<sup>3+</sup> contents (average =0.194). Of the various pyroxenes studied by Brown, one of the two samples (specimen H, Table 2, Brown, 1960) that failed to match the curves also had an abnormally high Al<sup>3+</sup> content (0.214). This suggests, therefore, that high total Al<sup>3+</sup> content so modifies the critical *b* and *a sin β* dimensions that these parameters cannot be used. Brown (1960, p. 27) implied this by indicating that his determinative diagram was to be used for those common clinopyroxenes with "average amounts of minor constituents." And Viswanathan (1966, p. 441), commenting on the usefulness of his modification of Brown's correlation diagram, cautions that it applies to those common clinopyroxenes containing "minor amounts" of such components as "Fe<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, MnO, Na<sub>2</sub>O, K<sub>2</sub>O, Li<sub>2</sub>O, TiO<sub>2</sub> and Cr<sub>2</sub>O<sub>3</sub>." For the Little Belt clinopyroxenes the critical Al<sub>2</sub>O<sub>3</sub> content seems to be about 3 percent. Above that figure the unit cell dimensions

TABLE 5. ATOMIC PERCENTAGES OF MAJOR CONSTITUENTS, IONS PER CELL, AND UNIT CELL PARAMETERS OF CLINOPYROXENES FROM INTERMEDIATE AND BASIC ROCKS

| Ident<br>no.<br>(See<br>table 2)       | Atomic percentage |                  |                  | Ions per cell    |                  | Cell parameters |           |          |                 |                   |                                | Degrees<br>of<br>freedom |
|----------------------------------------|-------------------|------------------|------------------|------------------|------------------|-----------------|-----------|----------|-----------------|-------------------|--------------------------------|--------------------------|
|                                        | Ca <sup>2+</sup>  | Mg <sup>2+</sup> | Fe <sup>3+</sup> | Al <sup>IV</sup> | Al <sup>VI</sup> | a, Å            | b, Å      | c, Å     | $\beta$         | a sin $\beta$ , Å | Cell<br>volume, Å <sup>3</sup> |                          |
|                                        |                   |                  |                  |                  |                  |                 |           |          |                 |                   |                                |                          |
| Clinopyroxenes from intermediate rocks |                   |                  |                  |                  |                  |                 |           |          |                 |                   |                                |                          |
| 3                                      | 45.1              | 42.1             | 12.8             | 0.060            | 0.014            | 9.722(2)        | 8.932(3)  | 5.378(2) | 74°43'<br>±2.1' | 9.378             | 450.5(2)                       | 9                        |
| 5                                      | 47.1              | 42.9             | 10.0             | .040             | .067             | 9.768(13)       | 8.935(18) | 5.250(4) | 74°43'<br>+6.0' | 9.422             | 442.0(9)                       | 4                        |
| 10                                     | 46.6              | 42.3             | 11.1             | .055             | .035             | 9.672(4)        | 9.000(3)  | 5.341(2) | 73°32'<br>±1.6' | 0.275             | 445.9(2)                       | 8                        |
| Clinopyroxenes from basic rocks        |                   |                  |                  |                  |                  |                 |           |          |                 |                   |                                |                          |
| 12                                     | 47.7              | 44.5             | 7.8              | .133             | 0.051            | 9.812(5)        | 9.005(5)  | 5.252(3) | 75°19'<br>+3.0' | 9.491             | 448.9(3)                       | 6                        |
| 13                                     | 46.6              | 45.4             | 8.0              | .084             | .018             | 9.769(13)       | 8.964(13) | 5.290(3) | 75°24'<br>±6.3' | 9.453             | 448.2(5)                       | 6                        |
| 14                                     | 48.2              | 41.9             | 9.9              | .814             | .005             | 9.858(13)       | 8.758(18) | 5.296(5) | 75°32'<br>+4.0' | 9.546             | 442.7(5)                       | 7                        |
| 15                                     | 48.6              | 34.2             | 17.2             | .162             | .041             | 9.835(7)        | 9.007(8)  | 4.250(2) | 74°59'<br>+3.6' | 9.500             | 449.1(4)                       | 8                        |
| 17                                     | 45.0              | 48.1             | 6.9              | .205             | .132             | 9.815(6)        | 9.001(7)  | 5.241(3) | 75°10'<br>+3.0' | 9.488             | 447.6(3)                       | 6                        |
| 18                                     | 46.2              | 47.4             | 6.4              | .103             | .037             | 9.829(4)        | 8.986(5)  | 5.235(1) | 75°09'<br>±1.4' | 9.501             | 447.0(2)                       | 7                        |



