STUDIES OF AMPHIBOLITES AND CONSTITUENT HORNBLENDES FROM AN AREA OF PROGRESSIVE METAMORPHISM NEAR LEAD, SOUTH DAKOTA

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ABSTRACT

The progressive metamorphism and origin of the amphibolites of the Lead-Deadwood area, S. Dakota, are considered in detail. Eighty specimens of amphibolite were collected along a belt 3 miles long extending across the entire garnet zone and part of the staurolite zone of the enclosing meta-sediments. These amphibolites were studied petrographically and from them thirty-four were used for modal analysis and chemical analyses for total iron (as Fe_2O_3), CaO, TiO_2, K_2O, MnO and trace elements. Twelve of the constituent hornblendes were analysed for all major and minor elements and trace elements. The other 22 constituent hornblendes were analysed for total iron (as Fe_2O_3), CaO, TiO_2, K_2O, MnO and trace elements. Seven of the constituent hornblendes and six constituent plagioclases were used for optical determinations and x-ray diffractometric studies.

On the basis of relict texture some of the amphibolites are concluded to be definitely ortho-amphibolites. Field relations of a few hornblende-bearing rocks suggest that they have meta-sedimentary origin. The origin of the remaining majority of the amphibolites is inconclusive.

The metamorphism of the amphibolites is essentially iso-chemical throughout the range of conditions represented by the appearance of successively the garnet and the staurolite isophases in the enclosing meta-sediments. What fluctuations in composition are observed appear to be random in character, attributable to minor variations in original composition or to retrograde alteration.

The compositions of the constituent hornblendes do not show

any significant correlation with intensity of metamorphism and the average composition remains roughly constant throughout the sequence.

The concentrations of the various components in the hornblendes seem to be closely related to the concentrations of the same components in the corresponding amphibolites. The ratios of the concentrations of the various components between hornblende and amphibolite do not show any significant trend with metamorphic rank and are reasonably constant over the range of metamorphic conditions represented here.

The composition of the hornblendes is closely related to specific gravity and broadly related to dimensions of unit cells but there is no close correlation between composition and optics. Size of unit cells in hornblendes appear to be unrelated to metamorphic rank.

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PART I

INTRODUCTORY PART

STATEMENT OF THE PROBLEM

Geochemical studies of metamorphic rocks and their constituent minerals have not been common. As a result, our knowledge of the effects of metamorphic processes on the distribution of elements and on the physical properties of rocks and minerals is very incomplete. Although the changes of phase that occur in various kinds of rocks under conditions of progressive metamorphism have been worked out in fair detail, studies on the exact chemical composition and physical properties of rocks and their constituent phases as they evolve through changing conditions of temperature, pressure and composition are, at present, inadequate. But this is precisely the kind of information necessary to resolve some of the major problems in metamorphic petrology, namely, the nature and extent of chemical mobilization caused by metamorphic processes, extent of the control of the bulk composition on the composition and stability of the constituent phases, the relative dominance of chemical composition and physical environment as a factor in the variation of physical properties of rocks and constituent minerals and so on. Instances have been reported where metamorphism has been concluded to be essentially isochemical (Shaw, 1956, p. 919-934) while in other instances marked chemical gradients have existed during metamorphism. These gradients have involved transfer and exchange of enormously large amount of materials over great distances (Engel and Engel, 1958, p. 1396-1403). It is possible that the two conclusions are not conflicting but are valid over two different regions of the metamorphic spectrum separated by some threshhold conditions at which large scale mobility of elements is possible.

The present study is an attempt to resolve a portion of the above mentioned problems in basic metamorphic rocks (amphibolites) of middle rank.

CHOICE OF THE FIELD AREA

The choice of a proper field area with the most favourable geological setting is of utmost importance for this kind of study. Besides the general considerations of accessibility and good outcrops, other primary requirements include the following: 1) an area of progressive metamorphism with at least several well-defined metamorphic zones; 2) presence of basic metamorphic rock in each of these zones distributed as evenly as possible; 3) excellent field and laboratory evidence indicating the original nature (especially composition) of the basic metamorphic rocks. This last named condition eliminates to a considerable degree the possibility that variations in composition of the rocks from place to place are wholly or in part due to original differences of composition rather than chemical mobilization caused by metamorphic processes*. The ideal situation would be in an area where one or more continuous metagabbroic dikes or sills cut across the metamorphic zones. The sills would, ideally, be thin enough to preclude the possibility of primary differentiation. An alternative unit might be a laterally continuous bed of mafic composition, which might be inferred to be constant in composition along the strike, prior to metamorphism. 4) The metamorphic history of the region must be simple. Areas of polymetamorphism and retrogression should be avoided. 5) The rocks should be fresh and coarsegrained and the constituent minerals as free of inclusions as possible.

A field area satisfying all these conditions is certainly not

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*The differences mentioned here are not the gross differences between rock types but the restricted differences in the composition of a similar rock type, which under similar conditions of metamorphism, evolves into the same or similar assemblages.

common. The area chosen on the basis of available information was a part of a pre-Cambrian inlier in the Northern Black Hills, in and around the Homestake Gold Mines, Lead, S. Dakota. Samples were collected from an area extending from near Kirk, a small hamlet near Lead, across the general area of the Homestake Mine in a NE direction to the town of Deadwood and slightly beyond--a distance of roughly three miles. Here a series of argillites (together with ankeritic and iron-magnesian carbonate rocks) with well-developed metamorphic zones (Noble and Harder, 1948) are associated with a series of amphibolites. Dodge, (1935, p. 214-222; 1942, p. 574) on the basis of structural and petrographic evidence, concluded that the amphibolites were metamorphosed gabbroic sills.

Three metamorphic zones, biolite, garnet and staurolite are represented in the argillites. The garnet zone is completely represented whereas the other two zones are only partially represented. Beyond the staurolite zone the metamorphosed rocks are covered by younger unmetamorphosed sediments. Samples of amphibolite collected for this study come mostly from various parts of the garnet zone. Only a few samples representative of the staurolite zone have been obtained, mostly from the cold end. The locations of the samples are shown in Plate I by numbers (e.g. A-1, A-2 and so on).

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The geological information and maps on the basis of which amphibolite samples were collected for this study, are primarily a product of the efforts of the Geology Department of the Homestake Mining Co. Most of the geological information and generalised maps are published (Noble et al., 1948, 1949). The detailed maps, including outcrop maps, prepared by the company mostly on 200' to the inch scale, are not meant for public information, but were very generously made available to the author. The geological map (Plate I) published with this dissertation has been compiled mostly from the maps prepared by the company. A few outcrops of amphibolite in the northeastern end, in areas not covered by the company geologists, were found by the author and are included in Plate I.

GENERAL GEOLOGICAL SETTING

The Black Hills are an oval, domelike structure with a core of metamorphosed pre-Cambrian rocks covering about a thousand square miles. The pre-Cambrian core is flanked on all sides by overlying, outward-dipping palaeozoic, mesozoic and tertiary sediments. On the north end of the pre-Cambrian core and separated from it by a band of tertiary intrusives, is a smaller inlier of pre-Cambrian crystalline schists, about 20 square miles in area. The area with which the present work is concerned lies in the eastern part of this smaller inlier and extends from Kirk, through the Homestake mine area and eastern part of Lead to the vicinity of the town of Deadwood--a distance of about 3 miles.

Amphibolites, the primary concern of the present investigation, occur as small and large lenticular masses enclosed in the various members of the pre-Cambrian meta-sedimentary schists. According to Dodge (1935, p. 214-222; 1942, p. 574) who studied their petrography and structural relations in detail, these amphibolites are the metamorphic equivalents of original gabbroic sills.

Since the geological history of the amphibolites is inseparably related to that of the enclosing rocks, it seems pertinent here to discuss briefly the salient features of the geology of the crystalline schists of the Lead-Deadwood area. For more detailed information the reader is referred to various publications mentioned in the following paragraph.

Over the last 60 years many authors have studied and discussed the geology of various parts of the Black Hills. The earlier publications that are more immediately concerned with the Lead-Deadwood area are those by Hosted and Wright (1923), Paige (1924), McLaughlin (1931), Gustafson (1933) and Dodge (1935, 1942). The latest and most detailed reports on the stratigraphy, structure and metamorphism of the pre-Cambrian rocks of this area are by Noble et al. (1948, 1949).

The synoptic stratigraphic column is given in Table 1.

The dominantly argillaceous pre-Cambrian rocks are characterised by progressive metamorphism seemingly like that described from the Scottish Highland (Barrow, 1893, 1912). Three well-defined zones, namely biotite, garnet and staurolite zones, are represented in the area. The zones run in a NW-SE direction across the area with rank of metamorphism increasing from SW to NE (see Plate I). Noble and Harder (1948) have mapped the metamorphic zones in great detail and have studied the mineralogical evolution of the different rock types involved. The impure iron-magnesian carbonate rocks represented in the biotite zone by sideroplesite schists (quartz, sericite and sideroplesite) evolve into cummingtonite schists in the garnet and staurolite zones.

The dominant structure of the pre-Cambrian rocks is a series of extremely tight, complex folds (Noble et al, 1949, p. 324-325). These folds are best defined by the comparatively thin Homestake formation which is easily distinguishable by its

Table 1

Synoptic Stratigraphic Column In Lead-Deadwood Area

Unmetamorphosed		Tertiary, Quarternary and Recent gravel deposits
		----------------- Unconformity -----------------------
	Tertiary:	Intrusive rocks--Acid porphyries
	Cambrian:	Deadwood formation (300 to 500 ft.)- conglomerate, quartzite, dolomite, shale (in part glauconitic)
		----------------- Unconformity -----------------------
Metamorphosed	Pre-Cambrian	Basic Intrusives (amphibolites)
		Grizzly formation (possibly 3000 ft. or more)- dominantly argillaceous
		Flagrock formation (possibly 5000 ft.)- heterogeneous with argillites, impersistent quartzites and few thin impersistent impure iron-magnesian carbonate beds
		---Unconformity-----------------------
		Northwestern formation (possibly 4000 ft.)- dominantly argillaceous
		Ellison formation (3000 to 5000 ft.)- argillites and quartzites with a single bed of impure iron-magnesian carbonate
		Homestake formation (200 to 300 ft.)- dominantly impure iron-magnesian carbonate rocks; mineralised
		Poorman formation (possibly 2000 ft. or more)- dominantly argillaceous with a few thin impersistent beds of impure iron-magnesian carbonate

Base not seen----------

unique composition. The axial planes of the major anticlines and synclines strike a little west of north except in the northeastern part of the area where they strike north or a few degrees east of north; the folds are for the most part isoclinal; their axial planes and limbs dip about 65° E or ENE (see Plate I). The direction of plunge of the folds changes from SSE in the southwestern part of the area to about due S in the northeastern part. The amount of plunge of the folds is about 10° to 15° in the southwestern part of the area but increases gradually to about 45° in the northeastern part.

Superposed on these major isoclinal folds at an angle to their axes, are a series of lesser "cross folds" which have given the outcrops of the limbs a peculiar sinuous appearance in plan. As a consequence of "cross folding" some very narrow isoclinal folds became so tightly closed that some formations became detached into lenticular masses.

No major fault with large displacement is known in the general area of the Homestake mine (Noble et al., 1949, p. 325). The most important fault, traceable throughout the whole length of the mapped area, is in the eastern part of the district. It strikes a little west of north and dips probably eastward at a steep angle. The vertical displacement on this fault ranges from about 120 feet in the southern edge of the mapped area to about 600 feet at the northern end, the eastern side being the upthrown side (see Plate I). Another fault in the southwestern edge of the map, near Whitewood Creek, has a displacement of about 100 feet and has offset several limbs of the Homestake formation. Other faults show no appreciable offset in the pre-Cambrian formations. Most of the important faults are tertiary in age. Several of the larger tertiary porphyry dikes are intruded along these fault planes.

There is evidence from underground mapping that the surface of the garnet isophase dips towards WSW at an angle of about 45° (oral communication from G. C. Mathisrud, Geology Department, Homestake Mining Co.). This conclusion is also corroborated by the shapes of the surface trace of the garnet isophase across the Deadwood and Whitewood Creeks (see Plate I).

NOMENCLATURE

The outcrops mapped as amphibolites by the Homestake Mine geologists, or shown as amphibolites in the maps of Dodge (1935) and Noble et al. (1948, Plate I) include hornblende-bearing rocks with considerable variation in composition and proportion of minerals. All of these rocks are referred to as amphibolites and a great majority of them are dominated by hornblende-plagioclase. Extreme types such as quartz-biotite schists or calcite-epidote-chlorite schists with only minor or accessory hornblende have also been mapped as amphibolites. The reason for doing so was to facilitate field mapping. But if we adhere to the definition of amphibolite as a hornblende-plagioclase (oligoclase-andesine) rock with other minerals only as accessories, then some of these outcrops should not be called amphibolites; nor is it valid to argue that all these rocks should be grouped together because they are derived from the same kind of parent rock. Available evidence suggests two or more parent rocks may be involved.

Since the map attached to this report has been prepared mainly from the maps supplied by the Homestake Company the nomenclature of the original workers is preserved on the map. The variations in mineral composition and mineral proportion which suggest diverse parentage for some of the amphibolites will be pointed out in the descriptive part of the report.

DISTRIBUTION AND FIELD RELATIONS OF THE AMPHIBOLITES

The distribution and structural relations of the amphibolites have been described by Dodge (1935, 76-87). In the Lead-Deadwood area most of the amphibolites are confined to the eastern half of the area mapped. A majority of them are enclosed in the Flagrock formation, although some are in Northwestern formation and a few occur in the Grizzly formation. There is one outcrop of amphibolite in the Poorman formation near Central City. In the underground mines amphibolites are common in the Poorman, Homestake and Ellison formations.

The amphibolite bodies are discontinuous and occur as lenticular masses enclosed in the schists. The visible contacts between amphibolites and enclosing schists are sharp. In every instance where the contact can be seen or surmised, the amphibolites are found to be concordant with the schists. Some of the amphibolites wrap around folds. After a detailed investigation for any cross-cutting relationship Dodge (1942, p. 567) notes that

> "a most careful search for such relationship in the Lead area has proved fruitless although on a large scale certain bodies appear to be cross-cutting".

The last part of Dodge's statement is probably based on the inferred irregular shape of some of the larger bodies in the southeastern part of the area; the argument being that if these bodies are really of this shape then on a smaller scale they most be cross-cutting the schists somewhere even though the contacts showing this relation are not exposed. A certain amount of interpretation is involved in any statement of size and shape of the three large bodies of amphibolites shown in the southeastern part of the map. The size and shape of these bodies would depend on the extent to which one wishes to interpolate between outcrops. Without changing the known detailed outcrop data each of these same bodies can be interpreted as one or more bodies of more regular lenticular shape conformably enclosed in the schists.

Since it is intended in a later section of this report to discuss the origin of the amphibolites in the light of integrated evidence from field, petrographic and chemical viewpoints, further details of structural relations of the amphibolites are omitted here.

SCOPE OF THE WORK

Eighty samples of amphibolite were collected from as many outcrops. Samples of other rock types in the area were not collected but some hand specimens and thin sections of these rocks from the collection of the Homestake Mining Company were studied by the author.

After examining the thin sections of the 80 specimens of amphibolite, 34 specimens were chosen on the basis of freshness, coarseness of grain size, lack of inclusions in the constituent grains and evenness of distribution over the area. These were used for the following operations and studies:

1) Modes of the rocks
2) Separation of about 15 gms. of clean hornblende mineral from each of the rocks
3) Separation of about 8 gms. each of plagioclase from 6 of the rocks
4) Wet chemical analyses for major and minor elements of 12 hornblende samples
5) Analyses for Fe, Ca, Ti, Mn and K in 22 hornblende samples by fluorescent x-ray spectrometric method. (Analyses of Si, Al and Mg were also attempted but results were unsatisfactory.)
6) Analyses for Fe, Ca, Ti, Mn and K in 34 amphibolites by fluorescent x-ray spectrometric method
7) Analyses of 34 hornblendes for trace elements by emission spectrographic method
8) Analyses of 34 amphibolites for trace elements by emission spectrographic method

9) Determination of Mg-Fe contents of 22 hornblendes by emission spectrographic method
10) X-ray diffractometric studies on 5 hornblende and 6 plagioclase samples
11) Determination of the specific gravities of 10 hornblende samples
12) Optical properties of 7 hornblende and 6 plagioclase samples

Attempts have been made to decipher any possible relation between the chemical compositions of the minerals and their optical data, specific gravities and crystal-structure data; and finally the relations of the chemical and physical properties of the rocks and their component minerals to metamorphism are discussed.

PART II

AMPHIBOLITES

GENERAL PETROGRAPHY

The petrography of the amphibolites of the Lead-Deadwood area has been described by Dodge (1935, p. 88-155) and need not be repeated. Only a few salient textural and mineralogic characters will be mentioned here. A purely descriptive classification, based on texture, mineralogy, size and shape of grains of the amphibolites will be attempted. Wherever the characteristics of the classes are genetically significant, these will be pointed out.

There are several amphibolites in the area which show textural evidence of derivation from basic igneous rocks. These are:

Class I - a) A-49, A-52
b) A-16, A-18, A-23, A-31, A-32
c) A-26, A-27
d) A-54

The common group characteristics are palimsest gabbroid or diabasic texture, high content of accessories ilmenite and apatite and deep bluish green color of hornblendes.

Class I-a is very coarse-grained with hornblende crystals averaging 5 to 6 mm length and 2 mm in width. A large part of the plagioclase is also as coarse grains while the rest occurs as mosaics of finer grains evolved from single crystals. Most of the large grains of plagioclase show twinning. The twin lamellae have somewhat irregular outlines and the twinning in parts of some grains is either destroyed or shadowy due to recrystallisation. Many of the plagioclase grains occur as large randomly oriented laths. Others form more equidimensional grains. The texture of the rock as a whole is gabbroid. A little biotite and chlorite replace hornblende.

Class I-b is texturally pretty much the same as Class I-a but is somewhat finer grained and has more slender laths of plagioclase. The laths are intergrown with themselves and with hornblendes in typical sub-ophitic texture of diabases and fine-grained gabbros. The average grain size of the hornblendes in this group is about 3 m.m. by 2 m.m. Apatite is common as euhedral and subhedral grains completely enclosed in hornblende. Much of the hornblendes in this group contain cores of ilmenite in a lattice-work pattern. The cores are usually bounded by straight edges parallel to the straight boundaries of the hornblende grains. The cores make up most of the hornblende crystals with a rim of opaque-free hornblende (or chlorite or biotite where these replace hornblende) around the lattice work.

Class I-c is compositionally and texturally very similar to Class I-b but is finer grained.

Class I-d contains more hornblende and less twinned lath-shaped plagioclase and ilmenite than other members of Class I. The grain size is comparable to that of Class I-b. In this group the gabbroid or diabasic texture is not as obvious as in the other members of Class I, but still quite recognisable.

No quartz was recognised in any member of Class I.

A second class of amphibolites which are similar in appearance, grain size, mineralogy and textural characteristics comprise the following specimens:

Class II - A-38, A-40, A-41, A-63, A-64, A-65, A-66,
A-68, A-72, A-73, A-75, A-76, A-77, A-78,

A-79, A-80.

Like members of Class I the members of this class are also characterised by numerous accessory grains of ilmenite and apatite and by deep color of the hornblendes. The rocks of Class II differ from those of Class I by lack of any relict gabbroid or diabasic texture. In contrast to the members of Class I and Class II, all other amphibolites in the Lead-Deadwood area contain considerably less ilmenite and apatite by volume and their hornblendes are much lighter in color than the hornblendes of Class I and Class II (except A-64). Because of the differences in color the hornblendes of Class I and II can easily be distinguished from the lighter colored hornblendes of other classes.

The hornblende grains in Class II amphibolites are generally 2 to 3 m.m. long and 1 to 1.5 m.m. wide. A-66 is somewhat finer grained than the rest. No twinned lath-shaped plagioclase is found in this class but some of the thin sections show a few grains of small equidimensional twinned plagioclase. All members of this class except A-64, A-65, A-72, A-73 and A-80 are garnetiferous. Biotite, present in considerable amount in specimens A-66, A-68 and A-73, is clearly secondary after hornblende. Quartz is very difficult to distinguish from untwinned plagioclase but a rough statistical survey of optic figures in a number of grains in each thin section shows that quartz is present in some of the sections, but in a very minor amount.

The third class which includes the majority of the amphibolites in the area comprises the following specimens:

Class III - a) A-5, A-13, A-15, A-20, A-21, A-33, A-35, A-39, A-42, A-46, A-47, A-59, A-61, A-67, A-69

b) A-1, A-7, A-14, A-17, A-24, A-30, A-34, A-71

c) A-3, A-4, A-6, A-9, A-19, A-28, A-36, A-50, A-56, A-57, A-70, A-74

d) A-2, A-55, A-58

The four subdivisions in this class are entirely on the basis of size of the hornblende grains and do not connote any other major difference. In Class III-a the average size of the hornblendes is about 5 to 8 m.m. in length and 3 to 5 m.m. in width. In Class III-b the hornblendes are approximately of 3-5 m.m. by 1.5 to 2.5 m.m. size and in Class III-c they are approximately 2-3 m.m. by 1 to 1.5m.m. The sizes described here are the approximate size of the majority of hornblende grains in a thin section. Besides these, almost every section contains some needles and irregular grains of much smaller size than the average. These smaller grains, however, comprise only a small percent of the total volume of hornblende in the rock.

Class III is characterised by considerably lesser ilmenite and apatite than members of the previous classes. No garnet has been found in this group. In contrast to the hornblendes of the previous two classes, the hornblendes of this class are usually of remarkably light color. Hornblendes from A-1, A-2, A-4, A-5, A-7, A-33 and A-69 show a somewhat deeper greenish color than is common for this class but still are much lighter than hornblendes of Class I and Class II. The plagioclase in members of

Class III occurs as mosaic of fine to very fine grains around the much coarser hornblende crystals or as inclusions in the hornblendes. Twinned plagioclase is mostly absent or is very rare. It is difficult to estimate correctly the amount of quartz (if any) because of the difficulty of distinguishing it from untwinned plagioclase. A statistical examination of optic figures shows that quartz, if present, is a minor constituent in most of the specimens. Specimens A-1, A-3, A-4, A-7 and A-67 seem to have more quartz than others in this class but even in these quartz probably does not exceed a few volume percent. A-20, A-21, A-67 and A-69 contain some K-feldspar, probably metasomatically introduced. A-71 contains considerable biotite secondary after hornblende. A-70 is a banded rock with alternate layers of highly biotitic and biotite-free amphibolite. The thin section used for modal analysis for this specimen was cut from a biotite-free band and therefore the mode does not show any biotite (see Table 2) although the rock contains appreciable biotite.

Class IV includes the following specimens:

Class IV - A-22, A-25, A-43, A-44, A-45, A-48.

Mineralogically, in color of hornblendes and petrographically these amphibolites are very similar to those of Class III except that in them the hornblendes are of a distinct needlelike form rather than more or less equidimensional hornblendes characterising Class III.

Class V comprises the following specimens:

Class V - A-29, A-37, A-51, A-53, A-60, A-62

These are highly schistose quartz-rich hornblende-bearing rocks usually with considerable biotite. The amount of hornblende in these is considerably less than in the amphibolites described above. Some of the biotites in them is definitely secondary after hornblende but whether all of the biotites are derived from hornblende or not is not clear. As far as can be estimated from statistical examination of optic figures, these specimens contain at least 10 volume percent of quartz. The outcrops from which these specimens were collected are much more heterogeneous across the strike than in all other amphibolites. The heterogeneity gives rise to many thin bands in a single outcrop, and is due to differences in amount and grain size of biotite and hornblende. Three specimens collected by Dodge from the outcrop which yielded specimens A-51 and A-53 of the present collection, gave the following volume percents of hornblende, biotite, chlorite, quartz and plagioclase (1935, p. 146).

	(·21131)	(·21138)	(·21135)
Hornblende	60	35	6
Biotite	4	25	55
Chlorite	-	3	6
Quartz	12	17	17
Plagioclase	10	8	3

Hornblende in specimen A-37 is less than 10 percent by volume. Amounts of ilmenite and apatite in rocks of Class V are similar to those of Class III andIV and considerably less than those of Class I and II.

In the final class, to be called the 'Miscellaneous Class', are included the remaining four specimens which do not fit in any one of the above classes. It includes the following specimens:

Miscellaneous Class - A-8, A-10, A-11, A-12

Specimen A-11 is a very fine grained biotite-plagioclase rock with minor amounts of hornblende but no recognisable quartz. Other minor constituents are calcite, epidote and ilmenite. Biotite and plagioclase are by far the most dominant minerals. Specimen A-10 and A-12 are chlorite-plagioclase-calcite-epidote rocks with no hornblende. Chlorite is the dominant mineral. Specimen A-8 is a chlorite-plagioclase-epidote (zoisite)-calcite rock with considerable amount of a very pale bluish green amphibole.

Summarising the bearing of petrographic evidence detailed above, on the origin of the various types of amphibolites, it may be recalled that the amphibolites of Class I show definite textural evidence (relict gabbroid or diabasic texture) of derivation from basic igneous rocks. Mineralogically (though not texturally) and in color of hornblendes, the amphibolites of Class II are very similar to those of Class I. It is possible although not certain that these Class II amphibolites are also derived from basic igneous rocks and, in contrast to those of Class I, have undergone complete metamorphic reconstitution. The amphibolites of Class III and Class IV which are different from those of Classes I and II mineralogically and in color of hornblendes, do not show any particular evidence of their derivation. High quartz and biotite contents, heterogeneity of composition and field relations (to be discussed fully in a later section) of the Class V amphibolites suggest a meta-sedimentary rather than a meta-igneous origin.

MODAL ANALYSES

Modal analyses of 34 amphibolites were made from thin sections approximately 3/4 by 1 inch in size. These 34 amphibolites were chosen mainly on the basis of freshness, large grain size, lack of inclusions in hornblende and minimum retrograde effects. Some which do not entirely satisfy these specifications were also included to cover the various petrographic types encountered in the area. In specimens with strong lineation or foliation thin sections used for modal analyses were cut approximately normal to these linear or planar trends. In each thin section 1400 to 1500 points were counted with a point counter (Chayes F., 1949) adapted from a Leitz mechanical stage.

Since any quartz present could not be easily distinguished from untwinned plagioclase, particularly when they occur as fine-grained mosaic, plagioclase and quartz (if any) have been counted as one mineral*. But it is believed from qualitative examination of optic figures that quartz, when present, is a very minor constituent in this group of 34 amphibolites. Epidote, zoisite and sphene, when present, have been lumped together. In some thin sections chlorite occurs as very fine needles and it quite often becomes a matter of personal choice to decide whether the junction point of cross hairs is within or just outside the needle. In such circumstances, it is believed, there has been some tendency to exaggerate the count of small grains.

Modal analyses are given in Table 2.

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*Four specimens (A-20, A-21, A-67, A-69) contain K-feldspar. In modal analyses this has been lumped with plagioclase and quartz.

Table 2

Modes of Amphibolites

(in volume percent)

Sample No.	Feldspar + Quartz (if any)	Hornblende	Biotite	Chlorite	Garnet	Carbonate	Epidote + Zoisite + Sphene	Apatite	Ilmenite	Total
A-1	20.1	71.8		4.9		trace	0.8		2.4	100.0
A-3	14.9	74.0		4.8		1.2	1.9	0.3	2.8	99.9
A-5	18.3	55.2		22.7		0.4	0.4		3.1	100.1
A-7	14.4	77.3	1.3	2.2		trace	1.8	trace	3.0	100.0
A-13	20.6	73.2	trace	3.2		trace	1.5	trace	1.5	100.0
A-14	22.5	75.6	trace					trace	1.9	100.0
A-15	23.2	70.4		4.4			0.2		1.8	100.0
A-17	21.2	63.7		13.2				trace	1.9	100.0
A-20	*n.d.									
A-21	16.9	77.9		3.0					2.2	100.0
A-28	24.6	69.9		1.4		0.1			2.9	99.9
A-30	22.1	72.7	2.3	1.0			0.2		1.7	100.0
A-33	16.6	71.3		6.4		1.5	1.0	0.5	2.6	99.9
A-34	21.8	72.2		3.5			0.6		1.9	100.0

*n.d.--mode not determined.

Table 2 (Cont'd)

Sample No.	Feldspar + Quartz (if any)	Hornblende	Biotite	Chlorite	Garnet	Carbonate	Epidote + Zoisite + Sphene	Apatite	Ilmenite	Total
A-35	16.7	71.9		8.5		trace	trace	trace	2.9	100.0
A-36	26.3	67.6	0.2	2.6		0.4	0.8	0.2	2.0	100.1
A-39	21.8	70.1	trace	6.3			trace		1.8	100.0
A-46	15.1	75.2	0.9	5.7			trace	trace	3.1	100.0
A-50	15.7	80.0		0.6		0.2	1.1	0.1	3.4	100.1
A-52	47.2	35.8	2.8	0.1		7.2	1.0	0.7	5.3	100.1
A-57	26.5	67.2				3.1	1.2		2.0	100.0
A-58	22.6	75.3	trace	trace					2.1	100.0
A-59	18.2	78.8	0.7	0.1				trace	2.2	100.0
A-61	11.2	86.3					trace	trace	2.5	100.0
A-63	12.9	66.8		0.3	3.3	1.6	0.8	0.8	13.5	100.0
A-64	6.9	84.0		0.7		1.3	2.7	0.2	4.1	99.9
A-66	29.8	52.3	4.0		2.5	3.5		1.7	6.2	100.0
A-67	11.3	85.2		0.2		0.2	0.5	trace	2.6	100.0
A-68	16.9	46.4	20.5		trace	1.6	0.4	4.3	9.9	100.0
A-69	11.2	80.2				4.7			3.9	100.0
A-70	25.7	61.3		3.2		5.0	4.3		0.5	100.0
A-71	18.0	53.1	27.4			trace	trace		1.5	100.0
A-72	19.5	70.9	1.6			2.3	2.2	trace	3.5	100.0
A-78	23.2	63.6	trace	0.2	0.2	0.2	trace	2.1	10.6	100.1

CHEMICAL ANALYSES

To investigate (1) whether the petrographic classification detailed earlier is reflected in the bulk chemical compositions of the amphibolites, (2) whether chemical compositions may reflect origin and (3) in order to study the extent to which chemical composition of the amphibolites is a function of metamorphic conditions, 34 selected samples of amphibolites were analysed for 5 major and minor components and all trace elements. These are the same 34 samples for which modal analyses have been made. To study the effects of progressive metamorphic conditions on rock composition it is desirable to exclude specimens with relict textures (like those of Class I). In these rocks recrystallisation was very probably incomplete and hence the rock and minerals were not in equilibrium with the metamorphic environment. Only one specimen of Class I (A-52) has been analysed. Six specimens have been analysed from Class II. The other 27 specimens analysed belong to Class III.