may be so modified as to preclude their being compared with "common" clinopyroxenes.

Although there seems to be a correlation between high total  $Al^{3+}$  content and the spurious results, the amount of  $Al^{3+}$  in tetrahedral coordination may be the causative factor. Clearly the amounts of  $Al^{3+}$  in octahedral coordination are about the same in pyroxenes from both intermediate and basic rocks (B, Fig. 2; and Table 5). The major factor responsible for high total  $Al^{3+}$  in one set of pyroxenes and not the other is the amount of  $Al^{3+}$  in four-fold coordination. It seems to be the one factor common to most of the Little Belt pyroxenes that give unsatisfactory results. By contrast, the three samples that show some correlation with the compositional data contain relatively small proportions of  $Al^{3+}$  ion in four-fold coordination.

#### CLINOPYROXENES AND MAGMATIC DIFFERENTIATION

The presence of nearly identical pyroxenes in such diverse rocks as vogesite and rhyolite porphyry may substantiate, in part, the sequence of magmatic differentiation postulated by Larsen (1940) for the central Montana petrographic province. In essence, Larsen suggested that a basaltic parental magma differentiated slowly at depth by crystal settling to yield primary magmas, each of which characterized a specific subprovince in central Montana.

For the Little Belt Mountains subprovince, the differentiation sequence may have involved crystal settling, chiefly of plagioclase, olivine, and pyroxene to form a crystal-rich differentiate—the parental magma of the shonkinites and the other basic rocks. Clinopyroxenes from these intrusions contain much  $Al^{3+}$  ion in tetrahedral coordination. The crystal-poor differentiate, after assimilation of much siliceous material, became the parental magma which formed the bulk of the intrusions (Larsen, 1940, p. 943, 946). Clinopyroxenes from these bodies reflect the siliceous nature of such a host magma in that they contain large proportions of  $Si^{4+}$  ion and correspondingly small proportions of  $Al^{3+}$  ion in four-fold coordination.

#### CONCLUSIONS

The Little Belt clinopyroxenes are much alike whether from such silicic rocks as rhyolite porphyry, or such basic rocks as vogesite.

Although the clinopyroxenes from intermediate and basic rocks contain almost identical proportions of the major constituents  $Ca^{2+}$ ,  $Mg^{2+}$ , and  $(Fe^{2+} + Fe^{3+} + Mn^{2+})$ , they differ sharply in their content of  $Al_2O_3$ . The pyroxenes from the intermediate rocks have less than 2.5 percent  $Al_2O_3$ ; those from basic rocks have much more. This extreme variation in  $Al_2O_3$  content does not seem to be reflected by their optical properties.

The proportion of  $Al^{3+}$  ion in tetrahedral coordination is also different. Pyroxenes from intermediate rocks contain low  $Al_z$  percentages (average  $\sim 2.6$  percent), whereas those from subsilicic rocks are characterized by high  $Al_z$  percentages (average  $\sim 7.3$  percent). The Si:Al relations in the Z group probably mirror the molecular concentration of  $SiO_2$  in the parent magma.

The amount of  $Al^{3+}$  ion in octahedral coordination fails to show this sharp distinction—the average contents of  $Al^{VI}$  are about equal when pyroxenes from intermediate and basic rocks are compared.

New optical property curves, based upon the determined chemical and optical data, are believed to be suitable for predicting the composition of clinopyroxenes from the Barker quadrangle. It is unknown whether they are also suitable for clinopyroxenes from the other mountain complexes in central Montana.

If Viswanathan's (1966, Fig. 3) modification of Brown's (1960, Fig. 5) correlation diagram, based on the unit-cell parameters  $b$  and  $a \sin \beta$ , is used to estimate composition, in terms of  $Ca^{2+}$ ,  $Mg^{2+}$ , and  $Fe^{2+}$ , the results are unsatisfactory. Only some pyroxenes from the intermediate rocks containing low percentages of  $Al_z$  give consistent results.

The close similarity of pyroxenes from widely disparate rock types implies a genetic relationship of the parent magmas. As Larsen (1940) suggests, a parental magma probably differentiated by crystal settling into two primary magmas: a crystal-rich mafic differentiate consisting of plagioclase, olivine, and pyroxene, and a crystal-poor residue. The crystal-rich differentiate is the parent magma of the basic rocks, the shonkinites, syenites, and vogesites. The crystal-poor differentiate, after assimilation of much siliceous material, gave rise to the intermediate rocks; the stock, the laccoliths, and their related sills and dikes. Those clinopyroxenes from the basic rocks show the silica-deficiency of their parent magma as high  $Al_z$  percentages; those from quartz-bearing rocks show the silica oversaturation as low  $Al_z$  percentages.

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## APPENDIX

MINERAL SEPARATION TECHNIQUES, LABORATORY PROCEDURES AND  
OPTICAL DETERMINATIONS

*Concentration techniques.* The clinopyroxenes were concentrated into pure mineral separates by use of both methylene iodide heavy liquid and magnetic techniques. The crushed rocks were sieved and two fractions were retained: the  $-100$  and  $+120$  size for use in the optical studies and the  $-120 +200$  fraction for mineral separation purposes. After washing, both fractions were boiled for a few minutes in a solution of dilute hydrochloric acid and then immersed in the bath of an ultrasonic vibrator for a minute or two. Freed impurities, mainly limonite particles, were decanted, and the samples were then rewashed and dried. The  $-100 +120$  fraction was set aside; the  $-120 +200$  fraction was processed through methylene iodide several times to separate lighter impurities from the heavier pyroxene-rich fraction using centrifuge separation procedures much as described by Schoen and Lee (1964). After drying, magnetite was removed from the heavy separate by use of a hand magnet, and the remaining material was then cycled through a Frantz isodynamic magnetic separator several times to remove such minerals as ilmenite, olivine, apatite, sphene, and other minor accessories. For most of the samples a setting of forward tilt  $35^\circ$ , side tilt  $20^\circ$  and an amperage of 0.08 resulted in a separate estimated on the basis of grid counts to be 96–98 percent pure clinopyroxene.

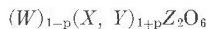
*Atomic absorption spectroscopy.*—Splits of the nine monomineralic separates were submitted to the U. S. Geological Survey laboratories in Denver, Colorado for analysis by atomic absorption spectroscopy. These splits, ranging in size from about a third of a gram to three grams, were analyzed for  $\text{Fe}_2\text{O}_3$ ,  $\text{MgO}$ ,  $\text{CaO}$ ,  $\text{Na}_2\text{O}$ ,  $\text{MnO}$ , and  $\text{Cr}_2\text{O}_3$  by Claude Huffman, Jr., and J. D. Mensik. Accuracy of the determinations is believed to be  $\pm 2$  percent of the amount reported for each element.

In atomic absorption spectroscopy total iron is reported as  $\text{Fe}_2\text{O}_3$ , and volumetric techniques were used, therefore, to determine the  $\text{FeO}$  values. From these values the  $\text{Fe}_2\text{O}_3$  percentages were then calculated. The  $\text{FeO}$  and  $\text{Fe}_2\text{O}_3$  determinations were made by H. H. Lipp, Violet Merritt, and Elsie Rowe of the Geological Survey, Denver laboratories.