Methods of sample preparation, methods and techniques used in chemical analyses and the data obtained are detailed in the following pages followed by discussions of the significance of the data.

Preparation of Samples

In all cases the material used for chemical analytical work was prepared from the same rock specimen from which a representative* thin section was made for petrographic study.

Each rock specimen, cleaned and dried, was first broken down to chips of 1 to 2 c.m. size on a steel plate. About 400 to 600 gms of these freshly broken chips--depending upon volume percent of hornblende--was then crushed by disintegration of rock chips between anvil-like slabs of the same rock sample. Crushing by machine was avoided to keep contamination of samples to a minimum. The resulting powder was screened through a 100 mesh sieve and the coarser fraction, up to about 0.2 m.m. size, was then further ground in an agate mortar and screened. The operation was repeated till the entire sample was brought down to -100 mesh size.

The entire -100 mesh fraction was then quartered down with a high purity aluminium microsplitter and about 12 gms of rock powder was split off for spectrochemical analyses.

The remaining bulk of the -100-mesh rock sample was then separated into three fractions, namely -100+150, -150+200 and -200-mesh sizes by screening with 150-mesh and 200-mesh sieves. Silk screens were used in all sizing operations to keep metallic contamination to a minimum.

Fluorescent X-ray Analyses For Five Major And Minor Components

Thirty-four amphibolites were analysed by fluorescent

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*Except in case of specimen A-70. It was a banded rock with alternate layers of biotite-rich and biotite-free amphibolite. The thin section in this case was prepared from a biotite-free band and was not representative of the rock as a whole. However, the rock powder used for chemical analyses was representative of the specimen as a whole.

x-ray spectrometric method for the following five components: Fe, Ca, Ti, K and Mn.

The methods and techniques used for fluorescent x-ray analysis are well known. The particular analytical conditions used in this laboratory for the analysis of basic silicate rocks and minerals were worked out by Mr. A. A. Chodos and his collaborators. These have already been published (Chodos et al., 1957).

The equipments used are as follows:

x-ray source -- Norelco (Tungsten target)
x-ray spectrograph -- Norelco
Analysing crystal -- Ammonium dihydrogen phosphate (2D = 10.648)
Collimator -- 0.02"
Counter -- Flow proportional; P-10 gas flow 0.02 cu.ft./hr.
Helium path for analysis of lighter elements -- flow 1 litre/minute
Linear amplifier -- Atomic Instruments, Model 510
Scaler -- Baird Atomic Model 134
High voltage power supply for counter -- Hamner Model N401
Sample holder -- Norelco polyethylene powder holder, sample cavity 35 x 22 x 1 m.m.

The following emission lines were used for analysis:

Element	Line
Fe	Kα (1.934 Å)
Ca	Kα (3.353 Å)
Ti	Kα (2.745 Å)

K	$K\alpha$ (3.735 Å)
Mn	$K\alpha 2^{o}$ (2.100 Å)

The second order reflection of Mn-line was used due to Fe $K\alpha$ interference in the first order.

2θ values for each element were determined empirically modifying them slightly from the theoretical Bragg angles due to slight errors in orientation of the analysing crystal.

Great care was taken in the choice of conditions for pulse height analysis. The base line and window settings of the analyser were chosen in such a manner that there was no other element with any portion of its energy distribution lying at or near the window edges. The settings were determined empirically for each element, using pure salts of the element as samples. Pulse height analyser was not used in the case of Fe and Ca. These two elements are present in amphibolites in amounts sufficient to give high intensities and background determinations are not necessary although they were routinely made.

The parameter of analysis was total intensity of the characteristic radiation from a sample of standard thickness and shape. The intensity was measured by making a fixed number of counts, measuring the time and calculating the counting rate. Background was measured at 1.0 to 1.5 degrees 2θ away from the peak on either side (a fixed location of measurement being chosen for each element). In all cases background was subtracted from the peak intensity to obtain net intensity of the characteristic radiation.

Potential complication from interelement effects in the matrix was simplified and largely eliminated by working within the limited concentration range of one rock type (amphibolite) and by using chemically analysed standards. Eight analysed amphibolites were used as standards for Ti, Ca and K; five were used for Mn and six for Fe. The standards were chosen to obtain maximum possible range in each element. The analysed amphibolite pulps used as standards were kindly loaned by Prof. A. E. J. Engel. These were amphibolites from the Grenville-like rocks (Northwest Adirondacks, N. Y.) analysed by Mrs. C. G. Engel.

To obtain precise and reproducible results rigid control of the electronics is absolutely necessary. The detector is both flow and pressure sensitive and undoubtedly contributes to the instabilities but probably the most important source of error is the high voltage dependence of the gas amplification. The instrument used, which was modified by the addition of a high voltage stabilizer, has approximately a stability of ± 0.01%. Supplies to the pulse height analyser, the high speed electronics and the filament of the preamplifier were also stabilized. With these modifications the drift in the pulse height was less than 0.5 volts per day and this drift could be easily compensated.

Instrument stability over a period of several hours was found to be very good. But there were some slight day to day shifts which were adjusted for each day (and every several hours, if necessary) by running a standard rock slab of amphibolite and making necessary adjustment of the high voltage and milliampere. By these adjustments conditions between samples in one set of determinations were kept at a certain chosen constant.

The importance of particle size in fluorescent x-ray analysis has been discussed by Claisse (1956). In this laboratory analyses by Mr. Chodos (Chodos et al., 1957) of a sample of amphibolite ground to successively finer fractions below 100 mesh showed an increase in the Fe/Ca intensity ratio which did not level off until minus 200 mesh material was ground about 1 hour in an automatic grinder. All analyses of amphibolites given in this report were made using extremely fine material. Twelve gms of representative minus 100 mesh rock powder were split off from 400 to 600 gms of each specimen and crushed to minus 100 mesh size. The 12 grams were first ground for 15 minutes and then approximately 3 gms were split off from it with the help of a pure aluminum microsplitter. This latter fraction was then ground for 2 1/2 hours in an automatic grinder (agate) and the resulting pulp was used for analysis. Each pulp sample was pressed into the shallow cavity of a sample holder and the surface carefully smoothed off with the help of a spatula.

To check reproducibility the standards were run twice, each time with a different pulp pack, ten days apart. The conditions in one case were a little different from the other thus giving somewhat different counts per second for the same sample in the two different runs; but the between-sample conditions in each run of the group were kept at a constant. The unknowns were analysed with the second run of the standards.

All working curves were drawn on the basis of least square calculations. The standard deviation of the wet chemical data, from the fluorescence data for each element in each run of the standards, was calculated. Two working curves for each element are shown in figures 1 to 10 together with the standard deviation in each case. The analytical values of the amphibolites are given in Table 3.

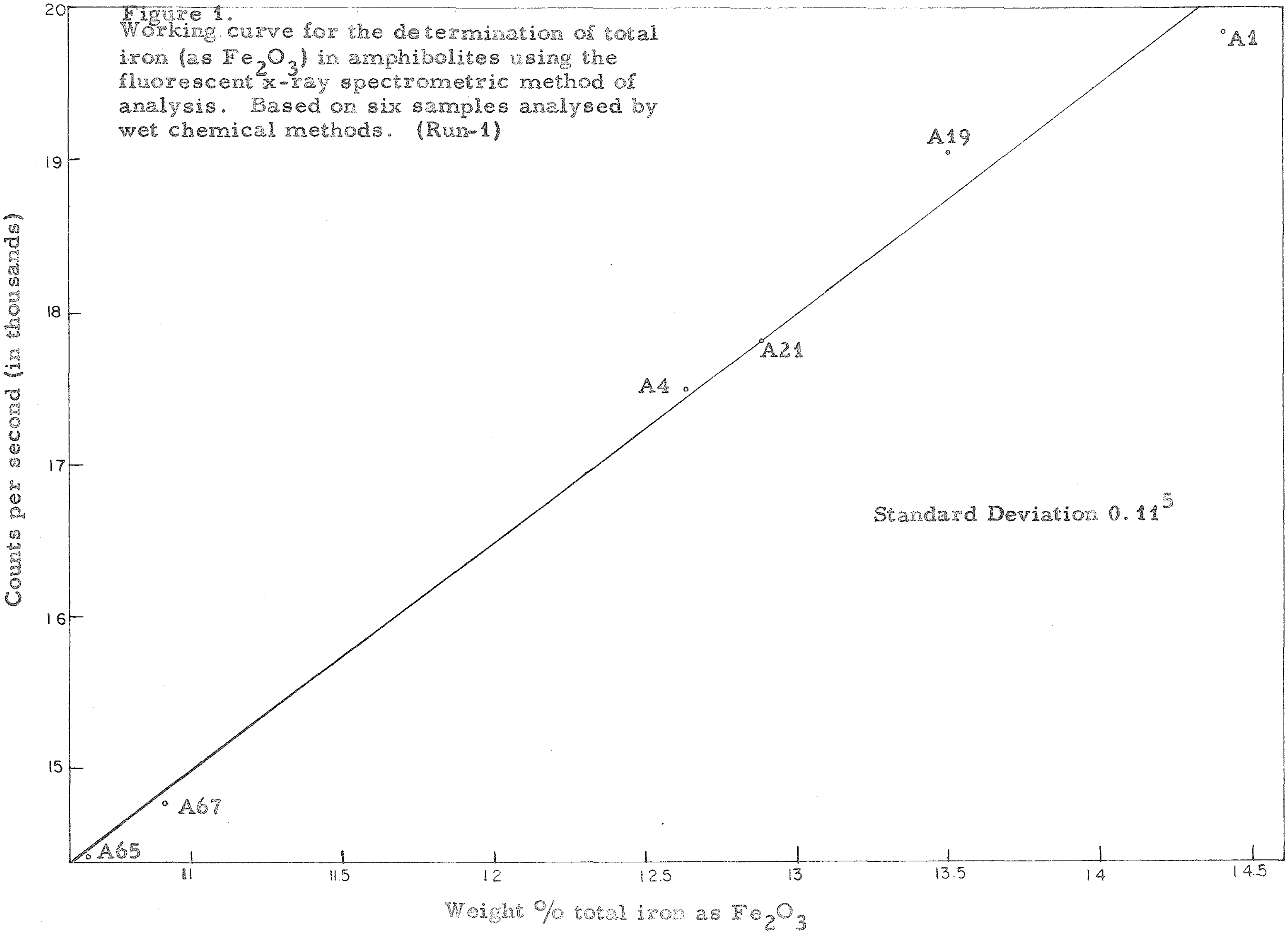
As can be seen from the standard deviations, the agreement between wet chemical and fluorescence data is excellent. The variations are, in most cases, comparable to the usual variations between duplicate wet chemical analyses of the same sample.

The reproducibility of the fluorescent analyses is also excellent. For each of the five major and minor components analysed, the average amount (present in the standards) and the mean of the variations between the values of two runs of the standards are given below.

Component	Average amount (in wt. %)	Mean variation (in wt. %)
Fe_2O_3	12.50 (Range 10.66-14.40)	0.02^{3}
CaO	10.18 (Range 7.96-12.76	0.05^{7}
TiO_2	1.31 (Range 0.99-1.60)	0.01^{1}
K_2O	1.44 (Range 0.35-2.29)	0.03^{6}
MnO	0.24 (Range 0.14-0.35)	0.00^{8}

Again the differences between duplicate analyses by fluorescent x-ray method are comparable to differences between duplicate wet chemical analyses.

Figure 1.
Working curve for the determination of total iron (as Fe_2O_3) in amphibolites using the fluorescent x-ray spectrometric method of analysis. Based on six samples analysed by wet chemical methods. (Run-1)



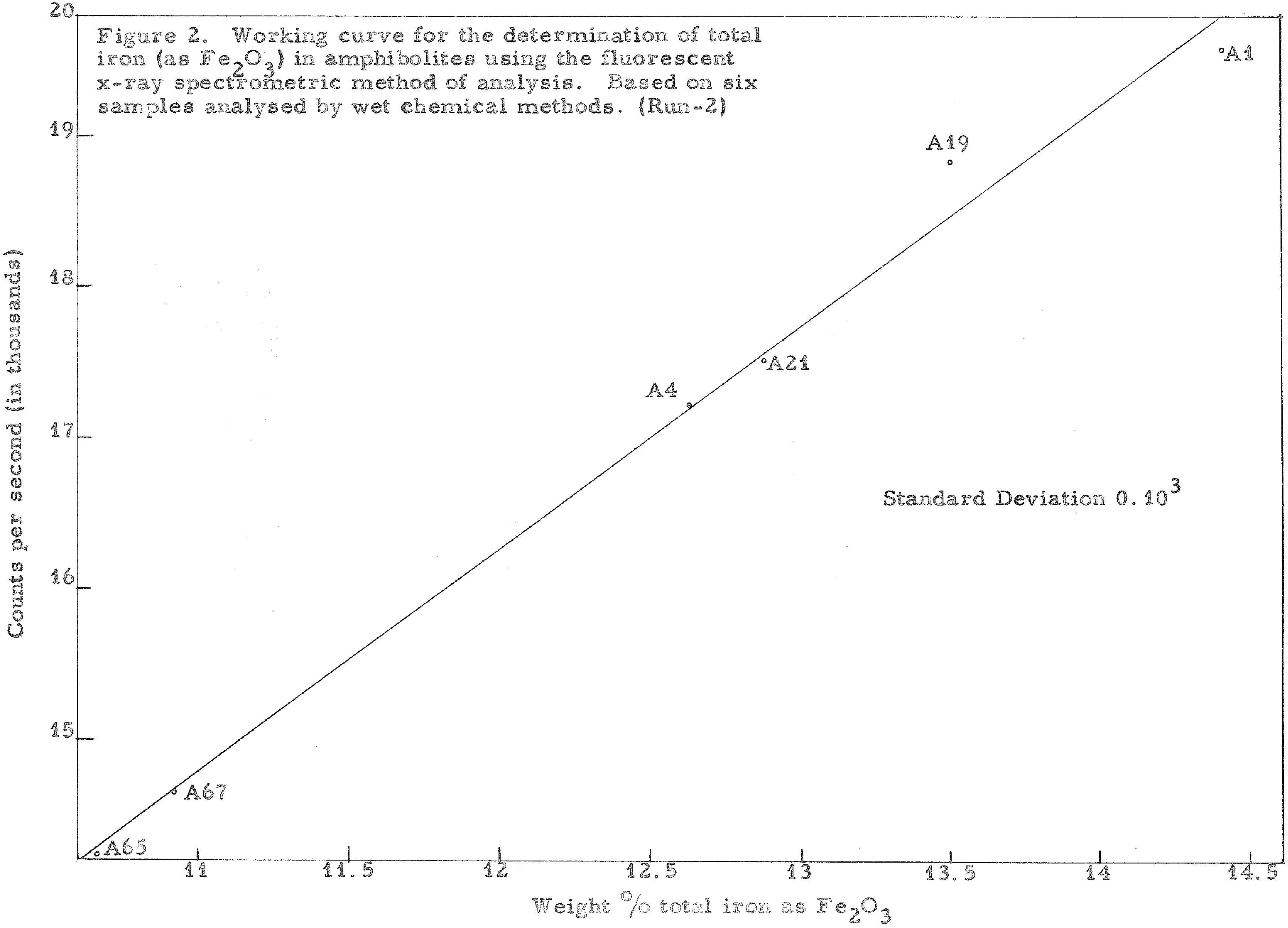


Figure 2. Working curve for the determination of total iron (as Fe_2O_3) in amphibolites using the fluorescent x-ray spectrometric method of analysis. Based on six samples analysed by wet chemical methods. (Run-2)

Figure 3. Working curve for the determination of CaO in amphibolites using the fluorescent x-ray spectrometric method of analysis. Based on eight samples analysed by wet chemical methods. (Run-1)

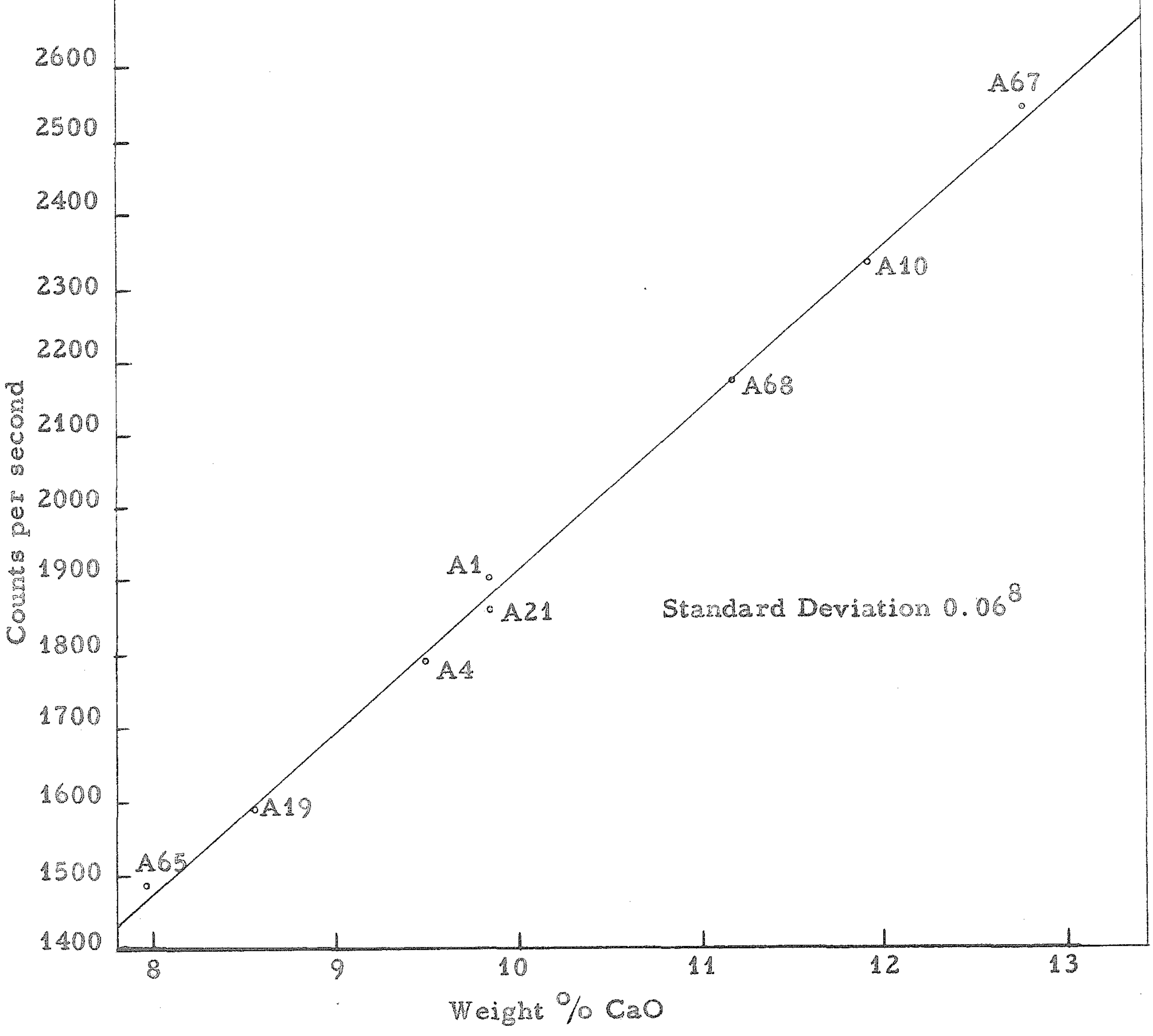


Figure 4. Working curve for the determination of CaO in amphibolites using the fluorescent x-ray spectrometric method of analysis. Based on eight samples analysed by wet chemical methods. (Run-2)

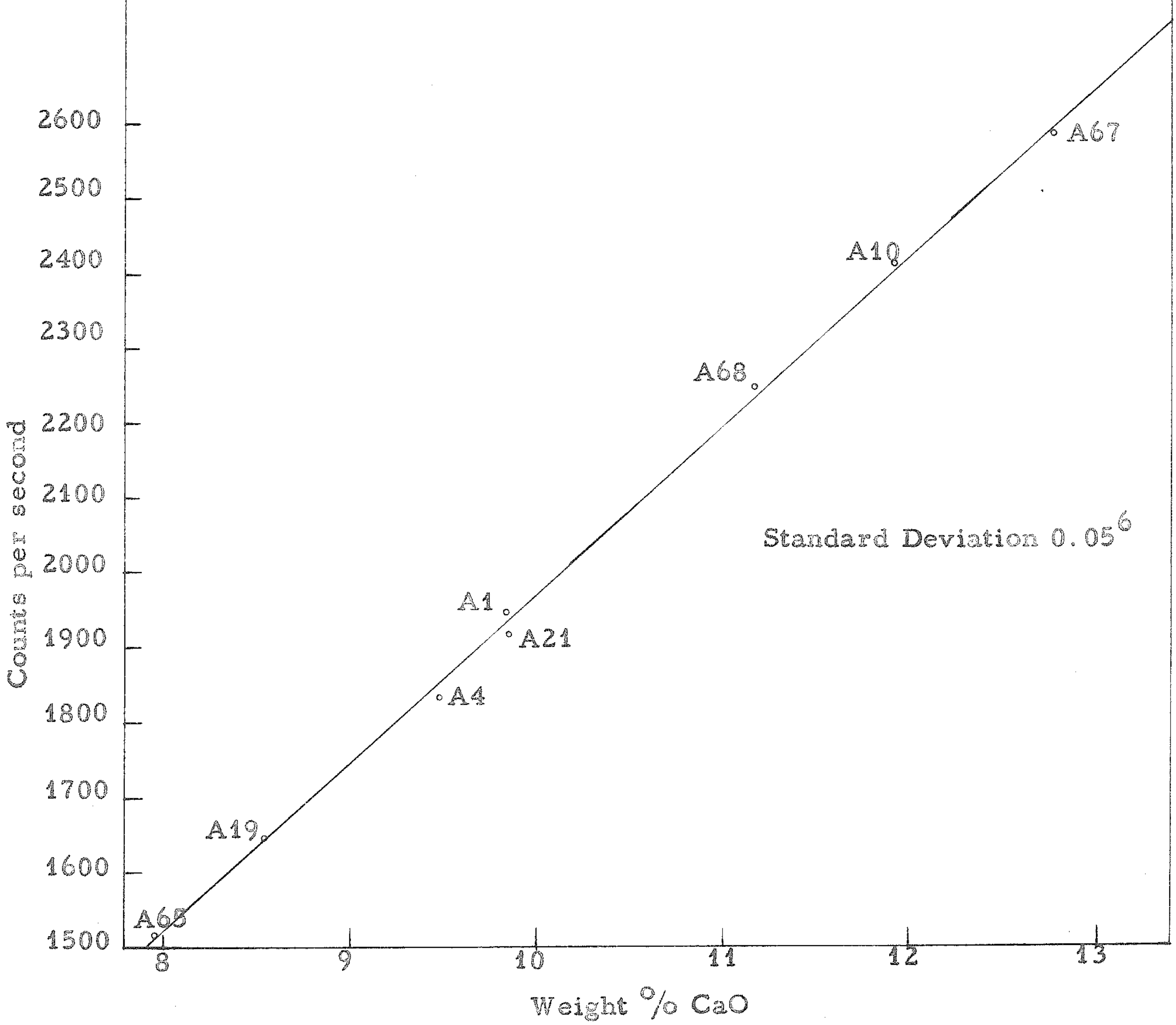


Figure 5. Working curve for the determination of TiO_2 in amphibolites using the fluorescent x-ray spectrometric method of analysis. Based on eight samples analysed by wet chemical methods. (Run-1)

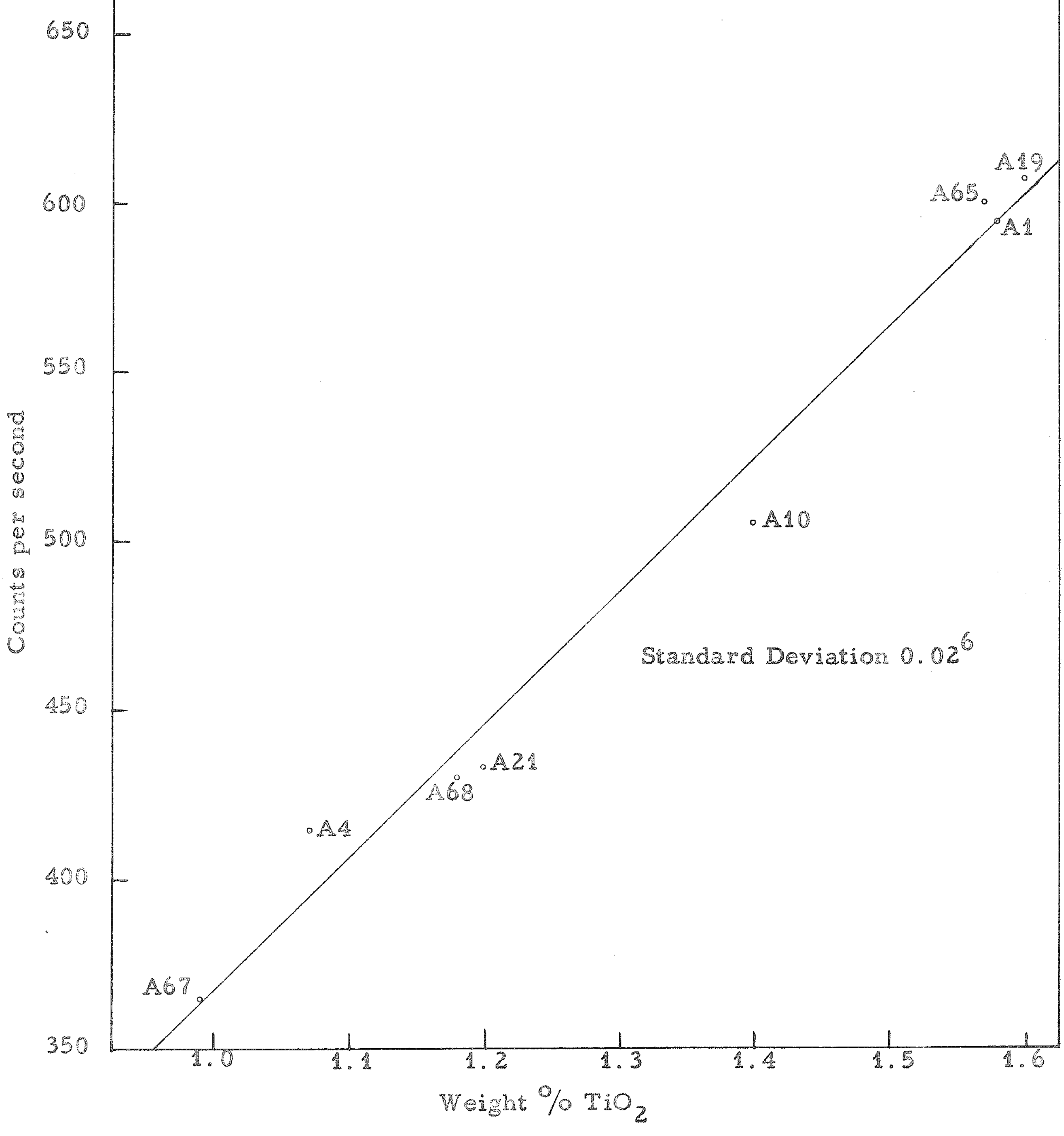
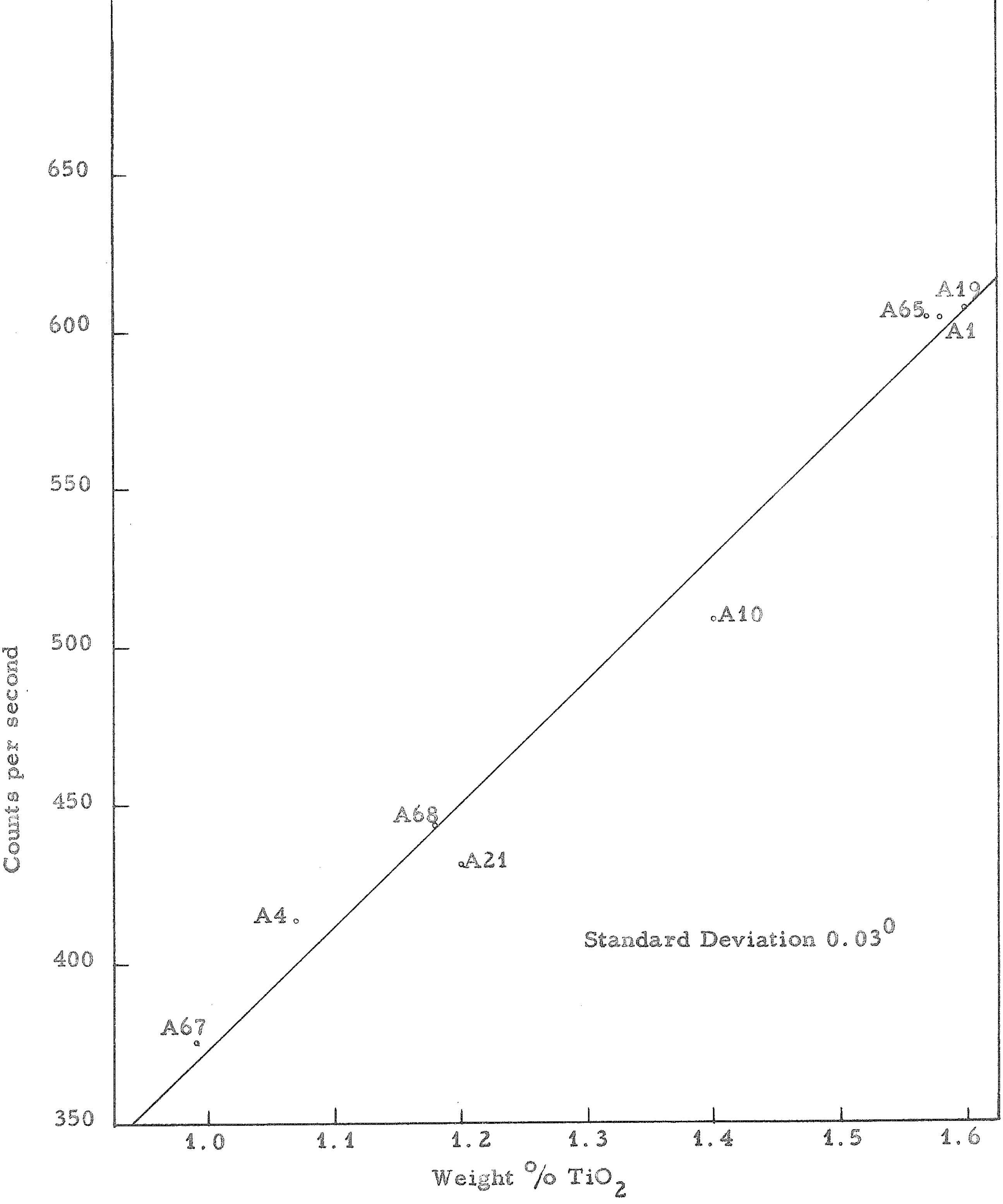


Figure 6. Working curve for the determination of TiO_2 in amphibolites using fluorescent x-ray spectrometric method of analysis. Based on eight samples analysed by wet chemical methods. (Run-2)



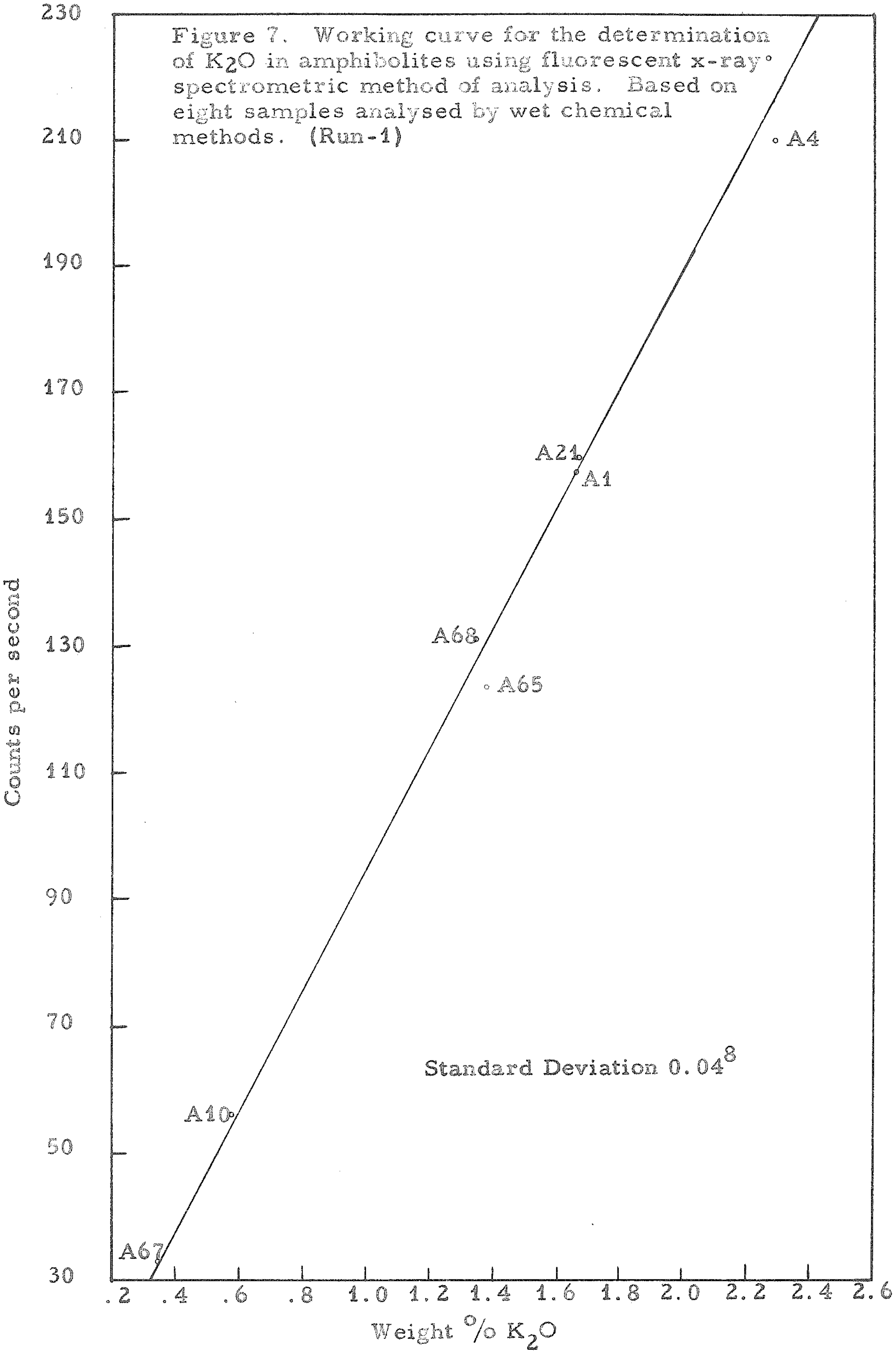


Figure 7. Working curve for the determination of K_2O in amphibolites using fluorescent x-ray spectrometric method of analysis. Based on eight samples analysed by wet chemical methods. (Run-1)

Standard Deviation 0.04[8]

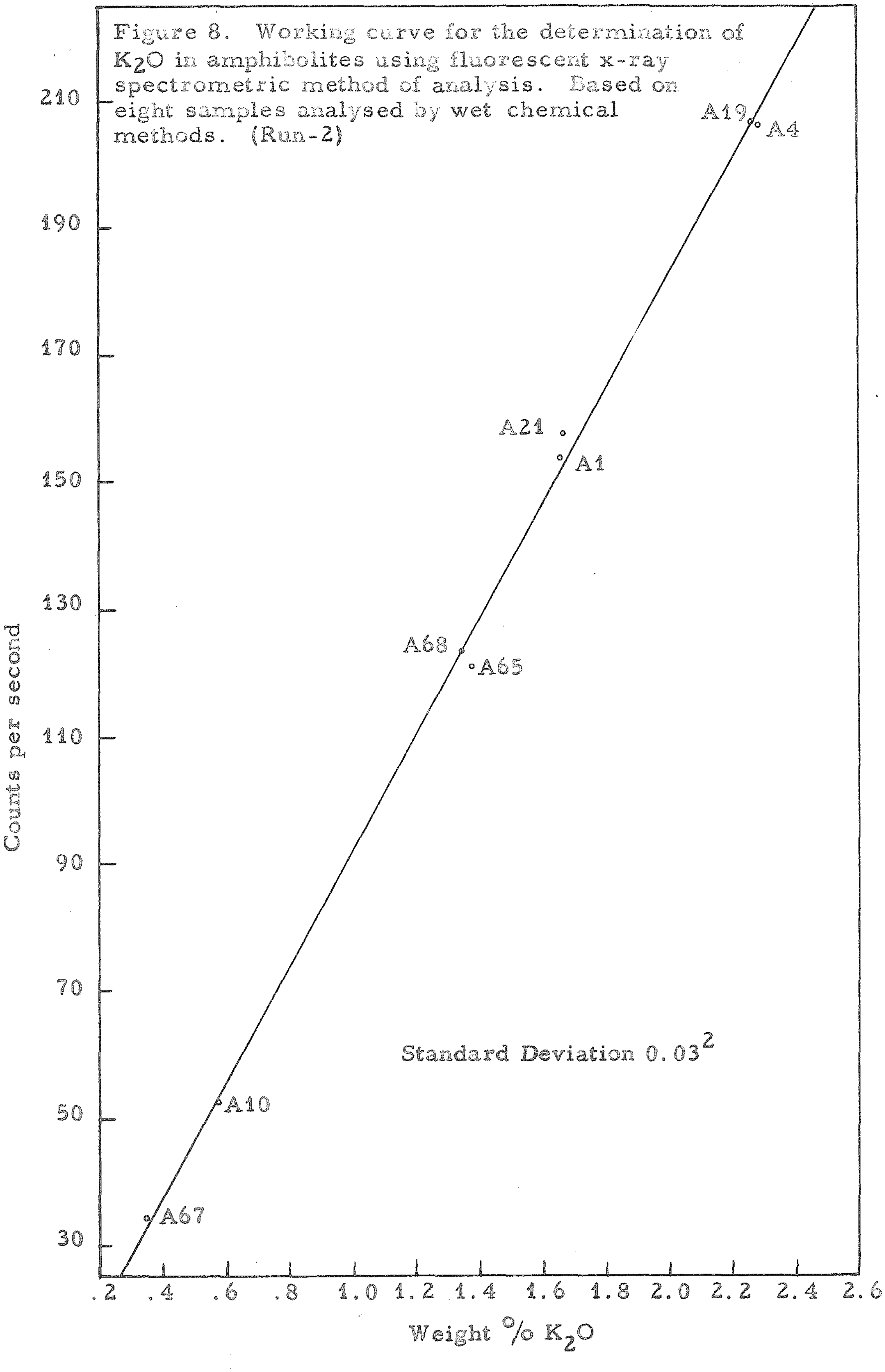


Figure 8. Working curve for the determination of K_2O in amphibolites using fluorescent x-ray spectrometric method of analysis. Based on eight samples analysed by wet chemical methods. (Run-2)

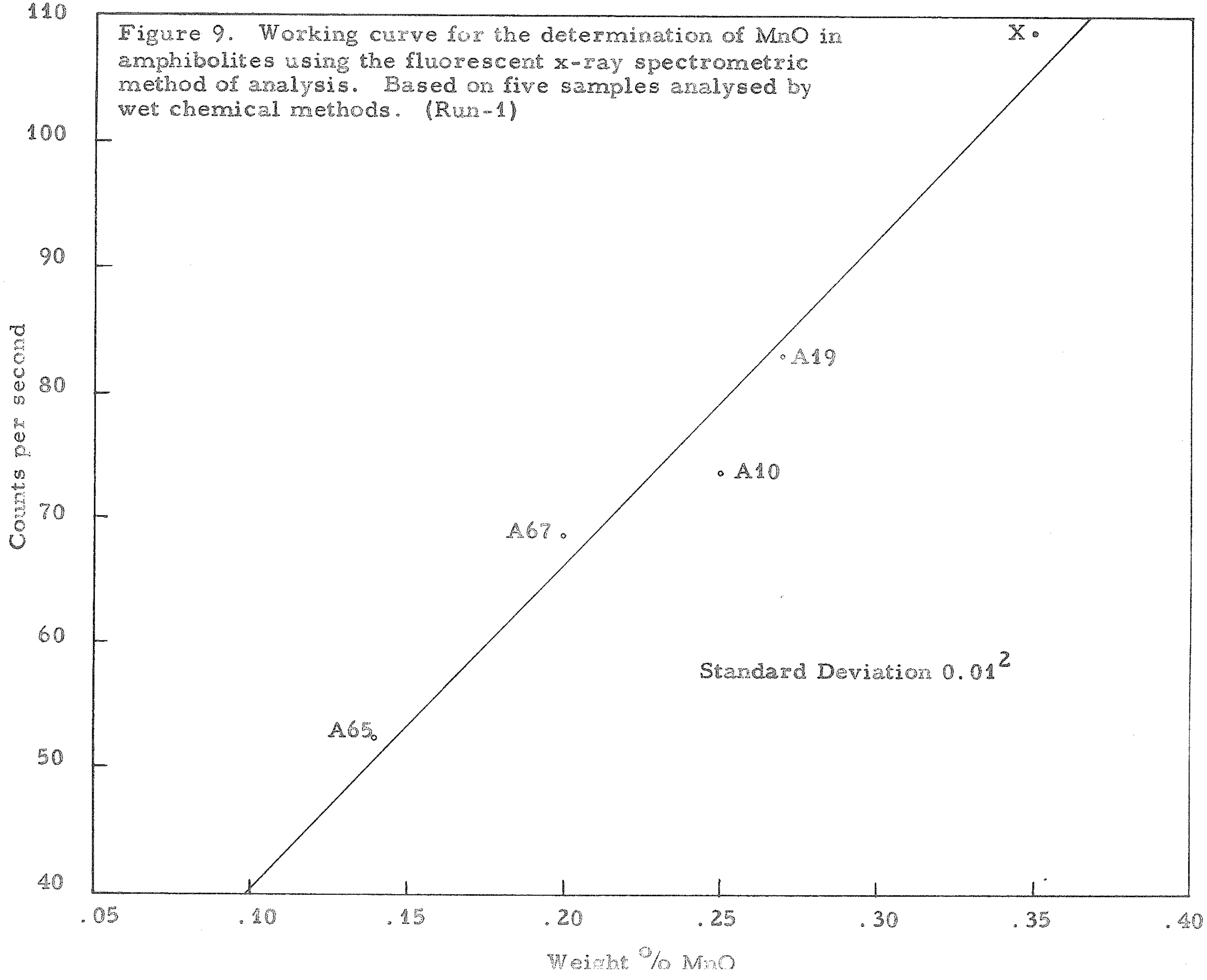


Figure 9. Working curve for the determination of MnO in amphibolites using the fluorescent x-ray spectrometric method of analysis. Based on five samples analysed by wet chemical methods. (Run-1)

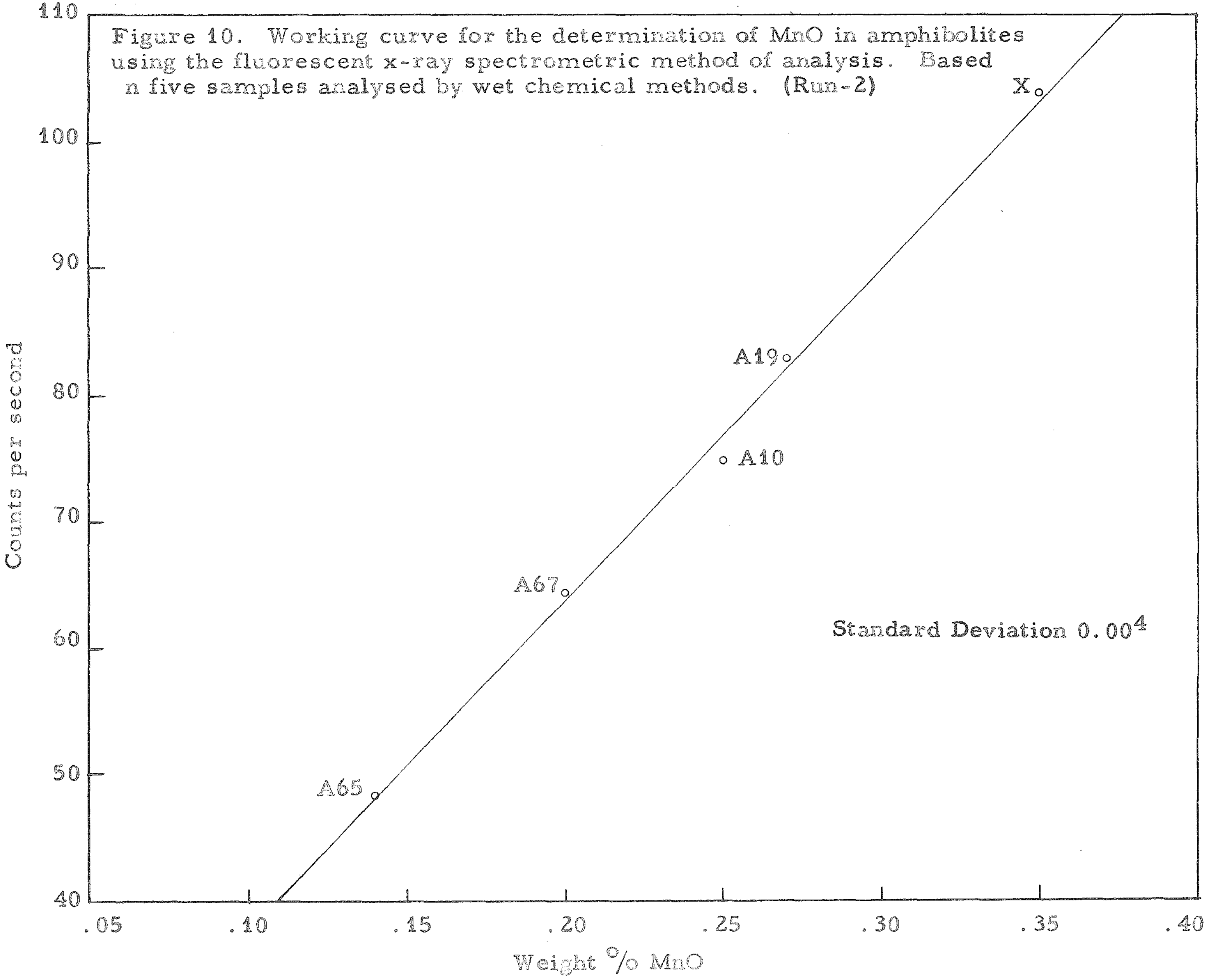


Figure 10. Working curve for the determination of MnO in amphibolites using the fluorescent x-ray spectrometric method of analysis. Based n five samples analysed by wet chemical methods. (Run-2)

Table 3

Five Major and Minor Components of Amphibolites

(in weight percent)

(Analysed by Fluorescent x-ray Spectrographic Method)

	Sample No.	Total Iron as Fe_2O_3	TiO_2	MnO	K_2O	CaO	
Class III	A-1	11.80	0.89	0.21	0.28	10.05	Low-TiO_2 Group
	A-3	13.07	0.88	0.17	0.30	10.42	
	A-5	13.61	0.92	0.18	0.35	8.97	
	A-7	11.90	0.79	0.19	0.31	11.46	
	A-13	12.79	0.86	0.20	0.24	10.53	
	A-14	13.07	0.87	0.21	0.22	10.62	
	A-15	12.79	0.80	0.20	0.20	10.65	
	A-17	13.73	0.90	0.18	0.34	8.79	
	A-20	13.12	0.86	0.22	0.93	10.82	
	A-21	13.30	0.90	0.20	0.67	10.61	
	A-28	11.46	0.95	0.17	0.21	10.67	
	A-30	13.54	0.92	0.20	0.26	9.59	
	A-33	13.09	0.84	0.20	0.20	10.26	
	A-34	12.55	0.92	0.20	0.22	10.79	
	A-35	12.97	0.87	0.20	0.31	10.03	
	A-36	12.65	0.84	0.20	0.23	9.88	
	A-39	11.74	0.70	0.18	0.25	11.26	
	A-46	12.49	0.88	0.21	0.21	11.42	
	A-50	13.19	0.80	0.23	0.22	10.15	
	A-57	12.00	0.80	0.18	0.44	12.74	
	A-58	12.69	0.67	0.19	0.16	9.72	
	A-59	12.59	0.82	0.20	0.21	11.41	

Table 3 (Cont'd)

	Sample No.	Total Iron as Fe_2O_3	TiO_2	MnO	K_2O	CaO	
	A-61	12.62	0.78	0.23	0.45	11.87	
	A-67	12.85	0.89	0.22	0.74	12.08	
	A-69	12.64	0.89	0.22	1.99	9.28	
	A-70	11.43	0.94	0.19	2.58	12.14	
	A-71	12.70	0.90	0.19	3.04	8.12	
Class I	A-52	9.85	1.82	0.16	0.23	9.58	High-TiO_2 Group
Class II	A-63	17.14	3.87	0.80	0.31	10.59	
	A-64	13.09	2.24	0.32	0.21	12.31	
	A-66	16.24	3.70	0.38	0.72	9.47	
	A-68	17.88	3.49	0.35	1.58	8.53	
	A-72	13.82	1.41	0.22	0.40	10.76	
	A-78	16.51	3.49	0.72	0.28	9.63	

Emission Spectrographic Analyses of Trace Elements

All the amphibolites analysed for major and minor elements by fluorescent x-ray method were also analysed for trace elements by an emission spectrographic method similar to that described by Murata (in Gordon and Murata, 1952). Minerals analysed chemically or pure oxides of elements mixed with a quartz-feldspar base (proportion of quartz to feldspar, 6:4) of known composition, were used as standards. Concentration steps of 10,000, 4640, 2150, and so on down to 2.15 ppm were prepared by dilution with the base and standard concentration vs. relative intensity curves were prepared. The emulsion was calibrated by means of a reference material which correlates the relative intensities of the unknowns to that of the working curves. This reference material was exposed in replicate on each plate. The equipment and methods used are as follows:

Spectrograph:	Jarrell-Ash 3.4 m grating instrument, Wardsworth mount, dispersion, 5.2 Å /mm. in the first order.
Excitation:	19-ampere short-circuit D.C. arc from a Jarrell-Ash Varisource. Sample as anode. Analytical gap, 4 mm magnified 5x and focused on the slit. Central 2 mm used with a slit width of 25 microns; 25 mg mixtures (4 sample: 1 pure graphite) were burned to completion. Total energy method with no internal standardization.

Electrodes: High purity one-quarter inch graphite rod as the anode. U.C.C. #3417. Pointed one-eighth inch cathode.

Wavelength Range: 2300-4800 A° in the first order.

Plates: Eastman Kodak III-O

Processing: 4 minutes in DK-50 developer at 20°C, 20 second short stop, 10 minutes in acid fix, 20 minutes wash.

Plate Calibration: Selected iron lines after method of Dieke and Crosswhite (Dieke and Crosswhite, 1943). Each plate is calibrated.

Densitometer: Applied Research Laboratories model #2250.

Each sample was exposed in duplicate and the values reported are an average of the two. Reproducibility is approximately 25 percent of the amount reported.

Matrix of the samples of amphibolite analysed are very different from the quartz-feldspar matrix of the standards used to prepare concentration vs. intensity curves. It is not known how far the difference in interelement effect--due to difference in matrix--would affect the absolute values of the analyses. But it is believed that the relative differences between samples are real since the effect of any matrix difference must be uniform for all samples.

The trace element analyses along with the sensitivities (i.e. average limit of detection) for the various elements are listed in Table 4.

Table 4

Trace Elements of Amphibolites

(in parts per million)

Analysed by Emission Spectrographic Method)

		Elements→	Ag	B	Ba	Co	Cr	Cu	Ge	Nb	Ni	Sb	Sc	Sr	V	Y	Zn	Zr
	Sample No.	Sensitivity→	0.5	10	1	2	5	1	20	15	2	200	2	2	2	10	80	2
Low TiO_2 Group	A-1	Class III	-	-	36	44	115	1	-	-	100	-	32	185	155	-	pt	37
	A-3		-	-	19	55	78	21	-	-	120	-	31	275	155	-	pt	33
	A-5		pt	-	14	85	130	70	-	-	190	-	38	190	235	13	pt	44
	A-7		-	-	26	81	96	68	-	-	240	-	30	225	205	13	pt	44
	A-13		-	-	52	61	125	52	-	-	140	-	31	300	305	26	pt	37
	A-14		pt	-	48	44	70	54	-	-	120	-	27	225	165	-	pt	29
	A-15		-	-	8	79	130	61	-	-	155	-	32	145	270	14	pt	37
	A-17		-	-	5	45	46	12	-	-	100	-	29	110	95	-	pt	24
	A-20		-	-	38	74	71	66	-	-	160	-	29	170	155	-	pt	27
	A-21		-	14	21	15	39	60	-	-	30	-	33	280	30	-	pt	pt
	A-28		-	-	26	59	115	3	-	-	120	-	30	190	265	15	pt	33
	A-30		-	-	52	59	68	27	-	-	115	-	32	150	155	-	pt	18
	A-33		pt	-	69	110	155	76	-	-	370	-	46	200	265	20	88	56
	A-34		-	-	13	67	96	1	-	-	190	-	43	155	200	18	pt	41
	A-35		-	-	15	56	62	36	-	-	100	-	29	230	120	-	pt	26
	A-36		-	-	71	66	170	88	-	-	160	-	37	205	335	14	pt	33
	A-39		-	-	51	86	105	36	-	-	300	-	30	245	135	-	pt	36
	A-46		-	-	26	84	96	6	-	-	195	-	33	235	285	pt	pt	48

Table 4 (Cont'd)

		Elements→	Ag	B	Ba	Co	Cr	Cu	Ge	Nb	Ni	Sb	Sc	Sr	V	Y	Zn	Zr
	Sample No. ↓	Sensitivity→	0.5	10	1	2	5	1	20	15	2	200	2	2	2	10	80	2
	A-50		pt	pt	21	105	125	27	-	-	275	-	33	205	295	13	pt	36
	A-57		-	-	8	54	66	32	-	-	120	-	23	225	85	-	pt	17
	A-58		-	-	10	43	62	1	-	-	85	-	25	145	135	19	pt	19
	A-59		pt	-	12	84	140	30	-	-	210	-	36	235	305	-	pt	42
	A-61		-	-	16	58	50	7	-	-	150	-	24	145	90	pt?	pt	27
	A-67		pt	25	92	65	135	38	-	-	195	-	39	155	245	pt	pt	49
	A-69		-	55	37	44	50	28	-	-	90	-	26	150	130	-	pt	29
	A-70		-	37	46	38	43	-	-	-	65	-	28	295	70	-	pt	24
	A-71		-	-	94	43	56	11	-	-	65	-	21	160	100	-	pt	pt
High TiO_2 Group	A-52	Class I	-	-	235	49	80	8	-	pt	85	-	34	765	260	31	92	260
	A-63	Class II	1.5	-	20	69	32	46	-	pt	15	-	41	370	820	35	134	155
	A-64		pt	pt	26	98	1400	74	65	pt	405	-	27	330	450	16	96	113
	A-66		-	-	130	28	6	1	-	pt	6	pt	27	190	130	47	100	175
	A-68		1	-	405	45	50	47	-	pt	10	-	45	460	285	71	136	185
	A-72		pt	-	30	71	180	105	-	pt	145	-	49	165	340	36	93	80
	A-78		1.5	-	13	39	39	10	-	pt	10	-	41	290	300	59	144	235

Also looked for but absent or below sensitivity: As, Au, Be, Bi, Cd, Ga, In, La, Mo, Pb, Pt, Sn, Th, U, Yb

'pt' means approximately at the level of sensitivity
'-' means absent or below sensitivity

ORIGIN OF THE AMPHIBOLITES IN THE LIGHT OF FIELD, PETROGRAPHIC AND CHEMICAL DATA

In the following discussion the various outcrops of the amphibolites would have to be referred to again and again. To avoid lengthy description of their locations in terms of geographical or geological reference points, the outcrops would be referred to simply by the numbers of the specimens collected from them. Since the locations from which the specimens were collected are indicated on the map (Plate I) serially from south to north, there will be no difficulty in finding the outcrops referred to.

The major problem in the origin of amphibolites is the distinction of ortho- from para-amphibolites. That there are ortho- and para-amphibolites was first conclusively proved by Adams and Barlow (Adams, 1909; Adams and Barlow, 1910) and has since been confirmed by many workers. But whether the amphibolites of a particular region are ortho- or para-amphibolites often becomes a highly debatable question in the absence of very obvious and definite evidence. If very direct evidence pointing to one or the other origin is absent, then there is so far no universally accepted and universally applicable criteria to settle the issue definitely.

Dodge (1935, p. 214-222; 1942, p. 574) and Noble et al. (1948, p. 965) believe that the amphibolites of the Lead-Deadwood area are all metamorphosed gabbros. They were impressed by the relict gabbroid and diabasic texture of some of the amphibolites (like members of Class I) and though no definite cross-cutting relations could be found, they point out that the amphibolite zone as a whole cross-cuts the structural trend and bedding at a low angle. In the present author's opinion the latter conclusion involves a considerable amount of interpretation and opinion.

As has been mentioned in the section of petrography, the amphibolites of Class I (A-16, A-18, A-23, A-26, A-27, A-31, A-32, A-49, A-52, A-54) showing palimpsest gabbroid and diabasic texture, are definitely derived from basic igneous rocks. Though this finding is in favour of a meta-igneous derivation for other amphibolite outcrops in the area because of their close spatial association, it is also significant that impure ferriferous carbonate sediments of the right bulk composition to to produce para-amphibolites, occur quite frequently in discontinuous beds and lenses in almost all the stratigraphic units (pre-Cambrian) in the area. Thus a meta-sedimentary origin for some of the amphibolites should at least be considered as a strong possibility.

In an area in which the structure is as complicated as the present one and with only a few impersistent horizon markers, it is not an easy task to reconstruct stratigraphic horizons. Nevertheless, there is at least one instance of stratigraphic continuity which probably is significant. Very close to the base of the Flagrock formation there is a zone, about 30 to 40 feet thick, consisting of thin bands of cummingtonite schists and amphibolites (or quartz-hornblende-biotite-plagioclase schists) in intimate association with pelitic schists and quartzites. This zone can be traced from the City Creek area in the northeast to a point east of Kirk in the southeastern part of the mapped area. Within this zone narrow (3 to 4 feet) bands of amphibolite or more commonly quartz-hornblende-biotite-plagioclase schist (e.g. A-37, A-51 and A-53 of Class V) adjoin bands of cummingtonite schist of similar thickness. In closely spaced outcrops along the strike the two types sometimes cannot be recognised separately and apparently merge into one or the other type. Thin, impersistent cummingtonite-bearing schists and quartzites may also be found in very close proximity to some of the larger bodies of amphibolites in the southeastern part of the area. In an outcrop in Whitewood Creek thin bands (1 to 4 feet) of amphibolite (e.g. A-43, A-44, A-45 of Class IV) occur in intimate association with thin bands of typical pelitic schists and there is no structural discordance between these bands. In the same outcrop two narrow bands, about 1 foot thick, of carbonate rock (about 80% calcite and 20% rounded quartz grains) occur in the amphibolite.

Several authors have attempted to distinguish ortho- from para-amphibolites on chemical basis. Lapadu-Hargues (1953) plotted the analyses of 89 amphibolites in terms of weight percentages of oxides against frequency of occurrence. He found that FeO, MgO, CaO and Na_2O showed bimodal distributions. The type lower in FeO and higher in CaO, MgO and Na_2O was designated by him as para-amphibolite. But the bimodal peaks for the four oxides used to characterise ortho- and para-amphibolites are not formed by the same rocks and the average olivine basalt of the Pacific , in terms of these four oxides, is identical with Lapadu-Hargues' 'type para-amphibolite' (Wilcox, et al, 1958,

p. 1362). A. E. J. Engel and C. G. Engel (1951, p. 1435) suggested that ortho- and para-amphibolites can be distinguished by their contents of nickel, cobalt and chromium, but they discarded the suggestion on the basis of later work (Engel, A. E. J., 1956, p. 84-85). Wilcox and Poldervaart (1958, p. 1351-1352, 1362-1363) working on the amphibolites of Bakersville-Roan Mountain area of North Carolina found that ortho- and para-amphibolites cannot be distinguished by their bulk chemical composition or by their contents of trace elements Cu, Ga, Ba, Ni, Co and Cr. They noted, however, that the 'Roan type' para-amphibolites as well as the 'Quad Creek' para-amphibolites of the Beartooth Mountains (Eckelmann and Poldervaart, 1957) have a considerably lower TiO_2 content than that of the metadolerites and 'Toecane-type' ortho-amphibolites of North Carolina. From a limited number of analyses (8 each) they also found that the average Sr content of the para-amphibolites (144 ppm, standard deviation 87) was lower than that of the ortho-amphibolites (478 ppm, standard deviation 64.8).