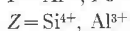
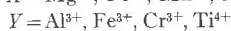
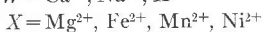
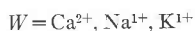
*Colorimetric analyses.*— $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  contents were furnished by G. T. Burrow using colorimetric techniques as described by Shapiro and Brannock (1962).  $\text{TiO}_2$  was determined by Claude Huffman, Jr., using the tiron colorimetric method described by Rader and Grimaldi (1961).

*Standard chemical analyses.*—Three splits of the pure separates were submitted for standard chemical analysis to check on the results and accuracy of the atomic absorption method. As the splits were small, only 10 of the constituents normally sought in an analysis of a silicate mineral were determined. These analyses, labeled "S.C.A." (*i.e.*, standard chemical analysis), are shown on Table 2. In general, there is good agreement between the results of the two methods. These analyses were made by George O. Riddle of the Geological Survey's Denver laboratories using procedures described by Peck (1964).

*Clinopyroxene formula.*—The theoretical formula for clinopyroxene, as modified by Hess (1949, p. 624), is:



Where



$p$  = Number obtained from analytical data.

Using this formula the theoretical structural formulas of the nine clinopyroxene separates have been determined (Table 2). The calculations were made by an IBM 360 series computer following computer-based procedures described by Jackson, Stevens, and Bowen (1967).

Hess (1949, p. 626) states that "If the chemical analysis is accurate and the material analyzed pure, the total number of ions in the Z group (Si+Al) will come within about 2 percent of equaling the total number of ions in the W+X+Y groups, and these will be in the ratio of 2:2:6 as compared to the total number of O ions." All analyses of the Little Belt clinopyroxenes satisfy the requirements of this test (Table 2).

*X-ray diffractometry techniques.*—A split of each pyroxene concentrate was ground under acetone in an agate mortar. An internal  $\text{CaF}_2$  standard was added, and the whole then thoroughly mixed. The resulting fine powder was dusted through a 200-mesh screen onto a collodion membrane stretched across the rectangular opening of a standard diffractometer sample mount. The powdered sample and mount were then covered with another collodion film to form a secure sandwich which prevented any spilling of the powdered sample. The membranes were prepared using techniques proposed by Gude and Hathaway (1961).

A Norelco X-ray diffractometer with  $\text{CuK}\alpha$  radiation was used in this phase of the work. Each sample was rotated through an angle of  $58^\circ$  ( $2^\circ$ – $60^\circ$ ) at a scanning speed of  $1/4^\circ$ – $2\theta$  per minute. For each sample the observed interplanar ( $d$ ) spacings were processed through the "Least-squares unit-cell refinement" program to determine the major cell parameters (Evans, Appleman, and Handwerker, 1963, p. 42–43).

*Optical determinations.* All optical data were obtained on single grains selected from the  $-100$  +120 fraction, and studied by spindle stage procedures described by Wilcox (1959), and by Wilcox and Izett (1968, p. 269–277).

The grains were examined under a binocular microscope; those selected for study were untwinned, free of surface stain, contained few inclusions, and displayed good prismatic cleavage on short stubby crystals. The selected grain was moved about on the end of a spindle needle until the optic plane was normal or almost normal to the needle. In this position it was possible to determine all the major optical characteristics except the extinction angle that  $Z$  makes with crystallographic  $c$ . All determinations of the refractive indices were made using the focal masking techniques described in detail by Cherkasov (1955a and b; 1957).

To determine the extinction angle  $Z/c$  the grain was removed from the spindle needle and remounted, so that its length, and hence crystallographic  $c$ , was collinear with the spindle needle. The  $Z$  vibration direction was then brought both horizontal and north-south by combined movement of both microscope stage and spindle needle. The angle between this position and the one in which the grain's length (crystallographic  $c$ ) paralleled the north-south crosshair gave the desired extinction angle.