The major, minor and trace element compositions of the amphibolites of Lead-Deadwood area do not show any specific evidence pointing to a definite origin. The averages of their major, minor and trace element contents together with the compositional data of some basalts, gabbros and amphibolites collected from the literature for comparison, are given in Tables 5 and 6.

The 34 amphibolites of the Lead-Deadwood area have been divided into two groups on the basis of their chemistry and the

Table 5

Comparison of Compositions of Some Amphibolites, Basalts and Gabbros with Compositions (Partial) of Lead-Deadwood Amphibolites (in weight percent)

	1	2	3	4	5	6	7*	8*	9*	10*	11*	12*	13	14	15	16	17	18
SiO_2	50.00	50.83	46.25	47.25	47.33	47.38	47.9	48.7	49.7	51.2	50.3	47.1	45.78	48.36	43.94			
TiO_2	.82	1.10	1.83	1.97	1.62	1.40	2.9	2.4	.6	.6	1.6	3.0	2.63	1.32	2.86	2.86	.85	1.27
Al_2O_3	18.84	18.64	17.51	13.38	17.61	14.63	14.0	15.7	15.5	15.0	15.7	15.1	14.64	16.84	14.87			
Fe_2O_3	2.57	2.84	1.81	2.10	1.57	.66	3.8	2.6	1.7	2.0	3.6	3.7	3.16	2.55	4.35			
FeO	5.51	5.97	10.20	12.10	9.95	15.71	11.3	10.4	8.5	9.3	7.8	8.1	8.73	7.92	7.80			
MnO	.08	.10	.18	.26	.16	.15	.3	.2	.2	.2	.2	.2	.20	.18	.16	.42	.20	.25
MgO	4.63	4.90	9.34	7.52	7.39	9.07	6.4	6.2	10.0	8.8	7.0	7.9	9.39	8.06	9.31			
CaO	10.65	7.50	8.69	10.96	7.15	9.60	9.2	9.6	11.1	9.8	9.5	10.9	10.74	11.07	12.37	10.12	10.53	10.45
Na_2O	4.46	4.22	2.48	2.39	4.21	.64	2.9	2.8	2.3	2.2	2.9	2.7	2.63	2.26	2.32			
K_2O	1.18	1.83	.55	.61	.17	.78	.9	1.1	.3	.8	1.1	1.0	.95	.56	.92	(i) .28^6	(ii) .26^6	(iii) .27
P_2O_5			.28	.21	.15	n.d.	.4	.3	.1	.1	.3	.3	.39	.24	.44			
H_2O^+	1.00	1.40	.67	.92	1.10	.15							.76	.64	.66			
H_2O^-			.10	.07	.05	.60												
CO_2	.10	.11	.09	.16	1.18	.08												
Total			99.98			100.85	100.0	100.0	100.0	100.0	100.0	100.0						
Total iron as Fe_2O_3	8.69	9.47	13.14	15.54	12.62	18.11	16.4	14.2	11.1	12.3	12.3	12.7	13.0	11.35	13.02	(iv) 15.78	12.68	13.14

*Compositions reduced free of water and CO_2

Table 5 (Cont'd)

1. Amphibolite derived from marble of the “Grenville Series” and interlayered with marble at Maxwell's Crossing, Haliburton-Bancroft areas, Ontario (Adams and Burlow, 1910, p. 104, sample no. 2). Rock is composed of hornblende, pyroxene, plagioclase, scapolite and an “untwinned feldspar” with accessory sphene (ibid, p. 105).
2. Amphibolite “end stage” in amphibolization of marble, Haliburton-Bancroft areas, Ontario (Adams and Burlow, 1910, p. 104, sample no. 3). This amphibolite occurs as an inclusion in granite, in the same series of exposures as 1; mineral composition is hornblende, plagioclase and biotite (ibid, p. 105).
3. Garnetiferous meta-gabbro amphibolite, 2.5 miles ESE of St. Regis Falls, Nicolville Quadrangle, Adirondacks, N. Y., (Buddington, 1939, Table 44, No. 55, p. 185-186).
4. Amphibolite formed by interaction of fluids from granite upon clean dolomite of the “Grenville Series”, Gouverneur marble belt, 5.5 miles east of Gouverneur, N. Y. Composition-hornblende, clino-pyroxene, andesine with accessory biotite, quartz, magnetite and garnet (Engel, A. E. J., 1956, Table III, Specimen No. SK4-6, p. 86).
5. Feather amphibolite formed by skarnlike replacement of marble of the “Grenville Series”, 4.5 miles south of Bancroft, Ontario, from an area where all transitions exist between amphibolite and marble (Engel, A. E. J., 1956, Table III, Specimen No. FA-4, p. 86).
6. Ortho-amphibolite from the immediate neighbourhood of the Broken Hill Lode, New South Wales, Australia (Stillwell, F.L., 1922, p. 360, Specimen No. A-72). Mineral composition-hornblende and feldspar with accessory garnet, ores and apatite (ibid, p. 356).
7. Average of 8 Bakersville-Roan Mt. metadolerites (Wilcox and Poldervaart, 1958, p. 1351, table 6).
8. Average of 8 Toecane ortho-amphibolites (Wilcox and Poldervaart, 1958, p. 1351, table 6).
9. Average of 3 Roan type para-amphibolites (Wilcox and Poldervaart, 1958, p. 1351, table 6).
10. Average of 5 Quad Creek para-amphibolites (Eckelmann and Poldervaart, 1957, p. 1252).

Table 5 (Cont'd)

11. Average of 200 amphibolites (Poldervaart, 1955, p. 134).
12. Average Pacific olivine basalt (Green and Poldervaart, 1955, p. 185).
13. Average of 96 normal alkali basalts and dolerites (Nockolds, 1954, table 7, p. 1021).
14. Average of 160 gabbros (Nockolds, 1954, table 7, p. 1021).
15. Average of 42 alkali gabbros (Nockolds, 1954, table 7, p. 1021).
16. Average of 7 high-TiO_2 amphibolites (present study).
17. Average of 27 low-TiO_2 amphibolites (present study).
18. Average of all 34 amphibolites (present study).

(i) Average of 5 amphibolites - excludes specimens A-66 and A-68 which contain a considerable amount of retrograde biotite.

(ii) Average of 21 amphibolites - excludes specimens A-20, A-21, A-67, A-69, A-70, and A-71 containing retrograde biotite and/or metasomatically introduced K-feldspar.

(iii) Average of 26 amphibolites - excludes specimens A-20, A-21, A-66, A-67, A-68, A-69, A-70 and A-71 containing retrograde biotite and/or metasomatically introduced K-feldspar.

(iv) Average of 6 amphibolites - excludes specimen A-52 which is very low in iron.

Table 6

Comparison of Average Trace Element Contents of Lead-Deadwood Amphibolites with Those of Basic Igneous Rocks from Various Areas

		Ba		Co		Cr		Cu		Ni	
		Average	Range	Average	Range	Average	Range	Average	Range	Average	Range
High-TiO$_2$ Group (Present Study)		23	13-405	57	28-98	65 (i)	6-180	42	1-105	96	6-405
Low-TiO$_2$ Group (Present Study)		34	5-94	63	15-110	93	43-170	35	0-88	153	30-370
Both Groups Including (Present Study)		52	5-405	62	15-110	88	6-180	36	0-105	142	6-405
Ontario diabases (1)		280		40		220*		90	50-100	110	
Skaergaard (2)	Original magma	40									
	Dolerites and basalts	20									
	Gabbro										
Gabbros and dolerites (S. Lapland) (3)						410				45	
Mafic Rocks of Roslagen, Sweden (4)										65	
German Gabbro (5)											
Keweenawan basic flows (6)										180	
N. American diabases and basalts (7)				50							

Table 6 (Cont'd)

		Sc		Sr		V		Y		Zn		Zr	
		Average	Range	Average	Range	Average	Range	Average	Range	Average	Range	Average	Range
High TiO_2 Group (Present Study)		38	27-49	367	165-765	369	130-820	42	16-71	116	92-144	172	80-260
Low-TiO_2 Group (Present Study)		32	21-46	202	110-300	187	30-335	16	10-26	Pt(80)	Pt(88)	32 (ii)	17-56
Both Groups Including (Present Study)		33	21-49	235	110-765	223	30-820					60	17-260
Ontario diabases (1)		37		300		220						100	10-600
	Original magma			350								50	
Skaergaard (2)	Dolerites and basalts			100									
	Gabbro											30	
Gabbros and dolerites (S. Lapland) (3)		20		80		56							
Mafic Rocks of Roslagen, Sweden (4)				150		320							
German Gabbro (5)				170									
Keweenawan basic flows (6)													
N. American diabases and basalts (7)													

(i) Neglecting Specimen A-64 having concentration (1400 ppm) much too high compared to others
(ii) Neglecting 2 specimens having concentrations approximating sensitivity (i.e. 2 ppm)
*The average values for chromium in basic igneous rocks do not have the same significance as averages for many other constituents. Fairbairn et al. (1953) found extremely great scatter in chromium values of Ontario diabases.

(1) Fairbairn et al., 1953
(2) Wager and Mitchell, 1951
(3) Sahama, 1945
(4) Lundegardh, 1946
(5) Noll, 1934
(6) Sandell and Goldich, 1943
(7) Sandell and Goldich, 1943

two groups have been averaged separately and collectively. The high-TiO_2 group (7 samples) has a TiO_2 content more than three times that of the low-TiO_2 group (27 samples). In the latter group the TiO_2 content is very uniform and averages 0.85% (by wt.) while in the former it ranges from 1.82% to 3.87% and averages 2.86%. The high-TiO_2 amphibolites* are also considerably richer in total iron and MnO than those of the low-TiO_2 group.

The high-TiO_2 amphibolites also show some characteristic differences in contents of trace elements from the low-TiO_2 group. The Zr, Zn and Y contents of the high-TiO_2 group are distinctly and regularly higher than those of the low-TiO_2 group. The high-TiO_2 group shows presence of Nb while the low-TiO_2 group does not. Besides, the high-TiO_2 group is somewhat richer in average contents of V and Sr and poorer in average contents of Ni and Cr than the low-TiO_2 group. The trace element contents of the hornblendes from the high-TiO_2 amphibolites have similar differences from those of the low-TiO_2 amphibolites (see trace element contents of hornblendes, in Part III).

The TiO_2 content of the high-TiO_2 group (column 16) compares well with the average TiO_2 content of most basic igneous rocks and ortho-amphibolites (columns 7, 8, 12 and 13 of Table 5) while the TiO_2 content of the low-TiO_2 group (column 17) is not far from the average TiO_2 contents of most para-

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*Except sample A-52 which though high in TiO_2 is remarkably low in iron. The mode of this particular specimen is conspicuously different from that of all other amphibolites analysed in that it contains considerably less hornblende and considerably more feldspar. It perhaps represents an anorthositic differentiate and not a normal gabbro.

amphibolites (columns 1, 2, 9 and 10 of Table 5). Poldervaart's average of the TiO_2 content of 200 amphibolites (column 11) of both ortho- and para-types, has a value intermediate between the average TiO_2 contents of high-TiO_2 and low-TiO_2 amphibolites and compares favourably with the grand average of the TiO_2 contents of amphibolites of the two groups put together (column 18). It should, however, be noted that some amphibolites formed by interaction of fluids from granite upon dolomite (column 4) or by skarnlike replacement of marble (column 5) contain considerably larger amounts of TiO_2 than para-amphibolites of other areas (columns 9, 10). The TiO_2 contents of some ortho-amphibolites (columns 3, 6) and of average gabbro (column 14), though considerably higher than the TiO_2 contents of some average para-amphibolites (columns 9, 10), are comparable to the TiO_2 contents of some para-amphibolites of replacement origin (columns 4, 5).

Of the 7 specimens in the high-TiO_2 group A-52 belongs to Class I and the other six belong to Class II (see section on petrography). All 27 specimens of the low-TiO_2 group belong to Class III. It may be recalled here that specimen A-52 belonging to the high-TiO_2 group is considered to be definitely an ortho-amphibolite on the basis of its palimpsest gabbroid texture and that the amphibolites of Class I and Class II have some common petrographic characteristics (higher contents of ilmenite and apatite and deep color of hornblendes) different from those of Class III (lower contents of ilmenite and apatite and very light color of hornblendes). If, in addition, the striking chemical similarity between A-52 and the other members of the high-TiO_2 group is considered as a reasonable basis for correlation, then the entire high-TiO_2 group may be considered to be of meta-igneous origin. However, it should be pointed out that the average K_2O content of high-TiO_2 group is considerably lower than that of the ortho-amphibolites and basic igneous rocks from other areas.

If, again, high and low TiO_2 content is considered as a true distinction between ortho- and para-amphibolites then the TiO_2 rich amphibolites of the Lead-Deadwood area may possibly be meta-igneous and the low-TiO_2 amphibolites meta-sedimentary. But in view of the known variability of TiO_2 in basic igneous rocks it is doubtful if TiO_2 content can serve as a sure criterion to distinguish ortho- from para-amphibolites. The average TiO_2 content of the low-TiO_2 group is not impossibly low for gabbros and diabases.

As can be seen in Table 6 there is no aspect in the trace element distribution in either high-TiO_2 or low-TiO_2 amphibolites, which does not compare reasonably with the reported trace element contents of basic igneous rocks. It does not necessarily follow that all amphibolites from the Lead-Deadwood area are therefore derivatives of basic igneous rocks; merely that their trace element contents are compatible with their being ortho-amphibolites. Information on trace element in para-amphibolites is rare but the existing data give no sure clue to distinguish para- from ortho-amphibolites (Wilcox et al., 1958, p. 1365).

The average Sr content of the high-TiO_2 amphibolites

(367 ppm) is considerably higher than that of the low-TiO_2 amphibolites (202 ppm). Wilcox and Poldervaart (1958, p. 1358), on the basis of a limited number (8 each) of analyses of ortho- and para-amphibolites from the Bakersville-Roan Mt. area of North Carolina, found that the Sr content of ortho-amphibolites was distinctly higher than that of para-amphibolites. However, the average Sr content of the Bakersville-Roan Mt. para-amphibolites (144 ppm) as well as that of the low-TiO_2 amphibolites of the Lead-Deadwood area (202 ppm) are both higher than the Sr contents of basic igneous rocks reported by some workers (see Table 6, also Nockolds and Allen, 1956, p. 57-60).

If all the amphibolites in the Lead-Deadwood area are ortho-amphibolites then the high-TiO_2 and low-TiO_2 groups possibly represent two different suites of intrusions or differentiated fractions of one intrusive magma. Wager and Mitchell (1951) have shown that nickel in basic igneous rocks is very sensitive to fractionation and in a differentiated series a very wide scatter of nickel content is very possible. In the Skaergaard layered series they found 170 ppm Ni in marginal gabbro, as much as 1000 ppm in earliest olivine-gabbro, 40 ppm in so-called middle gabbro and less than 2 ppm in hortonite ferro-gabbro. It may probably be significant that of the Lead-Deadwood amphibolites the four (A-63, A-66, A-68, A-78) with the lowest nickel content have also the highest iron content. These, again, are the only four garnetiferous ones among all the amphibolites analysed.

In summary it may be said that the amphibolites of Class I (A-16, A-18, A-23, A-26, A-27, A-31, A-32, A-49, A-52, A-54) showing relict gabbroid and diabasic texture are definitely ortho-amphibolites. In case of some minor occurrences of hornblende-bearing rocks (A-37, A-51, A-53 belonging to Class V) the field relations are highly suggestive of a meta-sedimentary origin. In a majority of the remaining amphibolites available data are not unequivocally suggestive of one or the other origin.

METAMORPHISM

The mineral assemblages indicate that most of the rocks mapped as amphibolite in the Lead-Deadwood area belong to the uppermost part of the epidote-amphibolite facies or to the lower part of the amphibolite facies. The most common assemblage is hornblende-andesine-epidote (zoisite, sphene) with accessories like ilmenite, apatite, quartz, calcite and sometimes secondary chlorite and biotite. The furthest limit of amphibolite occurrence in the area is within the staurolite zone of the pelitic schists and staurolite is considered to be a typical guide mineral in the epidote-amphibolite facies (Vogt, 1927; Turner, 1948). The distinction between the epidote-amphibolite facies and the amphibolite facies is by no means clear. Eskola (1914, 1915) excluded epidote or zoisite from all of the stable mineral assemblages of his originally defined amphibolite facies. In his opinion, the epidote-amphibolite facies is characterised by the stable association of epidote or zoisite and practically pure albite, whereas in the amphibolite facies pure anorthite is stable. However, as pointed out by Ramberg (1952, p. 149-150), there is a considerable gap between the temperature at which epidote and pure albite can coexist stably and that at which pure anorthite is stable. To cancel the discrepancy Ramberg (1952, p. 150) suggested the use of epidote (zoisite)-$An_{30}(\pm)$ equilibrial association as the lowest boundary for the amphibolite facies. He also suggested that the lowermost stability border of diopsidic pyroxene in calcite milieu can be taken as another indication of the amphibolite$\rightleftharpoons$epidote-amphibolite facies transition. In the amphibolites of Lead-

Deadwood area plagioclase mostly reaches the An-content of a true andesine but no pyroxene has been detected in the amphibolites.

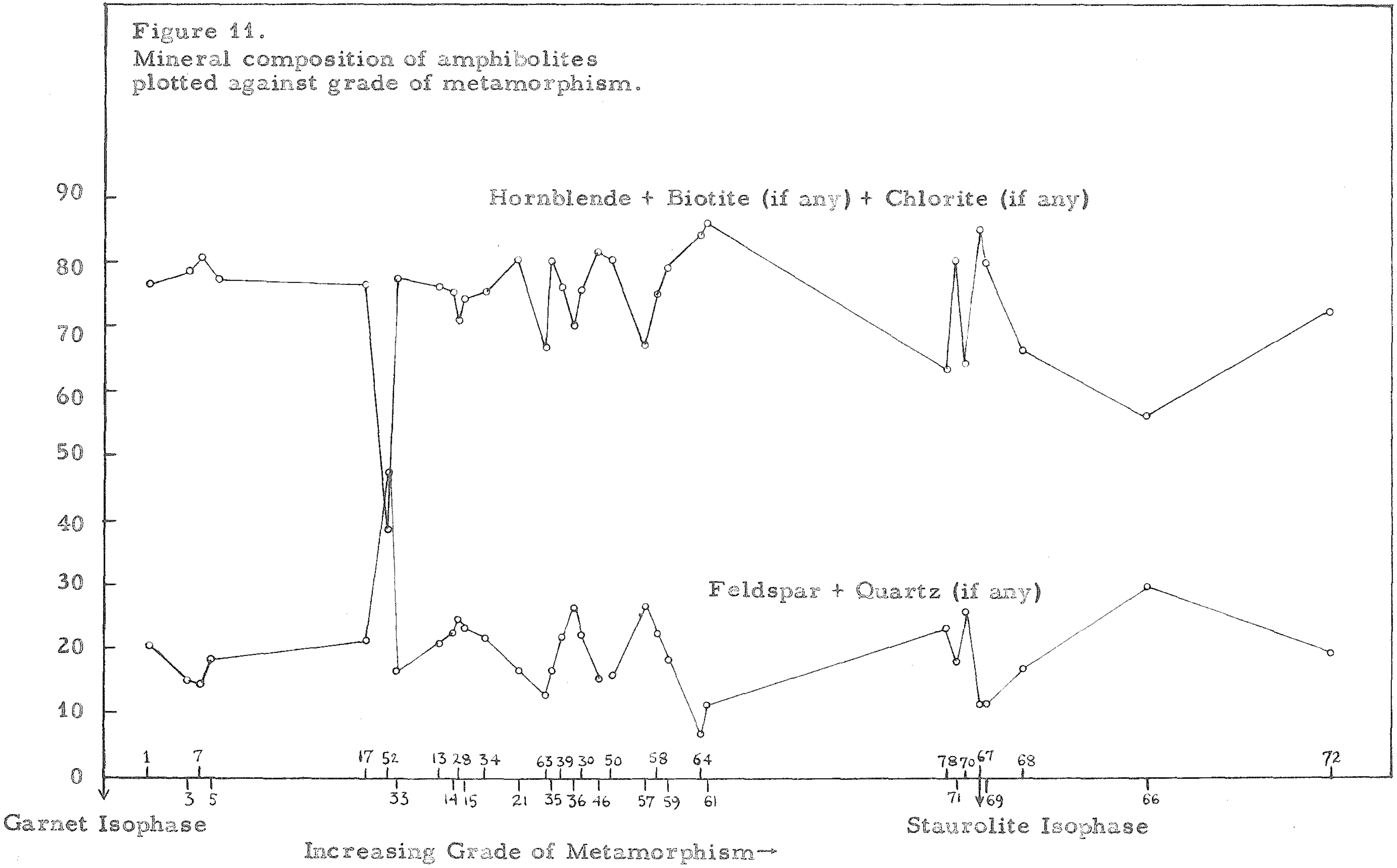
Specimens A-10 and A-12 comprise assemblages which are typical of the green-schist facies (chlorite-oligoclase-epidote-calcite).

According to Dodge (1942, p. 572) garnet occurs in all amphibolites in the northeastern part of the district and this, he concluded, is due to higher grade of metamorphism. But this conclusion is not verified by the present author. For instance, specimens A-67, A-69, A-70, A-71, A-72, A-74 etc. from the extreme northeastern part of the area are not garnetiferous. Garnet was found to occur only in amphibolites rich in Mn (e.g. A-63, A-66, A-68, A-78 and petrographically similar specimens as A-38, A-40, A-41, A-75, A-76, A-77, A-79). Specimens A-38, A-40 and A-41 come from the lower-middle part of the garnet zone, specimen A-63 is from the middle-middle part of the garnet zone and the rest of the garnetiferous amphibolites are from the uppermost garnet zone or from the staurolite zone. There seems to be a definite correlation between the presence of garnet and the Mn-content of the rock. This observation corroborates the finding of many workers that Mn has a considerable influence in lowering the temperature of formation of garnets.

In order to study the extent to which the mineralogical and chemical compositions of the amphibolites are affected by increasing metamorphic conditions, the modal and chemical data from the amphibolites were plotted against the varying ranks of metamorphism they represent (figures 11 to 18). Distances of specimen-locations on the horizontal coordinate were measured along horizontal lines drawn normal to the trace of the garnet isophase (all specimen-locations and the trace of the isophase being reduced to an arbitrary datum level). The locations of the garnet and staurolite isophases are indicated in the figures. Increasing distance from the garnet isophase in the direction of the staurolite isophase is assumed to indicate increasing intensity of metamorphic conditions.

In figure 11 volume percents of the major minerals in amphibolites have been plotted against increasing grade of metamorphism. Since quartz (if any present) could not be distinguished easily from untwinned plagioclase, the two minerals (and also K-feldspar, when present) have been lumped together and plotted as such. In the amphibolites plotted here quartz, when present, was found to be only a very minor constituent. Since biotite and chlorite are retrograde after hornblende, the total volume of these three minerals instead of the volume of hornblende alone, has been plotted. It is evident from figure 11 that in spite of occasional appreciable differences between individual specimens, the average volume percent of the minerals remains pretty much the same throughout the entire sequence of metamorphism represented here. If adjacent specimens are grouped together and values averaged, it can be seen that volume percents of hornblende (biotite, chlorite) and plagioclase (quartz, K-feldspar) remain effectively constant at around 76 and 20 respectively throughout the entire sequence.

Figure 11.
Mineral composition of amphibolites plotted against grade of metamorphism.



In figures 12, 13, 14 and 15 the weight percents of total iron (as Fe_2O_3), CaO, TiO_2, MnO and K_2O have likewise been plotted against increasing grade of metamorphism. The points representing the 7 high-TiO_2 amphibolites are indicated by 'HT' marked close to the points. As mentioned in a previous section, the general chemistry of the high-TiO_2 amphibolites are somewhat different from that of the low-TiO_2 amphibolites. It is highly probable that the two types of amphibolites were derived from rocks of somewhat different bulk composition and so they should be considered separately. In the low-TiO_2 group which contains the majority of the analysed specimens (27 out of 34), there is evidently no appreciable change in the abundances of the five components, total iron (as Fe_2O_3), CaO, TiO_2, MnO and K_2O with increasing rank of metamorphism. Whatever fluctuations are observed appear to be random in character, attributable to minor compositional variations in an approximately homogeneous parent rock. The high-TiO_2 group comprising only 7 specimens, shows much larger fluctuations in the abundance of the components but these again are random and do not constitute any persistent trend correlatable to metamorphism.

In order to get a statistical picture the low-TiO_2 amphibolites were divided into four sub-groups on the basis of closeness of their distances from the garnet isophase and the means of each of the five components (total iron as Fe_2O_3, CaO, TiO_2, MnO and K_2O) for each sub-group were plotted against the mean distances of the sub-groups from the garnet isophase. The four sub-groups are as follows:

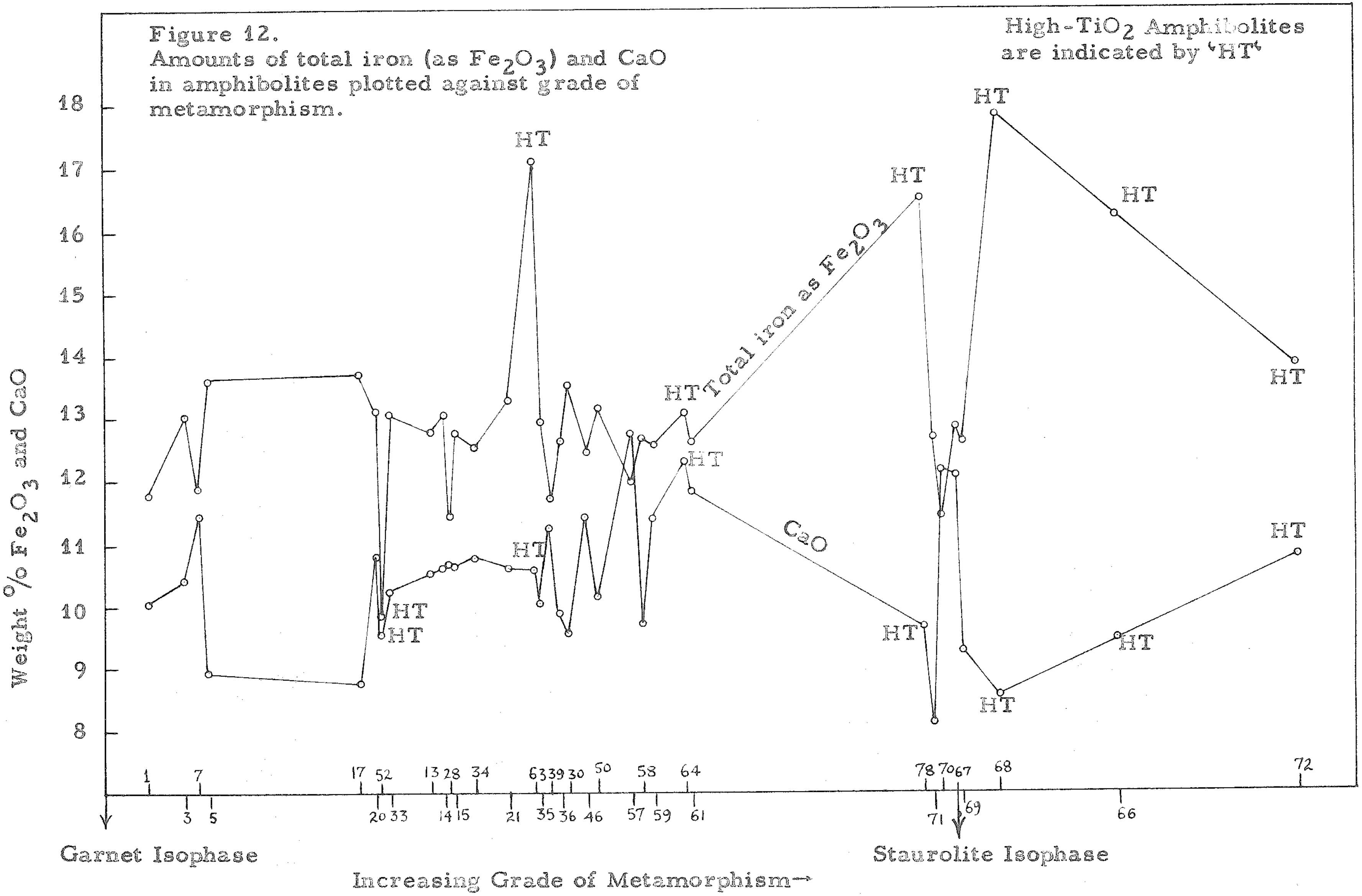


Figure 12.
Amounts of total iron (as Fe_2O_3) and CaO in amphibolites plotted against grade of metamorphism.

High-TiO_2 Amphibolites are indicated by 'HT'

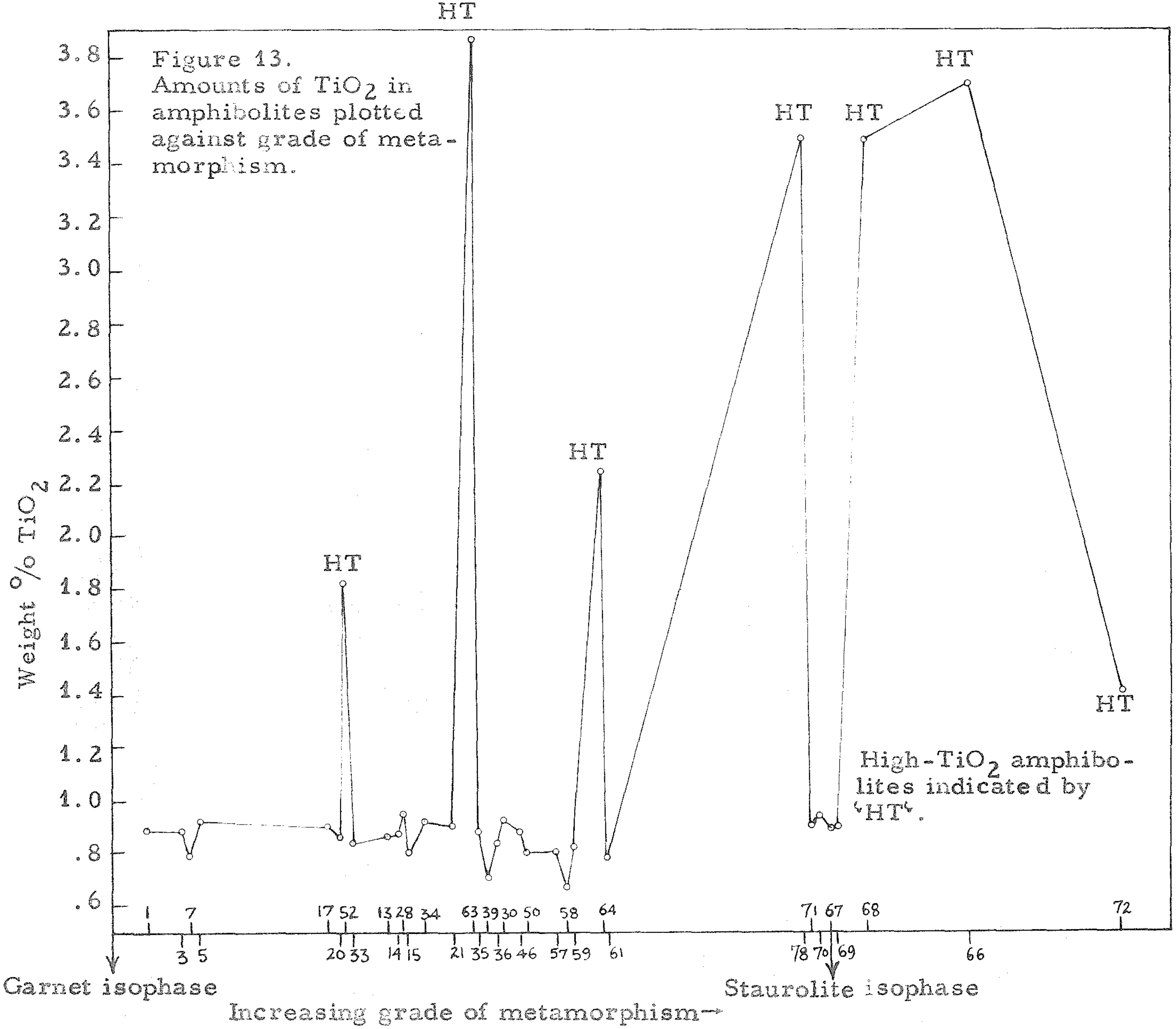


Figure 13.
Amounts of TiO_2 in amphibolites plotted against grade of metamorphism.

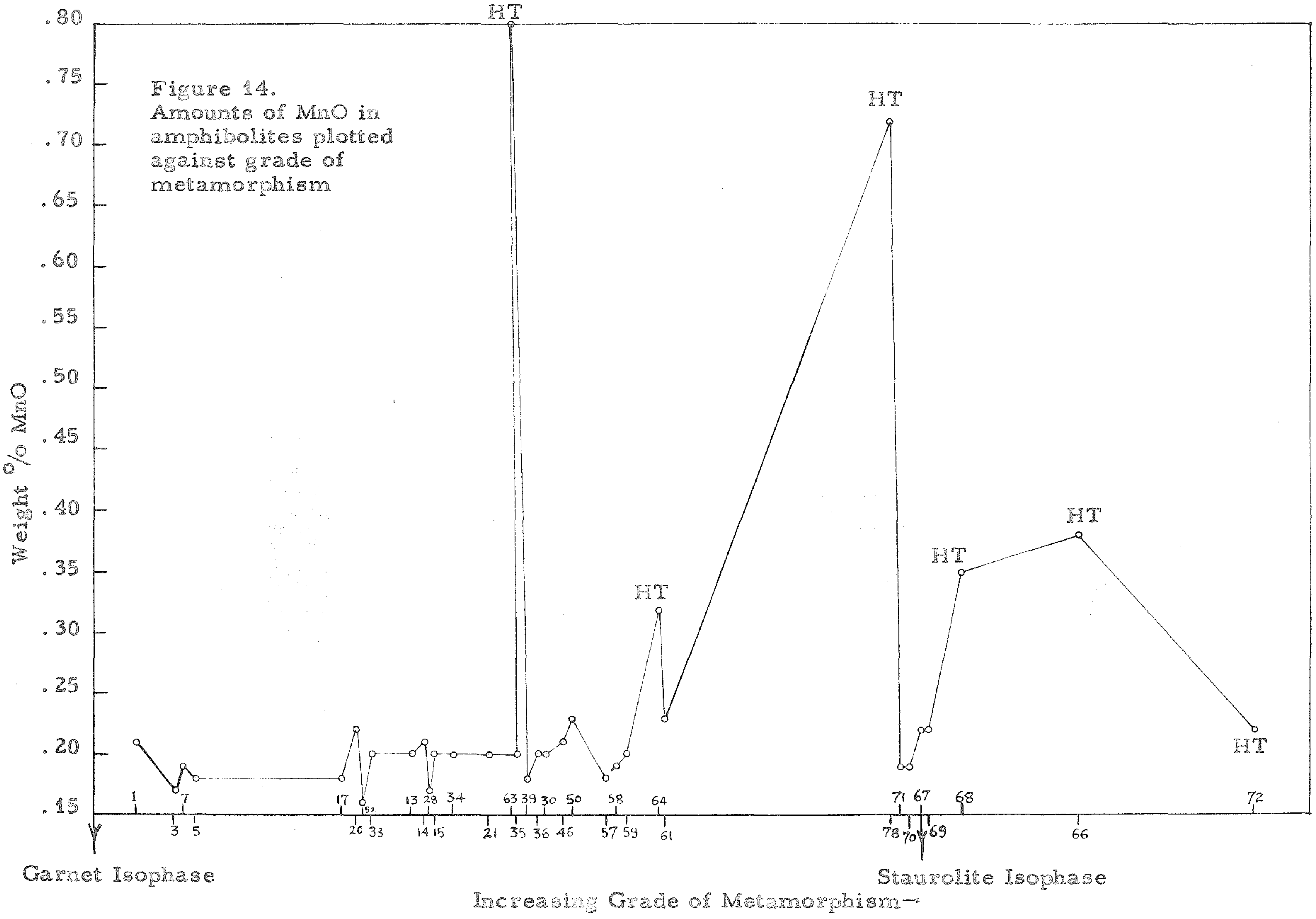


Figure 14.
Amounts of MnO in amphibolites plotted against grade of metamorphism

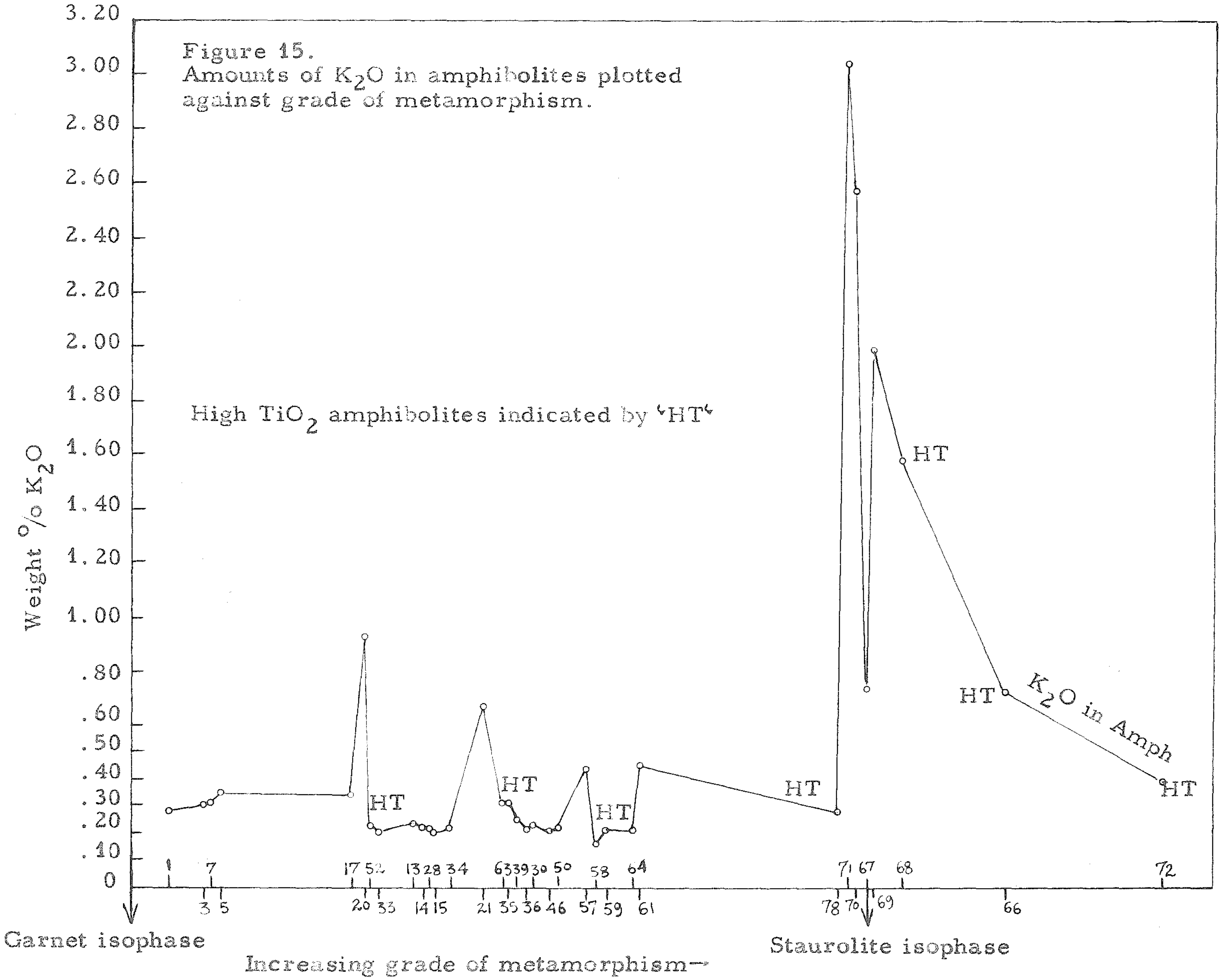


Figure 15.
Amounts of K_2O in amphibolites plotted against grade of metamorphism.

High TiO_2 amphibolites indicated by 'HT'

Sub-group A: A-1, A-3, A-5, A-7

Sub-group B: A-13, A-14, A-15, A-17, A-20, A-28, A-33, A-34

Sub-group C: A-21, A-30, A-35, A-36, A-39, A-46, A-50, A-57, A-58, A-59, A-61

Sub-group D: A-67, A-69, A-70, A-71

In the case of K_2O specimens A-20 of sub-group B, A-21 of sub-group C and A-67 and A-69 of sub-group D were omitted for these amphibolites contain K-feldspar of metasomatic origin. Specimens A-70 and A-71 of sub-group D were also omitted for K_2O as these amphibolites contain a considerable amount of retrograde biotite.

The mean values of the various components for the four sub-groups are given in Table 7 and are plotted in figures 16 and 17. In the figures the spread of the analyses in each sub-group is shown by a solid vertical line.

Table 7

Mean Values of Five Major and Minor Components of Low-TiO_2 Amphibolites (in weight percent)

	Total Iron as Fe_2O_3	CaO	TiO_2	K_2O	MnO
Sub-group A	12.60	10.23	0.87	0.31	0.19
Sub-group B	12.82	10.39	0.87^5	0.23	0.20
Sub-group C	12.71	10.79	0.81^6	0.27	0.20
Sub-group D	12.41	10.41	0.90^5	-	0.20^5

It is evident that going from garnet to the staurolite isophase the abundances of the five components total iron,

Figure 16. Mean amounts of total iron (as Fe_2O_3) and CaO in low-TiO_2 amphibolites plotted against grade of metamorphism.

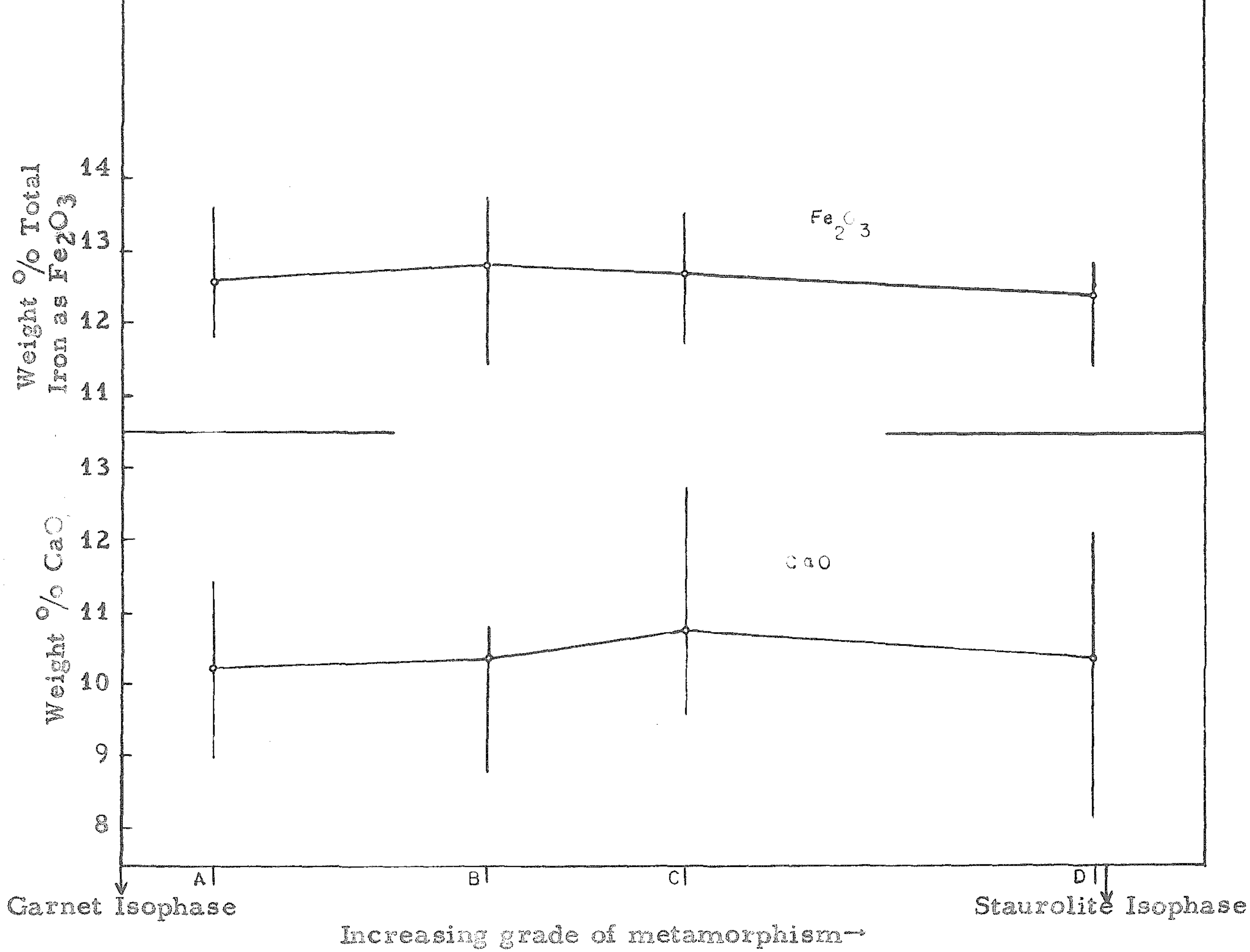
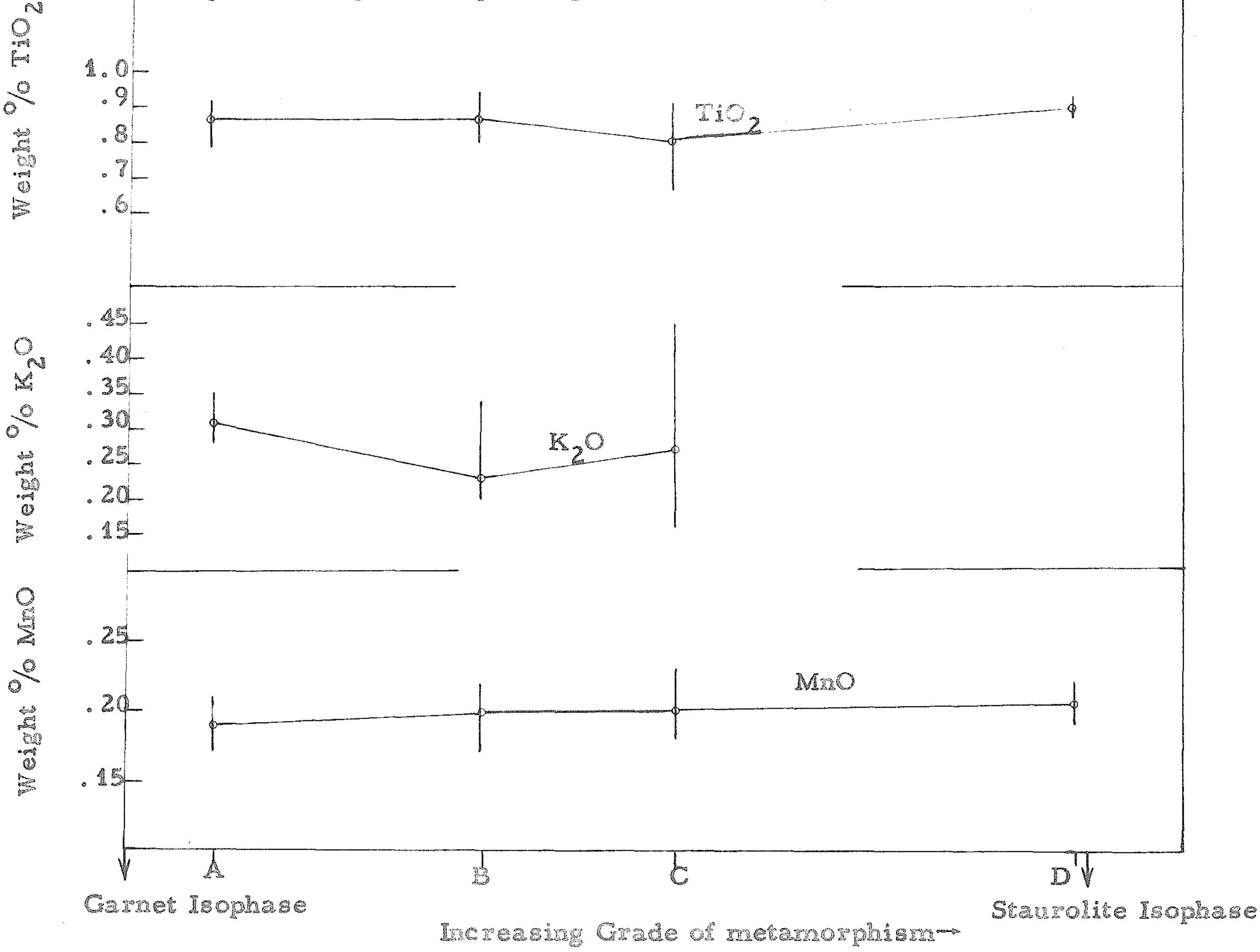


Figure 17.
Mean amounts of TiO_2, MnO and K_2O in low-TiO_2 amphibolites plotted against grade of metamorphism



CaO, TiO_2, MnO and K_2O in the amphibolites remain remarkably constant. Whatever small differences are observed do not constitute any systematic trend. A possible exception is MnO which appears to increase very slightly with increasing metamorphic rank. But here again the differences are within the limits of accuracy of the analyses and cannot thus be taken seriously.

The mean concentrations together with the standard deviations for the various trace elements in low-TiO_2 amphibolites (sub-grouped as mentioned earlier) are given in Table 8. The same mean concentrations of the trace elements in the different sub-groups are plotted in figures 18 and 19 against increasing metamorphic sequence. The spread of analyses in each subgroup is shown by a semi-vertical line. The small solid circles on the semi-vertical lines indicate individual analyses and the open circles indicate the mean values of the sub-groups.

As can be seen from Table 8 and from figures 18 and 19, the mean concentrations of the elements Co, Cr, Cu, Ni, Sc, Sr, V and Zr show a slight, though not always systematic, decrease with increasing rank of metamorphism. The concentration of Ba increases with increasing metamorphism. Whether these trends are real or not cannot be decided on the basis of present data. The differences constituting the trends are small and are comparable to the standard deviations in the various sub-groups. The weak trends thus cannot be justified on the basis of a stringent statistical analysis of the data.

Table 8

Mean Trace Element Concentrations of Low-TiO_2 Amphibolites (in ppm)

	Ba		Co		Cr		Cu		Ni		Sc		Sr	
	M	S.D.	M	S.D.	M	S.D.	M	S.D.	M	S.D.	M	S.D.	M	S.D.
Sub-group A	24	8	66	17	105	20	40	30	162	56	33	3	219	36
Sub-group B	32	22	67	20	101	34	40	28	169	80	34	5	187	54
Sub-group C	28	20	59	24	90	39	33	24	158	78	30	7	209	43
Sub-group D	67	26	48	10	71	37	29	11	104	54	29	7	190	61

	V		Zr	
	M	S.D.	M	S.D.
Sub-group A	188	34	40	5
Sub-group B	211	68	38	10
Sub-group C	179	101	27	12
Sub-group D	138	66	26	17

M -- Mean, S.D. -- Standard Deviation

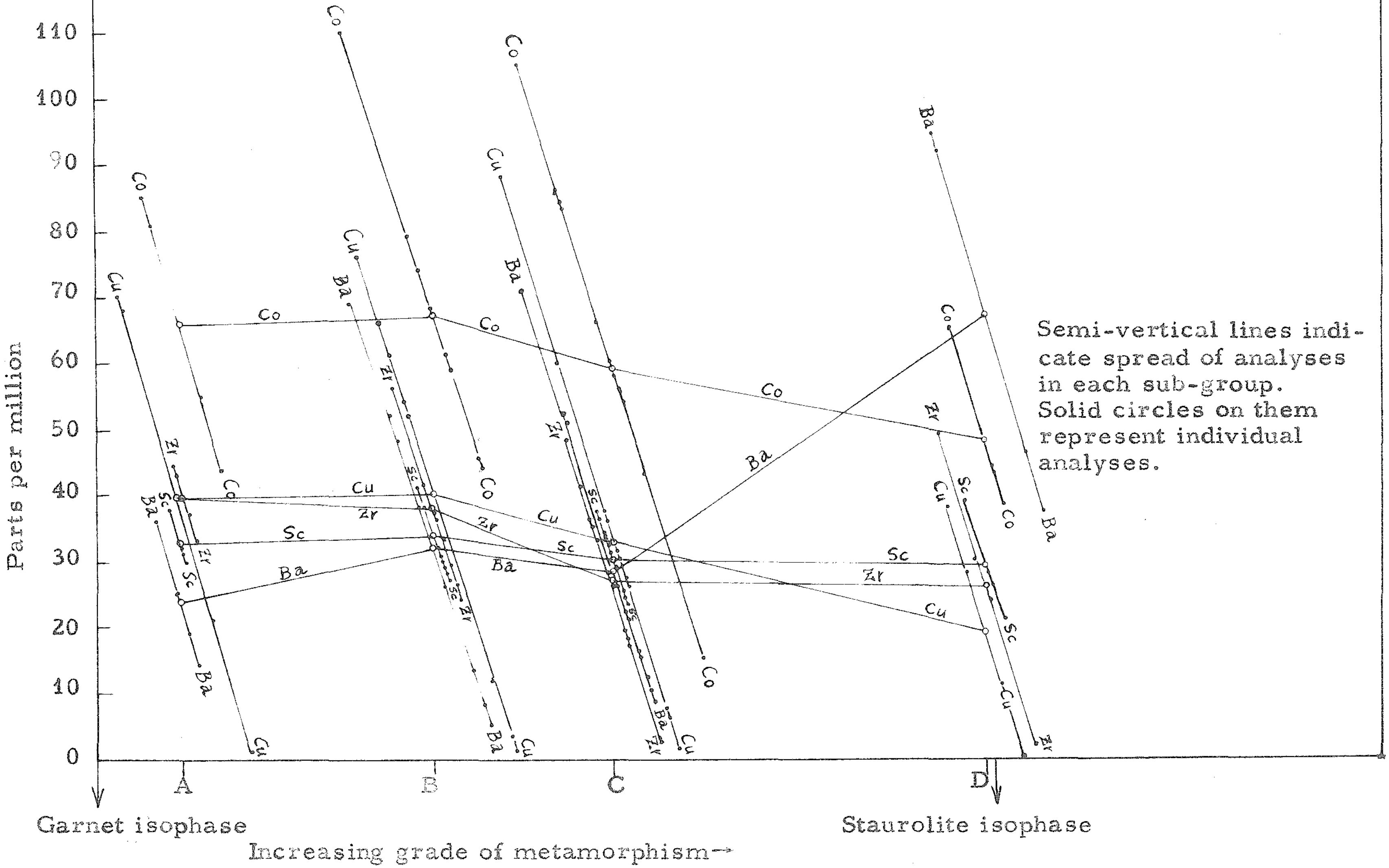


Figure 18.
Mean amounts of Ba, Co, Cu, Sc and Zr in low-TiO_2 amphibolites plotted against grade of metamorphism.

Semi-vertical lines indicate spread of analyses in each sub-group. Solid circles on them represent individual analyses.

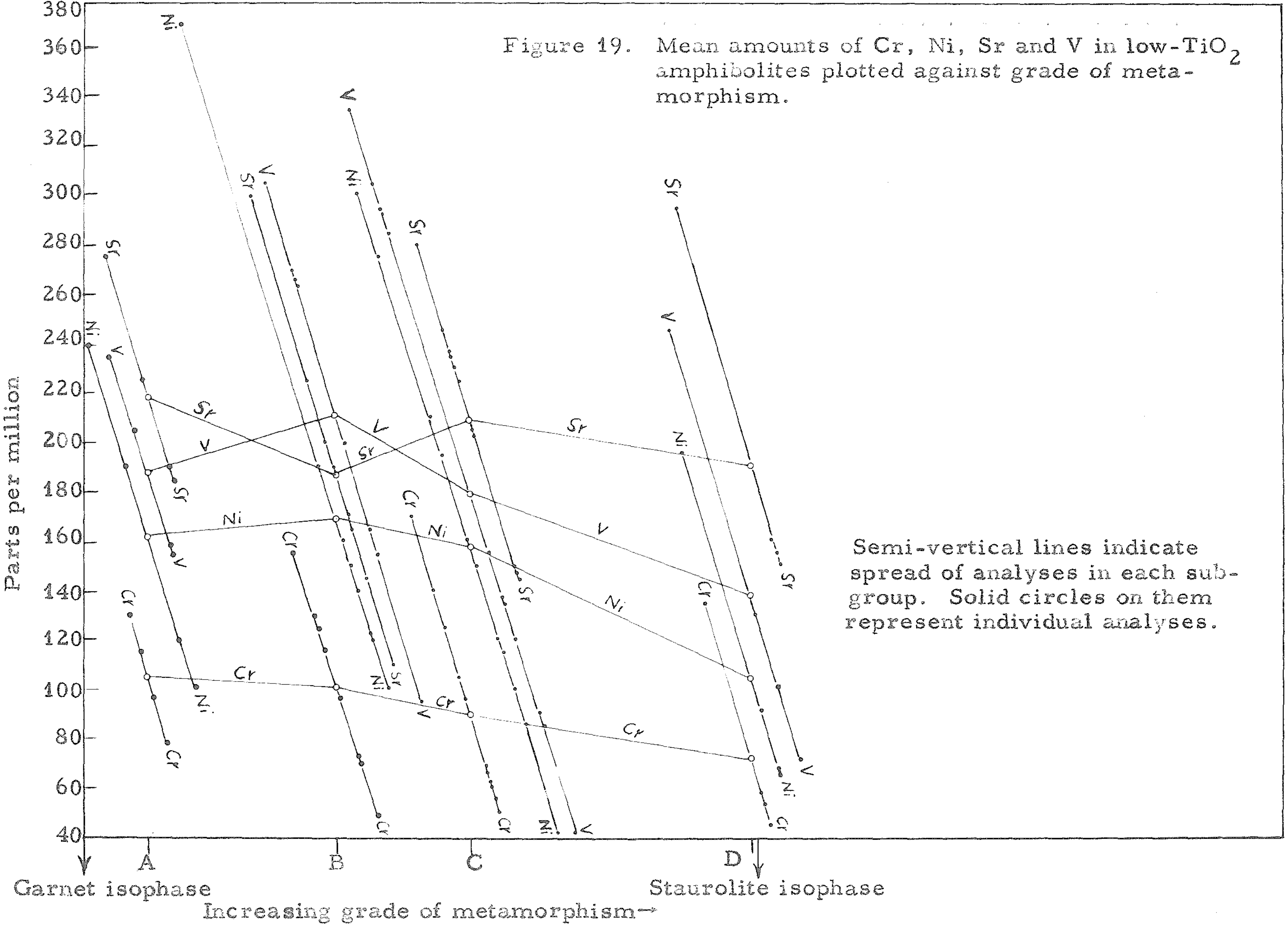


Figure 19. Mean amounts of Cr, Ni, Sr and V in low-TiO_2 amphibolites plotted against grade of metamorphism.

Semi-vertical lines indicate spread of analyses in each subgroup. Solid circles on them represent individual analyses.

The variations in the trace element contents of high-TiO_2 amphibolites (not plotted; see Table 4) are random and do not show any trend or correlation with metamorphic sequence.

In summary it may be said that metamorphism of the amphibolites in the Lead-Deadwood area is essentially isochemical throughout the range of conditions represented by the appearance of successively the garnet and the staurolite isophases in the enclosing metasediments. Several authors working in metamorphic terrains (e.g. Engel and Engel, 1958) have reported the existence of mineralogical and chemical trends in rocks correlatable to the intensity of metamorphism. The present study is limited in that no great mineralogical changes indicative of progressive metamorphism can be observed to occur in the amphibolites sampled. The appropriate metamorphic rank assignments must therefore be made on the basis of mineral assemblages observed in the pelitic schists enclosing these amphibolites. The great reconstructive transformations involving appearance of new phases and/or disappearance of old ones that are typical of progressive metamorphism in the pelitic rocks do not occur in the amphibolites studied. Whether or not significant changes in the bulk composition of amphibolite may occur when its constituent minerals are involved in similar drastic transformations, cannot thus be concluded from the present study. C. G. Engel and A. E.J. Engel (1958) studied the progressive metamorphism of amphibolite interlayers in the major paragneiss of the northwest Adirondack Mountains, New York. They report that in spite of marked and systematic mineralogical changes represented by the appearance of successively the clino- and orthopyroxenes with increasing rank of metamorphism, the chemical composition of the amphibolites varies little from that of a typical basalt even at the highest temperature of metamorphism represented there. In contrast lesser changes in mineralogical composition in the enclosing major paragneiss are accompanied by large changes in bulk composition (Engel, A. E. J. and Engel, C. G., 1958). It seems likely that the susceptibility of a rock to chemical change in response to progressive metamorphism, is critically related to its bulk composition. It seems probable that in examples of this type, progressive metamorphism is essentially a process of progressive "basification" with the basification being more obvious in rocks initially enriched in alkalis and silica. It may also be pointed out here that even in rocks susceptible to significant chemical changes in response to progressive metamorphism, the establishment of a chemical gradient possibly occurs only beyond some critical threshold conditions. Before these conditions are attained mobility of elements probably remains too low to make the chemical gradient conspicuous. It is interesting to note in this connection that excepting H_2O and CO_2 the mineralogic and chemical trends found by A. E. J. Engel and C. G. Engel (1958, fig. 4, p. 1394) in the Adirondack paragneiss do not show any linear relationship with metamorphic rank. The major part of the changes defining the trends occur only at relatively high grades of metamorphism. At the lower and middle grades the changes are very small or absent.

Shaw (1956) studied the progressive metamorphism of the pelitic Littleton formation and found its metamorphism to be essentially isochemical. Presumably the metamorphic conditions in the Littleton formation never attained the critical threshold values beyond which matter becomes mobile enough to make a chemical gradient conspicuous.

PART III

HORNBLENDES

INTRODUCTION

In order to investigate the chemical constitution of the hornblendes and also to study the extent to which chemical composition of the hornblendes is a function of metamorphic conditions and of bulk composition of the host rock, hornblende was separated from each of the 34 amphibolites whose modal and chemical compositions have been discussed in Part II. The methods and techniques of mineral separation and chemical analyses are described in the following pages followed by a discussion of the data obtained from the chemical analyses.

Specimen numbers used for hornblendes are the same as those of the corresponding amphibolites from which they have been separated. However, the prefix in case of the mineral samples is 'H' while the prefix used for the amphibolites was 'A'.

MINERAL SEPARATION

The -150+200 mesh fraction of the crushed rock was used for all mineral separatory work. The reasons for the choice of this size fraction are the following: the hornblendes of the amphibolites concerned in this study are in many cases poikiloblastic with inclusions mainly of plagioclase. To get an effective separation, therefore, the hornblende crystals must be broken down to a size approximating the average size of the plagioclase inclusions or smaller, thereby increasing the number of inclusion-free hornblende grains. On the other hand, the smaller the grain size the more difficult and time-consuming become the separatory procedures. The best compromise was obtained with -150+200 mesh grain size.

The crushed rock was first washed several times with acetone to free the grains from extremely fine rock powder attached to their surfaces.

A preliminary mineral separation was effected by treating the samples with tetra-bromo-ethene (density 2.965 at 20°C). The heavier fraction contained hornblende, ilmenite, some plagioclase and quartz dragged down along with hornblende grains, and any biotite, chlorite, garnet, epidote, etc. present in the rock. A good separation of hornblende from this mixture was effected with the help of a Frantz Isodynamic Magnetic Separator. Elimination of quartz, plagioclase and ilmenite was quite easy. Garnet, chlorite and epidote, though not as readily separable, were however separated quite effectively with proper adjustments of the magnetic separator and repeated cycling of the sample, all these minerals being more magnetic than hornblende. A major portion of biotite, when present, could be eliminated magnetically, but its separation was never as complete as chlorite, garnet or epidote. The most difficult problem in separation was provided by the binary grains, mostly of hornblende-plagioclase or hornblende-ilmenite binaries. These have magnetic properties close to pure hornblende, and are difficult to eliminate without sacrificing a considerable amount of all-hornblende grains in the process. However, it was found that with proper adjustments of the separator and a large amount of recycling, most of the binary grains can be separated without losing too many all-hornblende grains. Some of the more difficult samples were recycled 20 times to obtain an effective elimination of binary grains. After each cycle the purity of the sample was checked under a binocular microscope and cycling repeated till a desired purity was obtained.

The hornblende concentrates obtained after magnetic separation were again treated with heavy liquids for further purification. Two samples, from two garnetiferous amphibolites (A-63, A-78), were first treated with pure methylene-iodide to eliminate the remaining garnet grains.

The remaining hornblende-ilmenite binary grains with densities very slightly higher than pure hornblende grains, were eliminated by treating with methylene-iodide diluted with acetone, the density of the liquid being so adjusted that slightly heavier hornblende-ilmenite binaries sank to the bottom while the pure hornblende grains remained mostly suspended in the liquid. The process is very slow but effective.

Remaining hornblende-plagioclase (or quartz) binaries, biotite and chlorite were likewise separated from the hornblende concentrates by treatment with methylene-iodide of adjusted density. These are slightly lighter than pure hornblende and float while hornblende grains sink or remain suspended in the liquid. It was found that an appreciable amount of pure hornblende grains also was floating with the binaries because of the surface tension effects. Since the liquid treatment had to be repeated several times to get good separation, the loss of pure hornblende grains was considerable. To avoid this the procedure was modified in the following way. First the entire sample was kept floating on pure methylene iodide and then a thin layer of acetone was put on top of it. If not violently agitated, the diffusion between the liquids is slow and thus a two-layer liquid column could be maintained for hours with mineral grains hanging along the liquid-liquid interface. With gentle horizontal agitation along the liquid-liquid interface the mixing was enhanced in a controlled way, the upper layer becoming increasingly heavier and larger in volume and the lower layer increasingly lighter and smaller in volume but still maintaining an interface between them. With continued mixing the upper layer of liquid eventually reached a density which made the lighter binaries, biotites, chlorites etc. float upwards from the interface. Likewise pure hornblende grains from the interface started sinking because of increasing lower density of the lower layer. Eventually the interface was made to disappear completely by continued mixing. By repeating the procedure a number of times the purity of a sample could be brought to a desired point without too much loss of sample material.

Biotite and chlorite bearing samples of hornblende still contained a very small amount of these minerals after all the above mentioned operations. These were mostly separated by tapping the samples over an inclined surface of glazed paper whereby biotite and chlorite grains were left attached to the paper surface because of their flatness while the much more equidimensional hornblende grains easily rolled down the incline. The final elimination of biotite and chlorite was accomplished in the following way. The sample was put in a large separatory funnel with large amount of acetone and after vigorous shaking most of the settling grains were tapped very quickly out of the funnel leaving the bulk of the acetone in the funnel. The biotite and chlorite grains because of their flatness settled less easily than hornblende grains and were caught suspended in acetone. The quicker settling hornblende grains were almost entirely tapped out. By repeating the operation several times the flaky minerals were eliminated.

All hornblende concentrates were thoroughly washed with acetone before analysis. To avoid contamination only high purity Baker-Analysed acetone was used in all separatory operations.

PURITY OF MINERAL SAMPLES

The purity of the mineral samples was estimated from grain slides prepared from the mineral concentrates. The slides were examined under a binocular microscope and the volume percents of the impurities were estimated by a statistical count of the wholly or partially impure grains. In all estimates of purity average size of the impurities was taken into consideration. As is evident, the method is not entirely free from personal bias; but there is no known method which will eliminate personal bias and at the same time be simple and not time-consuming.

In a great majority of the cases the principal impurity is binary grains of hornblende-plagioclase or hornblende-ilmenite. However, in samples H-63, H-66, H-68, H-70, H-71 and H-78 a significant amount of impure grains was found. Samples H-63, H-66 and H-78 contain about 0.5% (by volume) of garnet. Samples H-66, H-70 and H-71 contain about 0.5% biotite and sample H-68 about 2%. Samples H-52, H-63 and H-78 contain about 1 to 1.5% ilmenite and sample H-72 about 0.5%. Ilmenite in all other samples is less than 0.3% by volume. Almost all samples contain about 0.5 to 1.5% of plagioclase as impurity. Sample H-68, considered as the least pure sample, is about 96% pure; samples H-63, H-66 and H-78 are about 97% pure and sample H-72 is about 97.5% pure. The purity of all other samples is 98% or better.

CHEMICAL ANALYSES

Wet Chemical Analyses

Twelve hornblendes were completely analysed (analyst: C. O. Ingamells) by the wet chemical methods. Five each were selected from extreme ends of the metamorphic grade and two from in between. Two of the hornblendes (H-72, H-78) are from the high-TiO_2 amphibolites, one (H-78) from a garnetiferous high-TiO_2 amphibolite and the other (H-72) from a non-garnetiferous high-TiO_2 amphibolite. The other ten hornblendes are from the low-TiO_2 amphibolites, one (H-71) being from an amphibolite with considerable amount of secondary biotite.

The wet chemical analyses are given in Table 9.

In chemical composition these hornblendes are very similar to eight metamorphic hornblendes from meta-gabbros described by Rosenweig and Watson (1954, p. 586) from the Pennsylvania-Delaware area. The Lead-Deadwood hornblendes contain, however, less TiO_2, Fe_2O_3, Na_2O and K_2O than those of the Pennsylvania-Delaware hornblendes. Hornblendes from the metamorphosed Adirondack gabbroic rocks (Buddington, 1952, Table 3) have 3 to 6 times more TiO_2 than Lead-Deadwood hornblendes. The Adirondack hornblendes are also richer in Fe_2O_3, K_2O and F than the Lead-Deadwood hornblendes.

Fluorescent X-ray Analyses of Selected Major and Minor Components

Major and minor elements of 22 hornblendes were analysed by fluorescent x-ray spectrographic method using the 12 completely analysed (wet methods) hornblendes as standards. Altogether the

Table 9

Complete Wet Chemical Analyses of 12 Samples of Hornblende

(in weight percent)

	H-1	H-5	H-13	H-14	H-17	H-39	H-61	H-69	H-70	H-71	H-72	H-78
SiO_2	45.20	45.20	44.46	44.37	44.56	44.44	45.00	44.91	46.01	45.26	44.17	42.71
Al_2O_3	13.49	13.00	14.70	15.24	13.10	15.54	14.66	14.53	11.88	13.48	13.29	15.15
TiO_2	0.43	0.44	0.43	0.43	0.47	0.43	0.48	0.50	0.43	0.51	0.78	0.66
Fe_2O_3	1.93	2.04	1.58	1.69	2.14	1.45	1.15	1.57	1.89	1.87	1.99	2.90
FeO	12.10	12.89	12.60	12.41	13.16	11.67	11.83	11.98	13.96	13.34	14.91	17.53
MnO	0.23	0.19	0.22	0.22	0.22	0.21	0.23	0.25	0.23	0.26	0.25	0.56
MgO	11.45	11.39	10.81	10.87	11.21	11.12	11.68	11.18	10.26	9.99	9.07	6.22
CaO	11.39	10.99	11.06	11.01	10.56	11.49	11.64	11.46	12.03	11.70	11.49	10.59
Na_2O	1.20	1.12	1.21	1.22	1.19	1.27	1.12	1.12	0.72	0.92	1.10	1.62
K_2O	0.25	0.25	0.26	0.22	0.30	0.28	0.22	0.24	0.59	0.56	0.37	0.26
H_2O^+	2.04	2.01	1.91	1.99	2.56	1.99	1.90	1.99	1.73	1.78	2.16	1.40
H_2O^-	0.00	0.04	0.02	0.01	0.07	0.04	0.00	0.00	0.02	0.00	0.02	0.00
F	0.04	0.03	0.03	0.02	0.04	0.02	0.04	0.03	0.20	0.11	0.04	0.20
Cl	0.01	tr	tr	tr	tr	n.d.	n.d.	0.01	n.d.	tr	n.d.	tr
	99.76	99.59	99.29	99.70	99.58	99.95	99.95	99.77	99.95	99.78	99.64	99.80
O (F and Cl	0.02	0.01	0.01	0.01	0.02	0.01	0.02	0.01	0.08	0.05	0.02	0.08
	99.74	99.58	99.28	99.69	99.56	99.94	99.93	99.76	99.87	99.73	99.62	99.72

tr -- trace
n.d. -- not determined

Table 9 (Cont'd)

Analyst -- C. O. Ingamells
Rock Analysis Laboratory
Department of Geology
University of Minnesota

H-1, H-5, H-13, H-14, H-17, H-39, H-61, H-69, H-70, H-71 -- Separated from low-TiO_2 amphibolites. All belong to petrographic Class III.

H-72, H-78 ———— Separated from high-TiO_2 amphibolites. Both belong to petrographic Class II.

H-78 -- Separated from garnetiferous amphibolite, others from non-garnetiferous amphibolites

H-70 and H-71 -- Separated from amphibolites with considerable amount of biotite; others from essentially biotite-free amphibolites concentrations of the 5 elements Fe, Ti, Mn, K and Ca were determined. Attempts were made to determine Si, Al and Mg unsuccessfully. The experimental techniques and analytical conditions have already been recorded earlier in the section on fluorescent analyses of major and minor elements of amphibolites, Part II.

To check reproducibility the standards were run twice, four months apart, each time with a different set of powder packs. The unknowns were analysed along with the second run of the standards.

All working curves (except in cases of Si, Al and Mg) were drawn on the basis of least square calculations and the standard deviation of the wet chemical data from fluorescent data for each element except Si, Al, Mg in each run of the standards was calculated. Two working curves for each of the five elements Fe, Ca, Ti, Mn and K together with the standard deviation in each case are shown in figures 20 to 29.

As can be seen from the figures the agreement between wet chemical and fluorescence data is excellent. The standard deviation for calcium and neglecting H-17 the standard deviation for iron are about 1% of the average amounts of these elements present. For Ti, Mn and K the differences between chemical and fluorescence data are comparable to usual variations between duplicate wet chemical analyses of the same sample. The average reproducibilities of the analyses are within respectively for Fe_2O_3, CaO, TiO_2, MnO and K_2O, 0.6%, 0.7%, 0.7%, 0.4% and 2% of the average amounts of the components present.

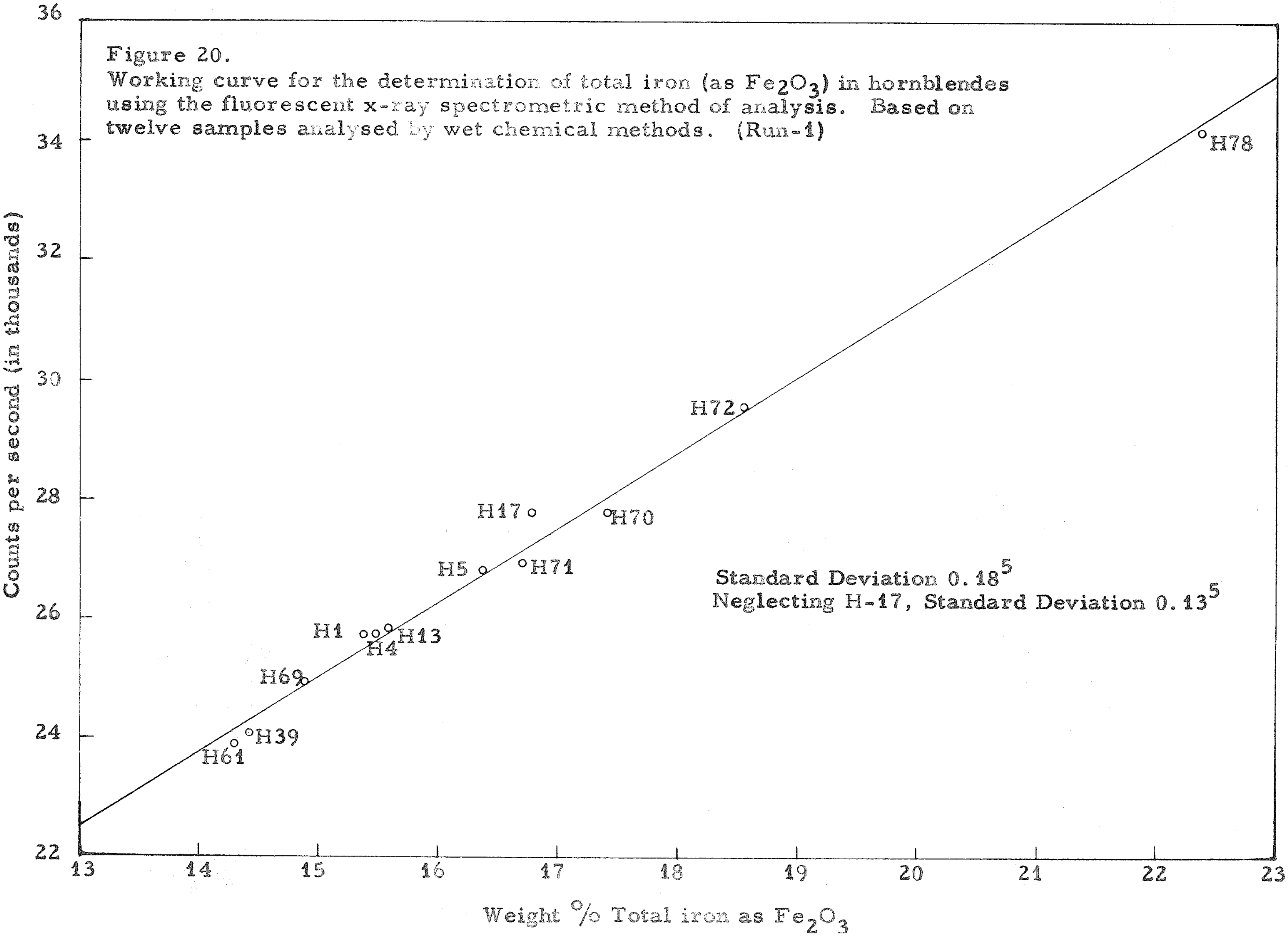


Figure 20.
Working curve for the determination of total iron (as Fe_2O_3) in hornblendes using the fluorescent x-ray spectrometric method of analysis. Based on twelve samples analysed by wet chemical methods. (Run-1)

Standard Deviation 0.18^5
Neglecting H-17, Standard Deviation 0.13^5

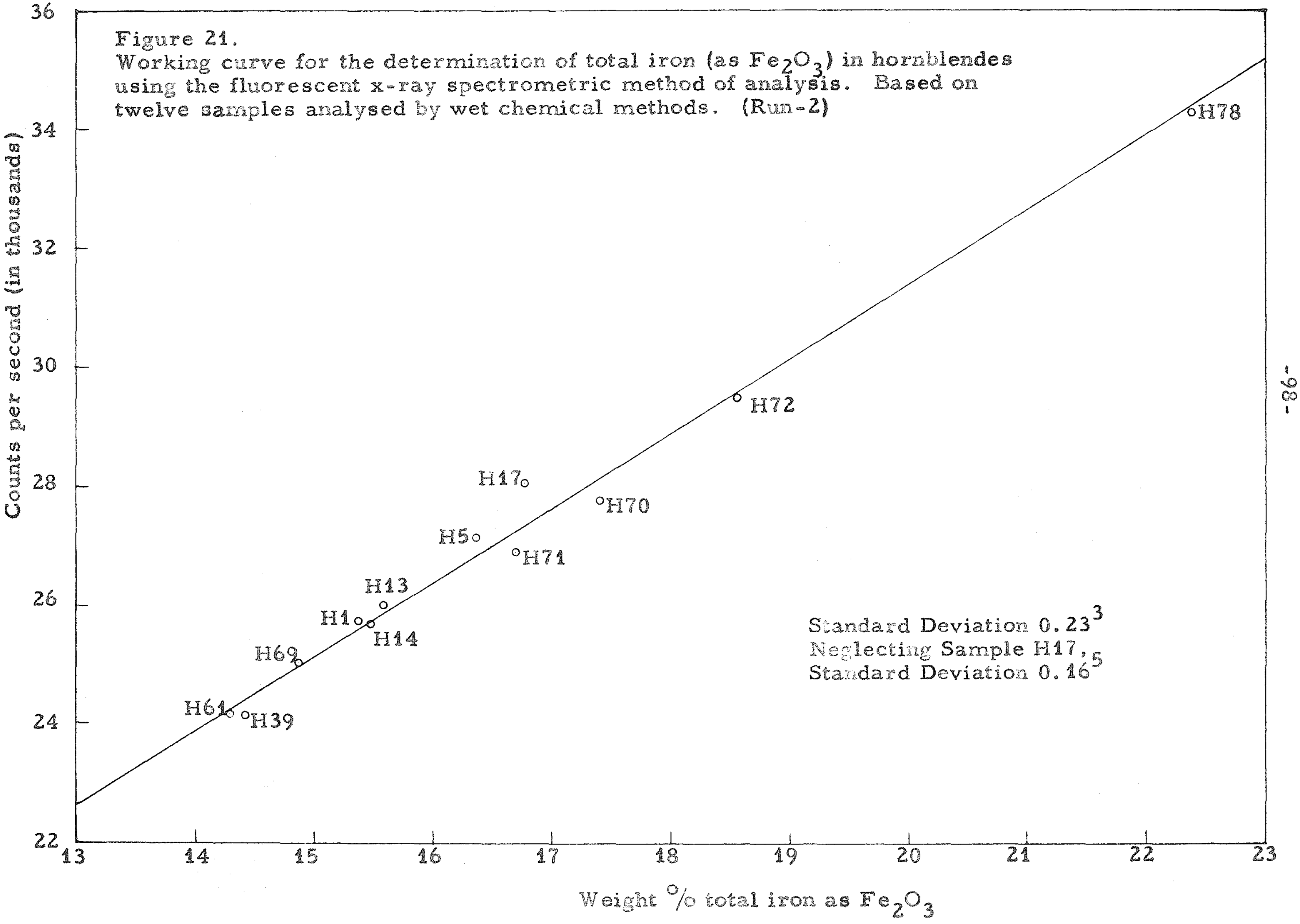


Figure 21.
Working curve for the determination of total iron (as Fe_2O_3) in hornblendes using the fluorescent x-ray spectrometric method of analysis. Based on twelve samples analysed by wet chemical methods. (Run-2)

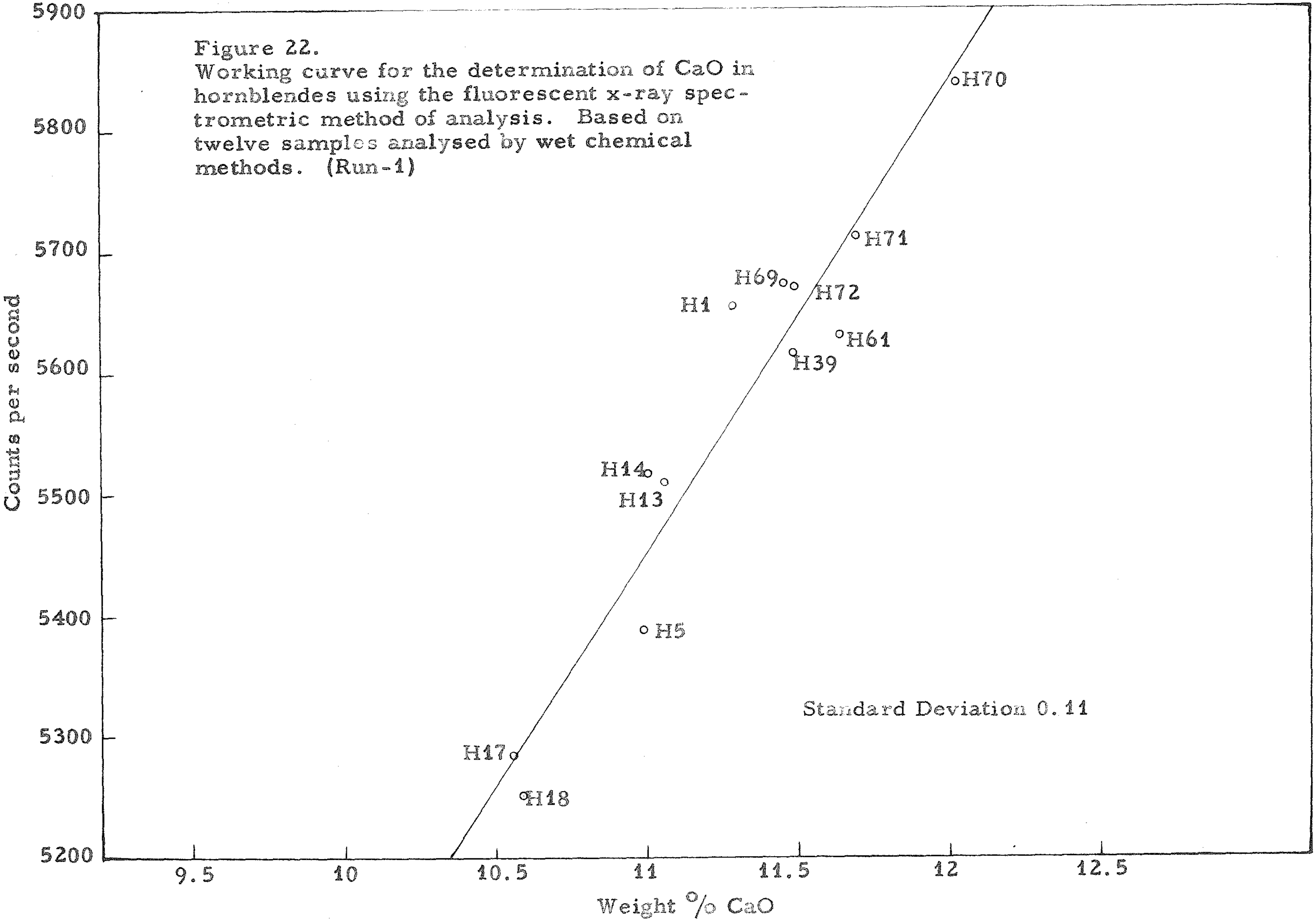


Figure 22.
Working curve for the determination of CaO in hornblendes using the fluorescent x-ray spectrometric method of analysis. Based on twelve samples analysed by wet chemical methods. (Run-1)

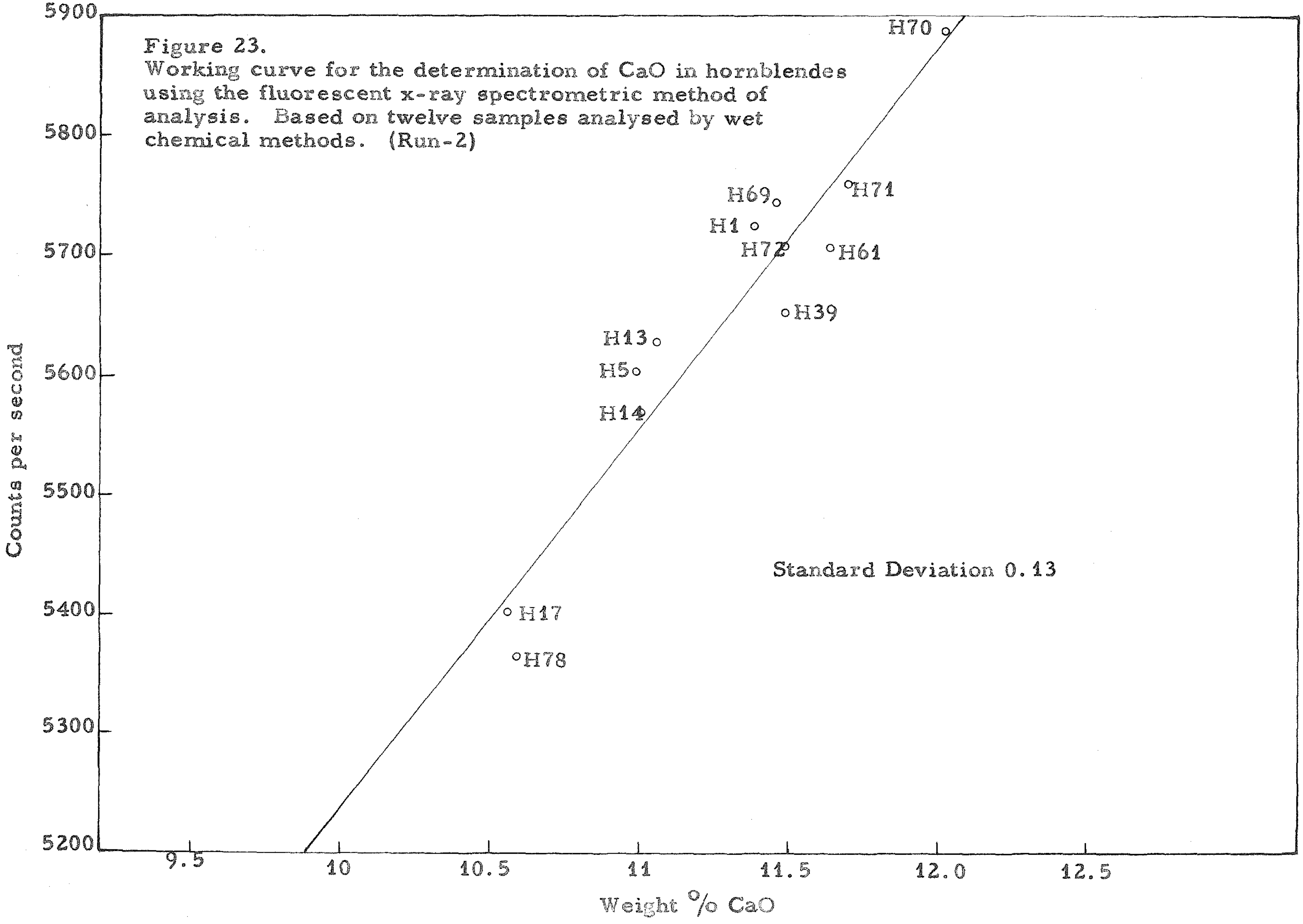


Figure 23.
Working curve for the determination of CaO in hornblendes using the fluorescent x-ray spectrometric method of analysis. Based on twelve samples analysed by wet chemical methods. (Run-2)

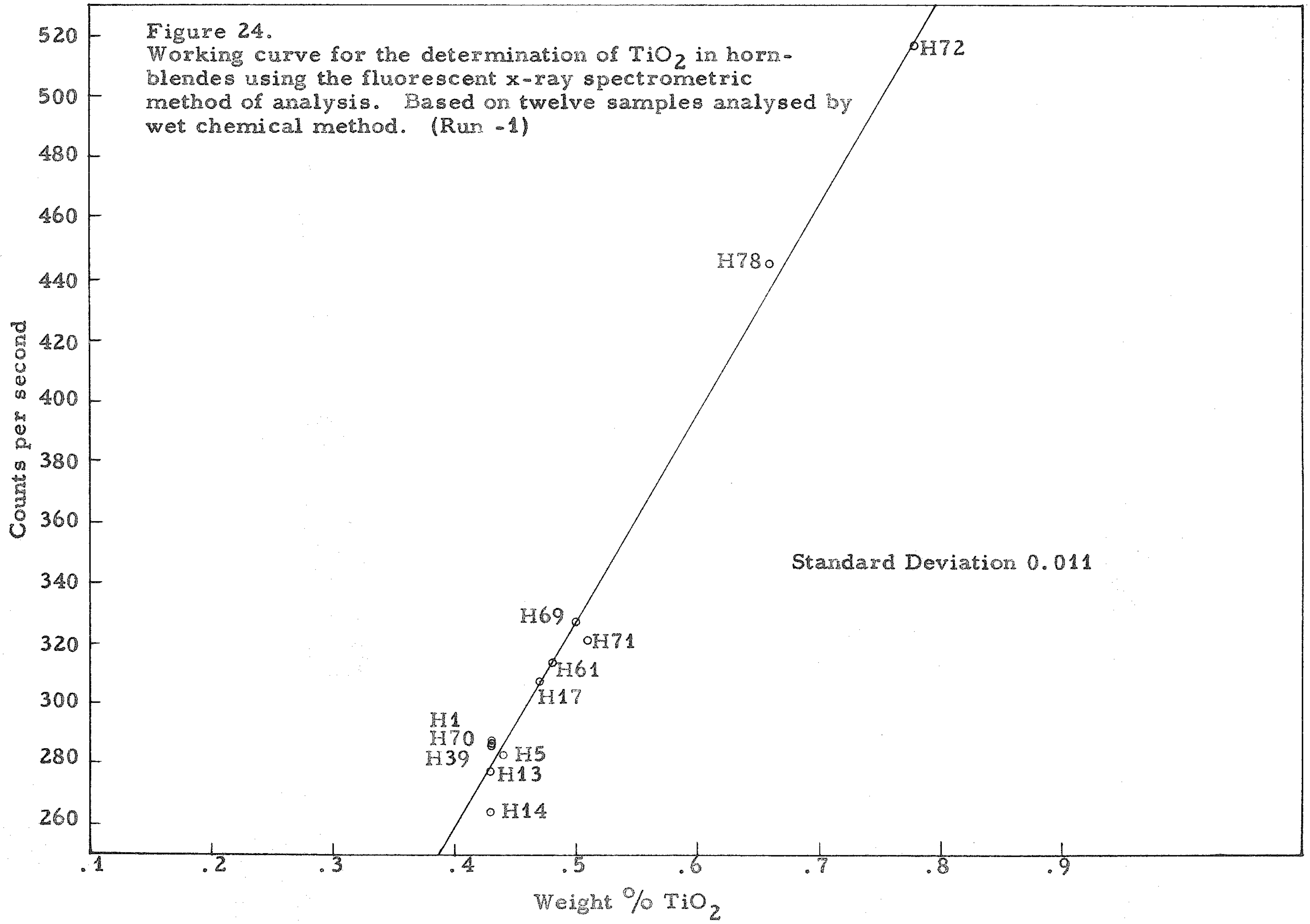


Figure 24.
Working curve for the determination of TiO_2 in hornblendes using the fluorescent x-ray spectrometric method of analysis. Based on twelve samples analysed by wet chemical method. (Run -1)

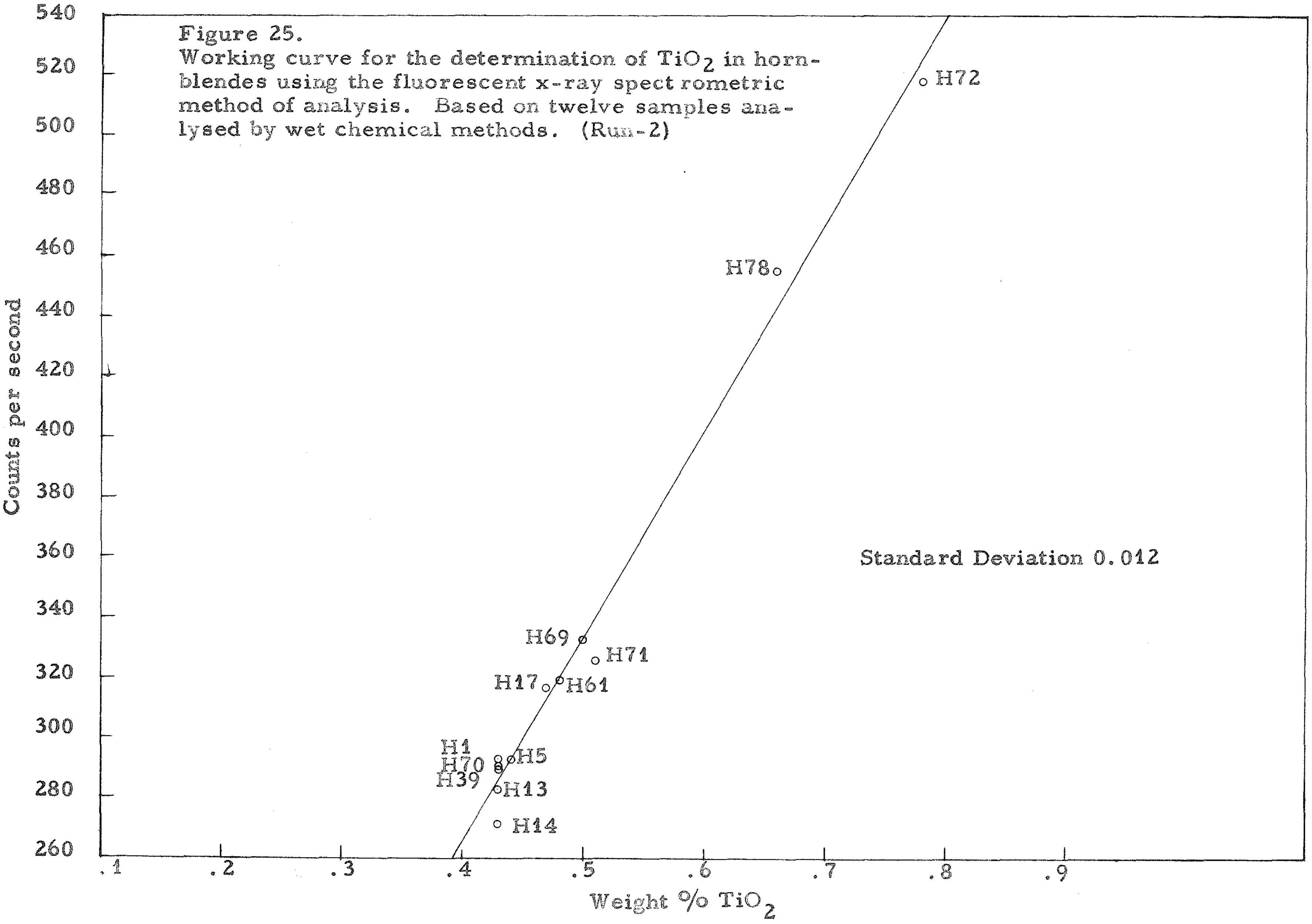


Figure 25.
Working curve for the determination of TiO_2 in hornblendes using the fluorescent x-ray spectrometric method of analysis. Based on twelve samples analysed by wet chemical methods. (Run-2)

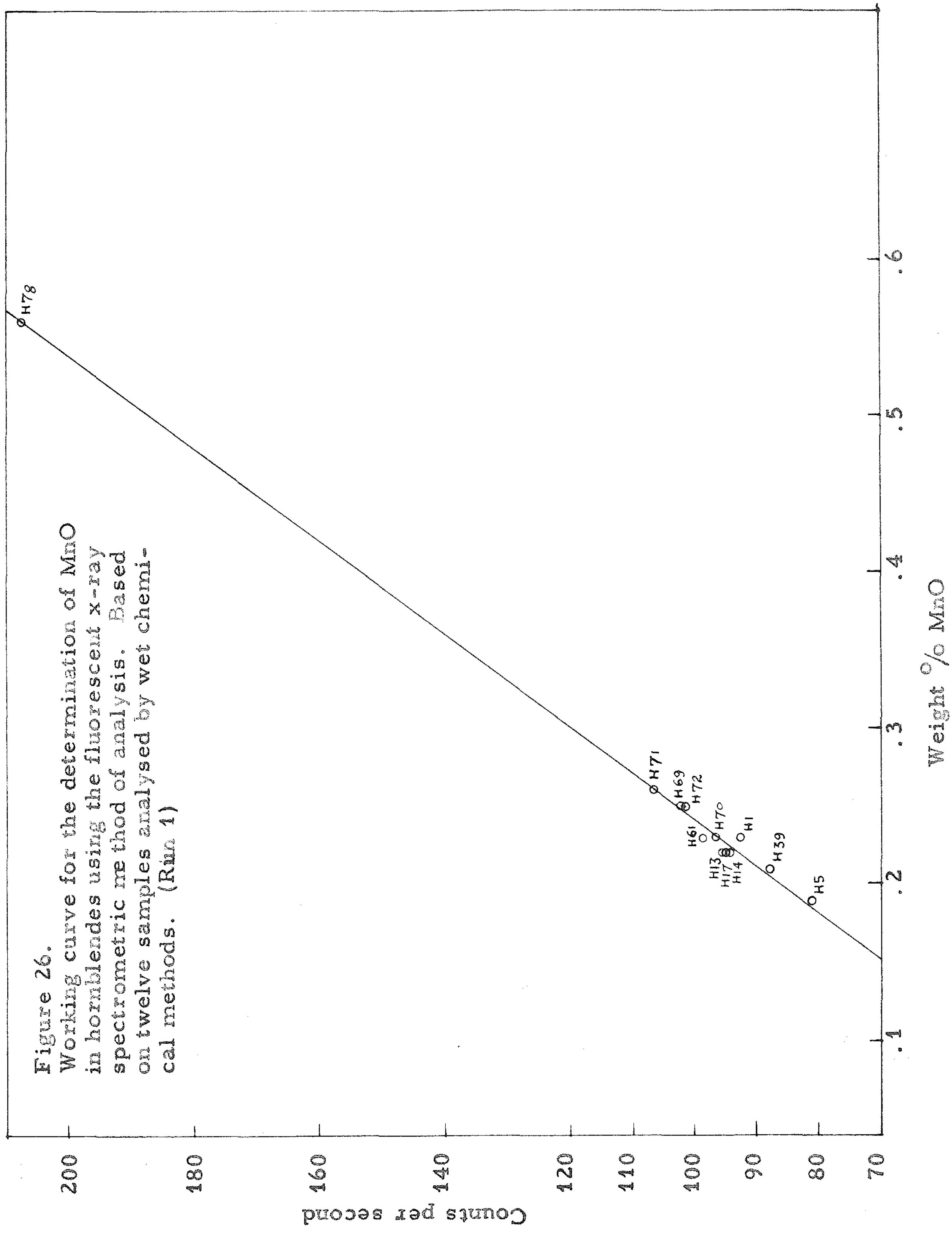


Figure 26.
Working curve for the determination of MnO in hornblendes using the fluorescent x-ray spectrometric method of analysis. Based on twelve samples analysed by wet chemical methods. (Run 1)

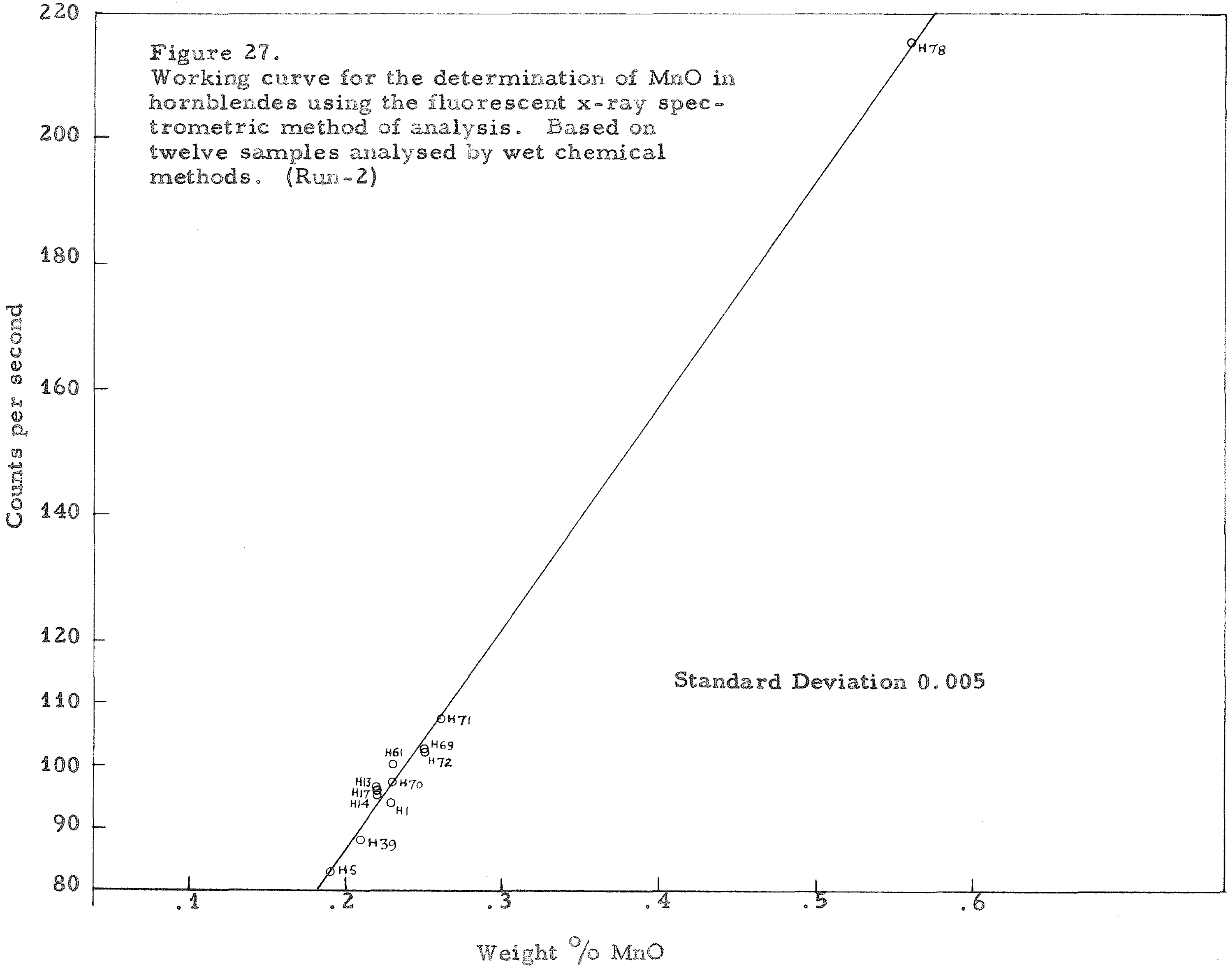


Figure 27.
Working curve for the determination of MnO in hornblendes using the fluorescent x-ray spectrometric method of analysis. Based on twelve samples analysed by wet chemical methods. (Run-2)

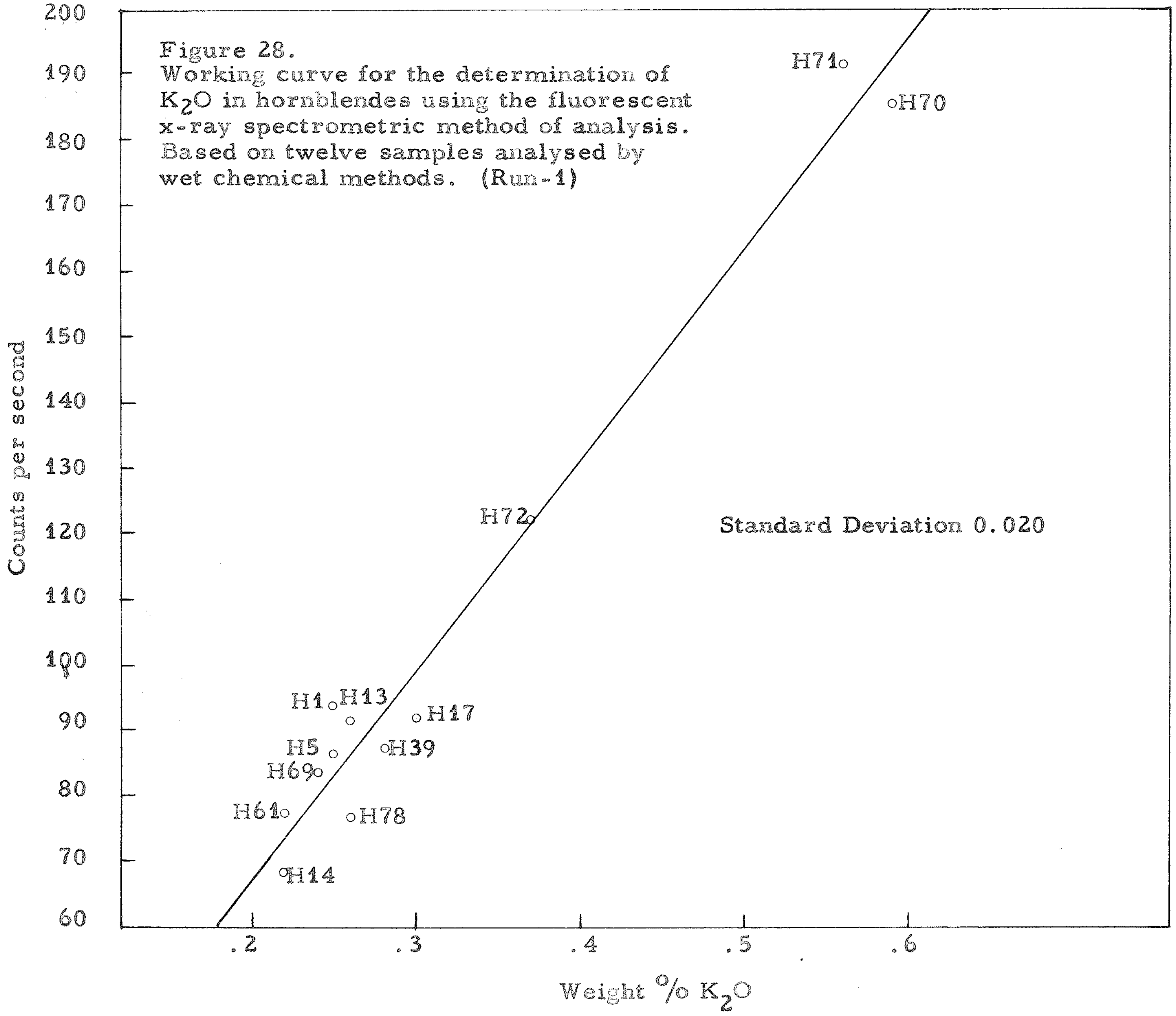


Figure 28.
Working curve for the determination of K_2O in hornblendes using the fluorescent x-ray spectrometric method of analysis. Based on twelve samples analysed by wet chemical methods. (Run-1)

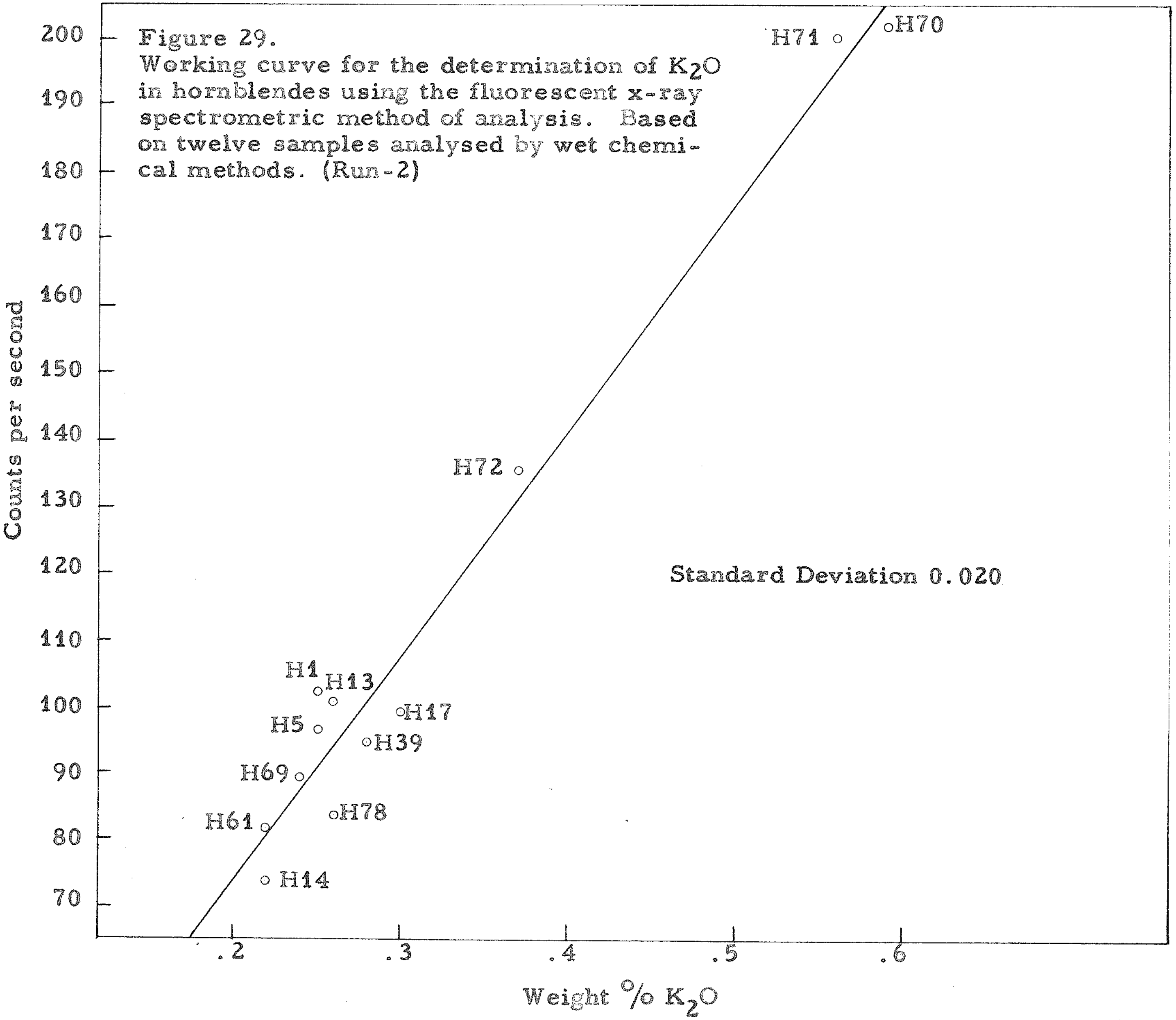


Figure 29.
Working curve for the determination of K_2O in hornblendes using the fluorescent x-ray spectrometric method of analysis. Based on twelve samples analysed by wet chemical methods. (Run-2)

No useful working curve could be obtained for Si, Al or Mg. The peaks of these elements are of very low intensity and any slight change in peak or background due to normal instrumental instability causes a considerable error in the analysis. To be able to analyse these elements much better instrumental stability is needed than was available. Figures 30, 31 and 32 show the experimental data obtained for these elements under the present instrumental setup.

The fluorescence analyses are given in Table 10.

Emission Spectrographic Analyses

Trace element contents of 34 hornblendes were determined by emission spectrographic method. The method, analytical conditions, sample preparation, and reproducibility have already been recorded earlier (see emission spectrographic analyses in Part II) and they apply equally here also. The trace element data of the hornblendes are given in Table 11.

An emission spectrographic method was also used to determine the Mg/Mg+Fe ratio of 22 hornblendes using the 12 hornblendes completely analysed by wet methods as standards. The analytical conditions were the same as those employed for trace element analysis except that 20 mg of mixtures of 1 part hornblende plus 9 parts graphite was used for each burn. This dilution of the sample was decided upon after several trials, and was necessary to get complete burns without loss.

Gower (1955, p. 42) used the ratio of intensities of 2929 Å iron line and 2779 Å magnesium line to determine Fe/Mg ratio in biotites. In the present work with hornblendes

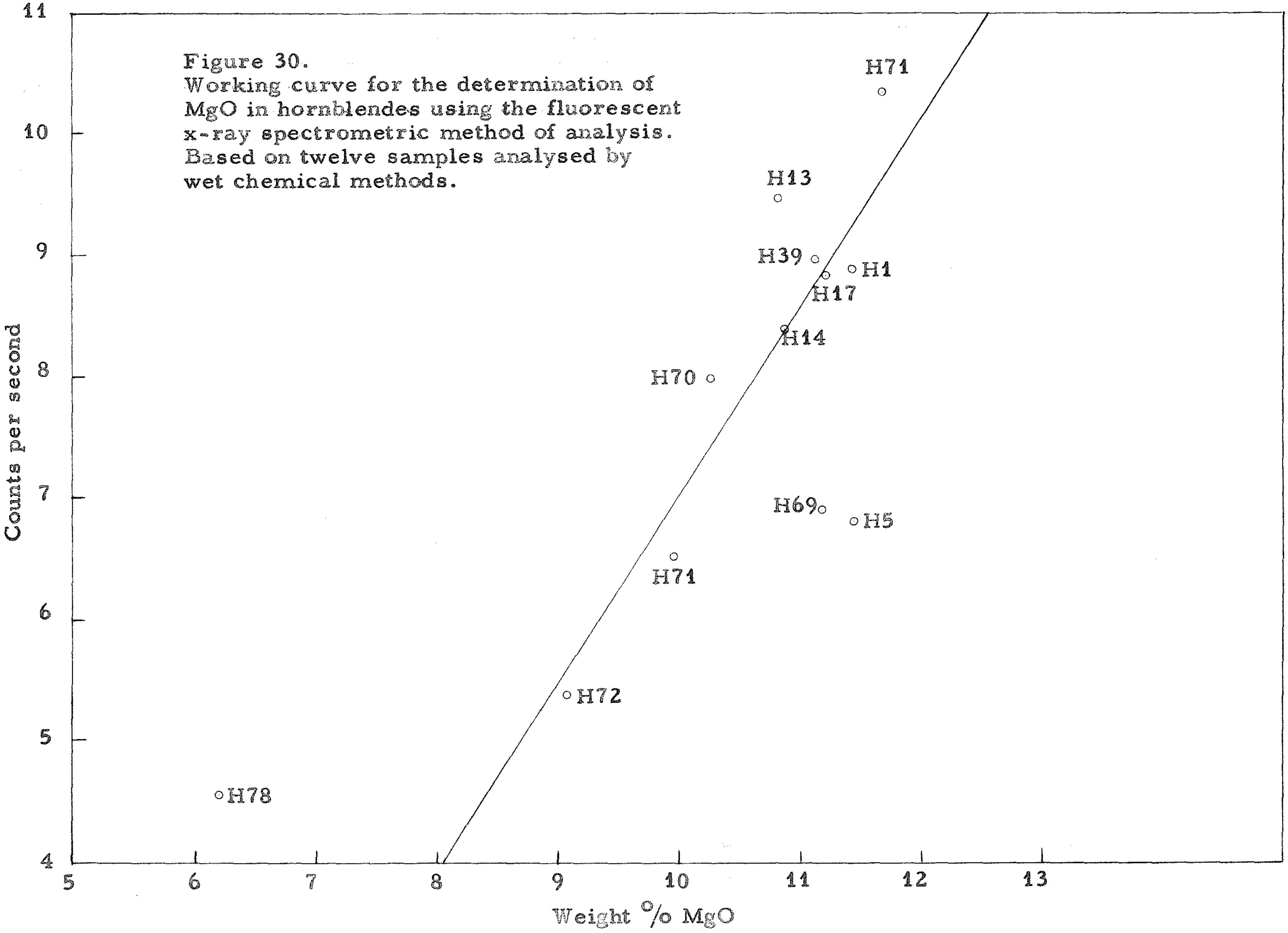


Figure 30.
Working curve for the determination of MgO in hornblendes using the fluorescent x-ray spectrometric method of analysis. Based on twelve samples analysed by wet chemical methods.

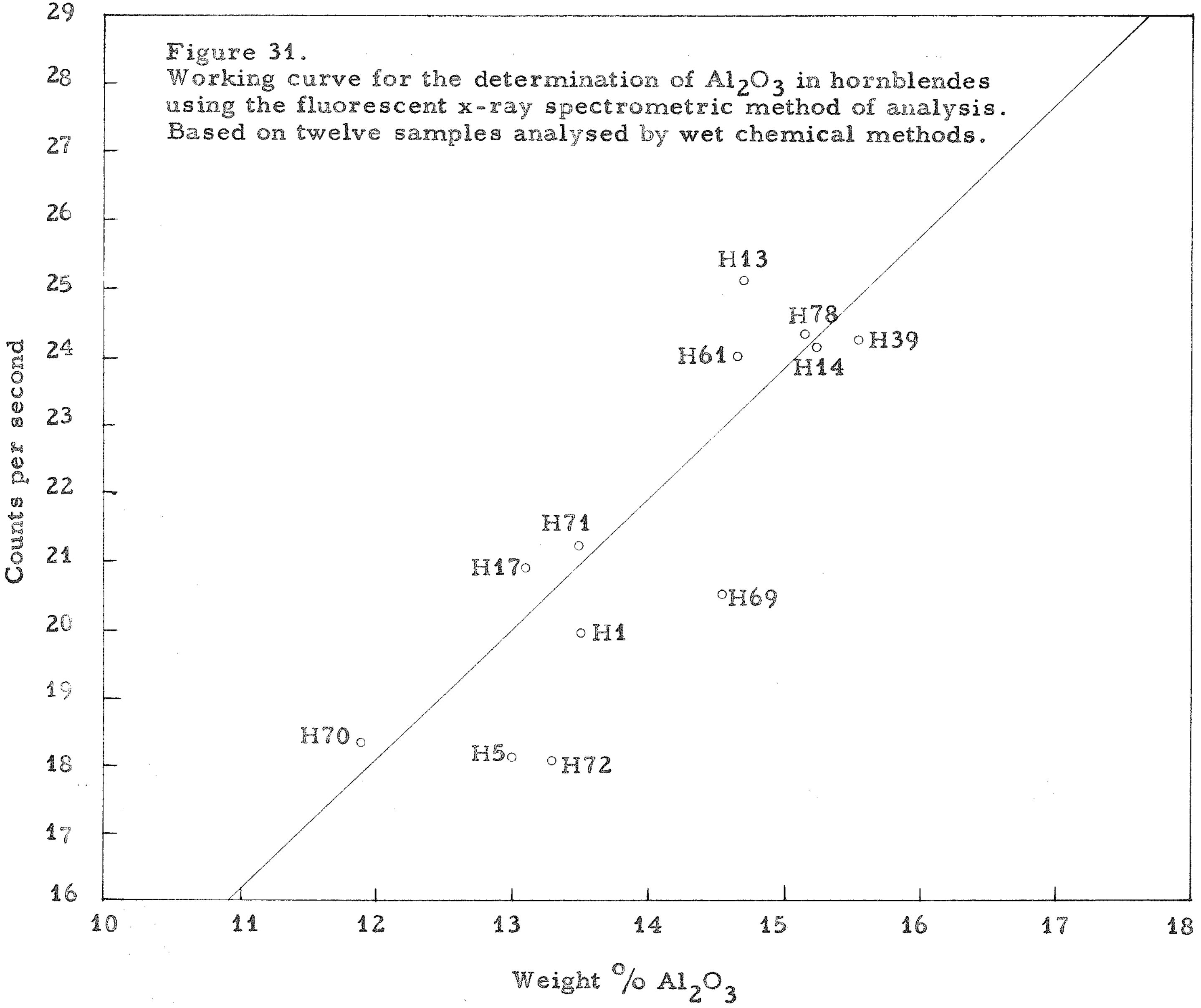


Figure 31.
Working curve for the determination of Al_2O_3 in hornblendes using the fluorescent x-ray spectrometric method of analysis. Based on twelve samples analysed by wet chemical methods.

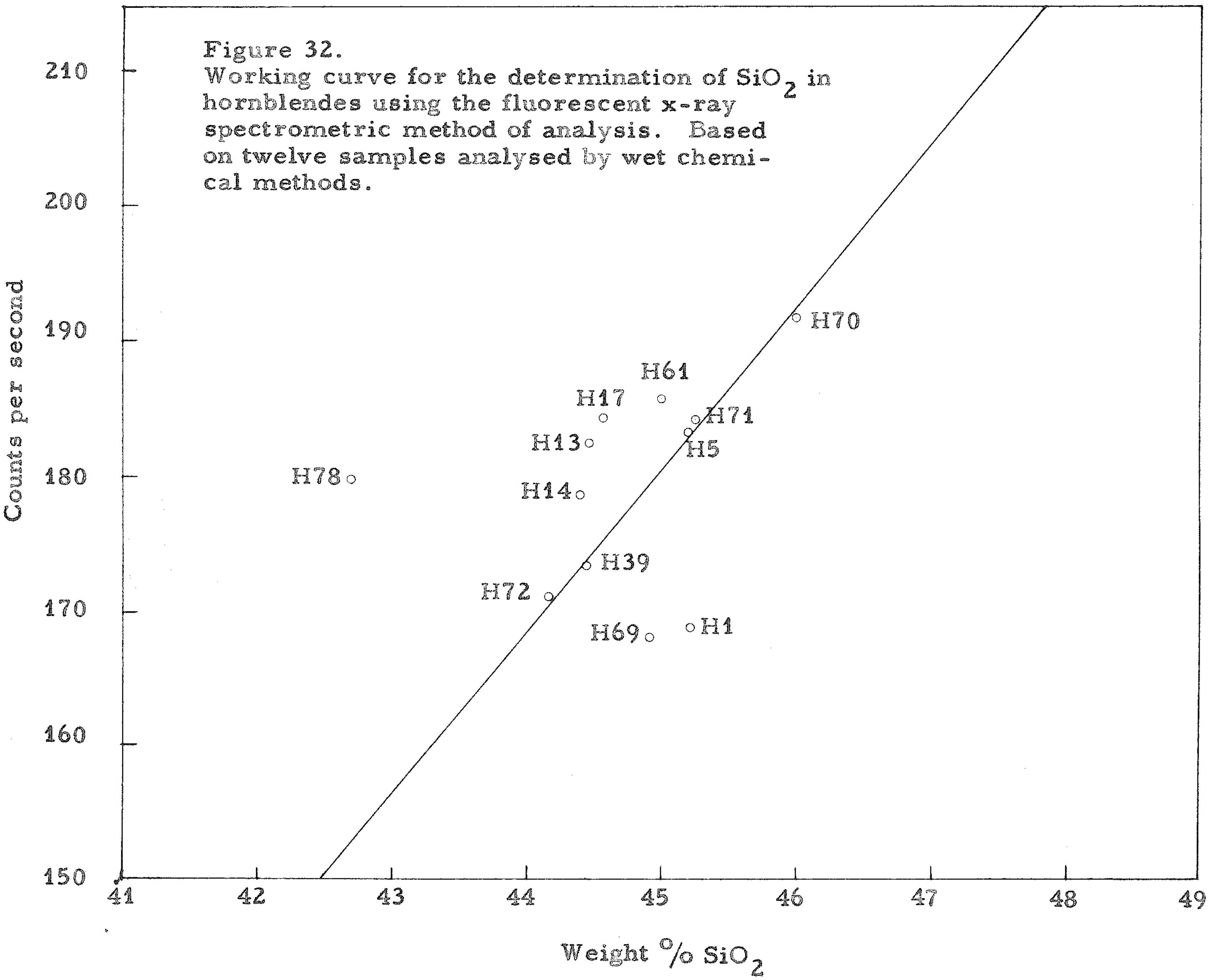


Figure 32.
Working curve for the determination of SiO_2 in hornblendes using the fluorescent x-ray spectrometric method of analysis. Based on twelve samples analysed by wet chemical methods.

Table 10

Five Major And Minor Components of 22 Hornblendes (in weight percent) (Analysed By Fluorescent x-ray Spectrographic Method)

Sample No.	Total Iron as Fe_2O_3	CaO	TiO_2	MnO	K_2O	
H-3	15.66	11.67	0.44	0.19	0.27	Hornblendes from Low-TiO_2 Amphibolites
H-7	15.11	11.93	0.46	0.23	0.30	
H-15	15.80	11.62	0.43	0.22	0.21	
H-20	16.01	11.71	0.47	0.23	0.35	
H-21	15.81	11.09	0.42	0.22	0.16	
H-28	14.91	11.75	0.52	0.20	0.20	
H-30	16.79	10.09	0.44	0.24	0.23	
H-33	16.09	11.46	0.50	0.25	0.22	
H-34	15.02	11.35	0.45	0.21	0.18	
H-35	16.13	10.77	0.53	0.21	0.24	
H-36	15.90	10.89	0.42	0.22	0.21	
H-46	15.04	11.60	0.52	0.22	0.21	
H-50	15.69	11.12	0.46	0.24	0.19	
H-57	15.82	12.46	0.64	0.21	0.15	
H-58	15.18	10.44	0.48	0.23	0.19	
H-59	15.00	11.13	0.42	0.22	0.20	
H-67	15.71	12.21	0.55	0.24	0.18	
H-52	18.73	11.22	0.63	0.21	0.20	Hornblendes from high-TiO_2 Amphibolites
+H-63	20.12	10.62	0.85	0.43	0.26	
H-64	13.72	12.04	0.59	0.29	0.14	
+ H-66*	22.71	10.84	0.74	0.23	0.57	
+ H-68*	25.56	8.46	1.03	0.38	1.09	

*Hornblendes from amphibolites with appreciable amount of biotite

+Hornblendes from garnetiferous amphibolites

Table 11

Trace Elements of 34 Hornblendes

(in parts per million)

(Analysed by Emission Spectrographic Method)

From low TiO_2 Amphibolites

From Class III amphibolites

Elements→	Ag	Ba	Co	Cr	Cu	Nb	Ni	Sb	Sc	Sr	V	Y	Zn	Zr
Sample No. ↓ Sensitivity→	0.5	1	2	5	1	15	2	200	2	2	2	10	80	2
H-1	.29	9	35	126	2	-	90	-	30	5	220	12	120	17
H-3	.10	5	26	75	6	-	66	-	23	3	95	pt	pt	15
H-5	.17	4	34	110	16	-	94	-	30	5	155	12	91	13
H-7	.15	8	30	47	8	-	71	-	19	5	110	pt	98	21
H-13	.38	13	25	70	8	-	70	-	26	6	180	13	100	21
H-14	.36	17	52	91	12	-	94	-	27	7	175	13	150	26
H-15	.24	3	39	94	34	-	100	-	20	6	220	pt	101	14
H-17	.10	4	21	72	21	-	64	-	28	4	135	pt	127	11
H-20	.18	14	33	71	37	-	70	-	21	5	160	pt	100	17
H-21	.13	6	35	77	17	-	82	-	21	4	150	pt	92	22
H-28	.13	7	42	131	6	-	97	-	27	5	280	13	110	26
H-30	.13	15	44	88	22	-	86	-	22	4	170	pt	92	18
H-33	.50	21	74	142	12	-	124	-	31	8	235	15	160	27
H-34	.21	5	39	102	1	-	88	-	27	5	190	13	92	28
H-35	.23	8	48	80	36	-	112	-	24	4	135	pt	111	19
H-36	.20	20	28	71	57	-	102	-	27	5	95	pt	92	18
H-39	.18	18	24	72	8	-	88	-	19	5	140	pt	98	17
H-46	.10	9	25	64	5	-	61	-	23	8	120	pt	91	18

Table 11 (Cont'd)

	Elements→	Ag	Ba	Co	Cr	Cu	Nb	Ni	Sb	Sc	Sr	V	Y	Zn	Zr
Sample No. ↓	Sensitivity→	0.5	1	2	5	1	15	2	200	2	2	2	10	80	2
H-50		.21	7	21	70	3	-	73	-	23	4	130	pt	102	19
H-57		.21	4	37	80	12	-	94	-	21	5	120	pt	95	25
H-58		.26	7	60	82	10	-	128	-	23	4	145	pt	97	23
H-59		.20	5	40	141	5	-	100	-	23	15	255	pt	122	21
H-61		.32	6	30	100	2	-	108	-	21	5	145	pt	200	26
H-67		.18	9	56	71	9	-	105	-	30	7	145	pt	192	36
H-69		.25	7	41	103	3	-	86	-	26	5	215	13	157	23
H-70		.33	46	49	152	1	-	122	-	34	101	235	pt	104	22
H-71		.29	6	58	84	9	-	98	-	38	8	195	pt	108	31
H-52	From high TiO_2 amphibolites From Class I amphibolite	.39	20	39	118	3	pt	82	-	37	16	320	20	145	94
H-63	From Class II amphibolites	.15	6	38	11	11	pt	12	-	25	9	260	pt	156	103
H-64		.21	3	39	360	15	-	180	pt	16	81	240	pt	98	105
H-66		.25	52	36	5	10	pt	8	-	38	8	185	50	235	233
H-68		.18	230	20	14	24	-	5	-	32	12	75	26	156	117
H-72		.40	11	33	175	27	-	63	-	34	8	330	19	123	53
H-78		.52	7	28	22	1	pt	18	-	32	7	125	26	172	123

Also looked for but absent or below sensitivity: As, Au, B, Be, Bi, Cd, Ga, Ge, In, La, Mo, Pb, Pt, Sn, Th, U, Yb

'pt' means approximately at the level of sensitivity
'-' means absent or below sensitivity

it was found that the 2779 Å Mg-line was rather too low in intensity compared to the 2929 Å Fe-line such that a small error in the determination of the intensity of the 2779 Å Mg-line caused large error in the intensity ratio. So 2782.97 Å Mg-line instead of 2779 Å Mg-line was used. It was chosen because of the closeness of its intensity to the intensity of 2929 Å Fe-line and because it has no appreciable interference from any line of the elements common in hornblende.

Each specimen was arced five times to give a correct average value. In the working curve (figure 33) the ratio (in percent) of intensities of the Mg-line to the sum of the Fe- and Mg-lines has been plotted against the Mg/Mg+Fe atom ratio (in percent) of the hornblendes. The range of the intensity ratio values obtained from five arcings of each specimen is indicated in the figure by solid lines, the point on the line representing the mean value. The spectrochemical values do not differ from the wet analytical values by more than 0.9% and the standard deviation is 0.6%.

The Mg/Mg+Fe atom ratios (in percent) are given in Table 12.

The hornblendes (H-63, H-66, H-68, H-78) from garnetiferous amphibolites are remarkably low in magnesium compared to all other hornblendes from garnet-free amphibolites. The obvious reason seems to be that in garnetiferous amphibolites part of the available magnesium is tied up by the garnets and as a result, the co-existing hornblendes become comparatively poor in magnesium.

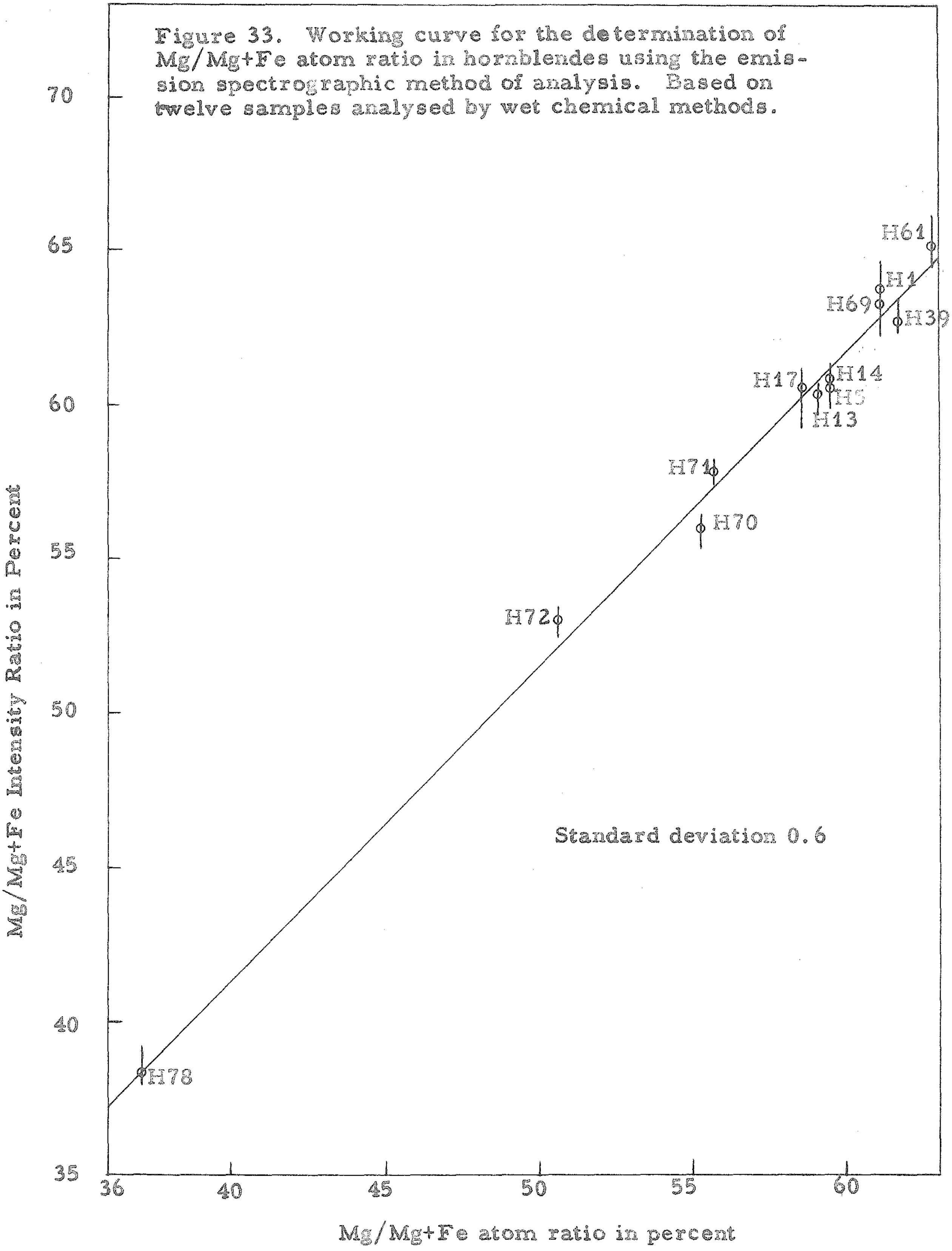


Figure 33. Working curve for the determination of Mg/Mg+Fe atom ratio in hornblendes using the emission spectrographic method of analysis. Based on twelve samples analysed by wet chemical methods.

Table 12

Atomic Ratio of Mg/Mg+Fe In Hornblendes (in percent)

	Sample No.	Mg/Mg+Fe Atom Ratio In Percent. From wet analytical data.	Mg/Mg+Fe Atom Ratio In Percent. From working curve (Emission Spec.)	Difference of emission values from wet analytical values. (In percent)
From low-TiO_2 amphibolites	H-1*	61.1	61.5	+0.4
	H-3		62.0	
	H-5*	59.5	59.1	-0.4
	H-7		61.8	
	H-13*	59.1	58.6	-0.5
	H-14*	59.5	58.8	-0.7
	H-15		60.2	
	H-17*	58.6	58.8	+0.2
	H-20		59.0	
	H-21		61.2	
	H-28		62.5	
	H-30		60.6	
	H-33		61.0	
	H-34		63.9	
	H-35		61.4	
	H-36		60.8	
	H-39*	61.7	61.0	-0.7
	H-46		62.4	
	H-50		62.3	
	H-57		60.6	
	H-58		62.0	
	H-59		63.5	
	H-61*	62.8	63.4	+0.6
	H-67		61.4	
	H-69*	61.1	62.0	+0.9
	H-70*	55.3	54.4	-0.9
	H-71*	55.7	56.2	+0.5

Table 12 (Cont'd)

	Sample No.	Mg/Mg+Fe Atom Ratio In Percent. From wet analytical data.	Mg/Mg+Fe Atom Ratio In Percent. From working curve (Emission Spec.)	Difference of emission values from wet analytical values (In percent)
From high-TiO_2 amphibolites	H-52		54.4	
	[+]H-63		44.4	
	H-64		65.6	
	[+]H-66		41.1	
	[+]H-68		33.8	
	H-72[*]	50.6	51.4	+0.8
	[+]H-78[*]	37.1	37.1	0

[*] Samples used as standards, analysed by wet chemical methods

[+] Hornblendes from garnetiferous amphibolites

ATOMIC CONSTITUTION OF THE HORNBLENDES

Structural formulae of the 12 hornblendes which were completely analysed (wet method), were calculated in the standard way on the basis of 24 O, OH, F and Cl ions in the unit cell. The formulae are given in Table 13.

After the standard amphibole formula was established by B. E. Warren (1929, 1930), various workers have attempted to classify amphiboles on the basis of chemical composition (Kunitz W., 1930; Berman H., et al., 1931; Berman H., 1937; Hallimond A. F., 1943; Sundius N., 1946; Boyd, 1958). Although the nomenclature of the ideal end members of the calciferous hornblendes are universally accepted, there is some confusion about the names of some natural types.

Next to the Mg—Fe^{2+} substituion in the octahedral site the other important substitutions in the lime-bearing hornblendes are $Na(K)Al^{IV}$ for Si^{IV} and $Al^{VI}(Fe^{3+})Al^{IV}$ for $Mg^{VI}Si^{IV}$. Starting with tremolite the ideal end members are built in the following way:

Tremolite

$Ca_2Mg_5Si_8O_{22}(OH)_2$

↓

Substitution

$NaAl^{IV}$ for Si^{IV}

↓

Edenite

$NaCa_2Mg_5AlSi_7O_{22}(OH)_2$

Table 13

Structural Formulae of 12 Hornblendes Analysed by Wet Chemical Methods

(Structure Type $X_{0-1}A_2B_5C_8Y_{24}$)

		H-1	H-5	H-13	H-14	H-17	H-39	H-61	H-69	H-70	H-71	H-72	H-78
X	Na^{1+}	.250	.243	.287	.284	.088	.286	.314	.250	.200	.210	.167	.447
	K^{1+}	.052	.053	.053	.035	.053	.052	.035	.052	.106	.106	.071	.054
	Ca^{2+}	-	-	-	-	-	-	.009	-	-	-	-	-
	0-1	.302	.296	.340	.319	.141	.338	.358	.302	.306	.316	.238	.501
A	Ca^{2+}	1.777	1.720	1.735	1.714	1.647	1.786	1.803	1.780	1.901	1.843	1.822	1.717
	Fe^{2+}	.114	.181	.174	.194	.082	.126	.171	.121	.061	.068	-	.185
	Na^{1+}	.083	.073	.065	.066	.245	.062	-	.064	.012	.054	.153	.025
	Mn^{2+}	.026	.026	.026	.026	.026	.026	.026	.035	.026	.035	.025	.073
	2	2	2	2	2	2	2	2	2	2	2	2	2
B	Mg^{2+}	2.487	2.475	2.360	2.361	2.436	2.404	2.526	2.417	2.246	2.187	1.999	1.399
	Fe^{2+}	1.357	1.390	1.367	1.319	1.521	1.285	1.266	1.336	1.655	1.572	1.848	2.032
	Al^{3+}	.902	.854	1.053	1.084	.762	1.111	1.034	1.021	.843	.976	.841	1.169
	Fe^{3+}	.210	.228	.176	.192	.228	.157	.122	.174	.212	.212	.213	.327
	Ti^{4+}	.044	.053	.044	.044	.053	.043	.052	.052	.044	.053	.089	.073
	Mn^{2+}	-	-	-	-	-	-	-	-	-	-	.010	-
	5	5	5	5	5	5	5	5	5	5	5	5	5
C	Si^{4+}	6.591	6.608	6.517	6.461	6.501	6.446	6.525	6.526	6.774	6.648	6.531	6.461
	Al^{3+}	1.409	1.392	1.483	1.539	1.499	1.554	1.475	1.474	1.226	1.352	1.469	1.539
	8	8	8	8	8	8	8	8	8	8	8	8	8
Y	O^{2-}	22.001	22.020	22.119	22.068	21.494	22.075	22.154	22.064	22.205	22.201	21.849	22.574
	OH^{1-}	1.978	1.966	1.867	1.923	2.488	1.916	1.829	1.919	1.698	1.746	2.133	1.417
	F^{1-}	.018	.014	.014	.009	.018	.009	.017	.014	.097	.053	.018	.009
	Cl^{1-}	.003	trace	trace	trace	trace	-	-	.003	-	trace	-	trace
	24	24	24	24	24	24	24	24	24	24	24	24	24

Tremolite

$Ca_2Mg_5Si_8O_{22}(OH)_2$

$\downarrow$

Substitution

$NaAl^{IV}$ for Si^{IV}

$Al^{VI}(Fe^{3+})Al^{IV}$ for $Mg^{VI}Si^{IV}$

$\downarrow$

Pargasite

$NaCa_2MG_4(Al, Fe^{3+})Al_2Si_6O_{22}(OH)_2$

Tremolite

$Ca_2Mg_5Si_8O_{22}(OH)_2$

$\downarrow$

Substitution

$Al^{VI}(Fe^{3+})Al^{IV}$ for $Mg^{VI}Si^{IV}$

$Al^{VI}(Fe^{3+})Al^{IV}$ for $Mg^{VI}Si^{IV}$

$\downarrow$

Tschermakite

$Ca_2Mg_3(Al, Fe^{3+})_2Al_2Si_6O_{22}(OH)_2$

With substitution of Fe^{2+VI} for Mg^{2+VI} these end members pass into their ferrous analogues with distinctive names, like:

Tremolite → Actinolite
Edenite → Ferroedenite
Tschermakite → Ferrotschermakite

There is however confusion with the name of the ferrous analogue of 'pargasite' and with the name 'pargasite' itself. Some authors use the name 'hastingsite' to designate the ferrous analogue of pargasite. The name 'hastingsite' was originally used to describe a hornblende rich in iron and aluminum with moderate amounts of alkalis. M. P. Billings (1928) later proposed the use of the name 'hastingsite' also for Mg-rich members and divided the relevant series into sub-groups named magnesio-hastingsites, femag-hastingsites and ferro-hastingsites. Thus Billings' 'magnesio-hastingsite' is synonymous with 'pargasite' and his ferro-hastingsite' is 'hastingsite' of other workers. As a compromise N. Sundius (1946, p. 22) suggested the retention of the terms 'pargasite' and 'hastingsite' as expressions for the Mg- and Fe^{2+}-extreme members of the hornblende series with tetrahedral Al-content approaching 2 and the use of the term 'femag-hastingsite' to designate the numerous members with intermediate $Mg:Fe^{2+}$ ratios.

According to their structural formulae (Table 13) all the 12 hornblendes should be classified as femag-hastingsite, both in Billings' and Sundius' sense. Sample H-78 is the most hastingsitic and sample H-61 is the least hastingsitic member of the group.

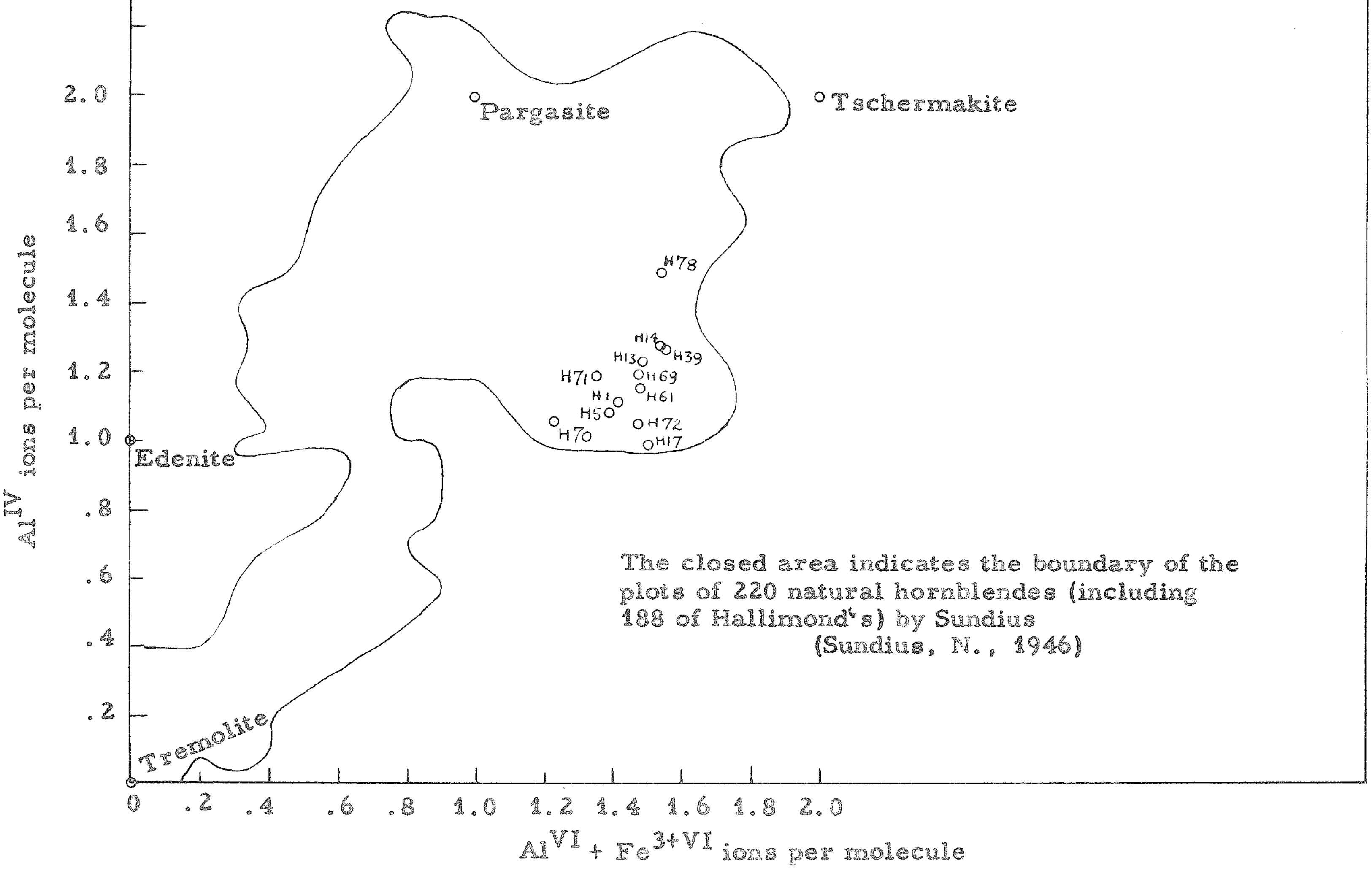
It is difficult to represent these formulae in terms of four ideal end-members of the calcic hornblendes because all these ideal members do not involve any substitution of their Ca-content whereas up to 18% of the lime in the hornblendes of the present case is replaced by Fe^{2+}, Mn and alkalies. Whether this substitution of Ca by Na is part of the paired substitution NaNa for Ca or $NaAl^{IV}$ for CaMg cannot be decided. As a consequence the exact extents of the substitutions $NaAl^{VI}$ for Si and $Al^{VI}(Fe^{3+})Al^{IV}$ for MgSi cannot be known. Ti replaces Mg probably as part of the substitution $TiAl^{IV}Al^{IV}$ for MgSiSi or TiNaNa for MgCaCa. In either case it brings in additional complications.

In figure 34 tetrahedral Al content has been plotted against octahedral Al and Fe^{3+} (because Fe^{3+} compensates Al^{VI}) for each of the 12hornblendes. The extent of the area which includes 220 similar plots of natural calcic hornblendes ($Ca > 1.5$) (Sundius, 1946, fig. 6) is also shown for comparison.

A comparison of the analyses (partial, Table 10) of 22 other hornblendes with those of the 12 which have been completely analysed (Table 9) and whose structural formulae have been calculated (Table 13) indicates that all of them are also femag-hastingsites.

In figure 35 Mg/Mg+Fe atom ratios (in percents) of the 34 hornblendes have been plotted against their total iron (as Fe_2O_3 in weight percent) contents. The well known substitution relationship between iron and magnesium is clearly demonstrated by the figure.

Figure 34.
Comparison of the compositions of hornblendes from Lead-Deadwood area with those from other areas (compiled by Hallimond and Sundius).



The closed area indicates the boundary of the plots of 220 natural hornblendes (including 188 of Hallimond's) by Sundius
(Sundius, N., 1946)

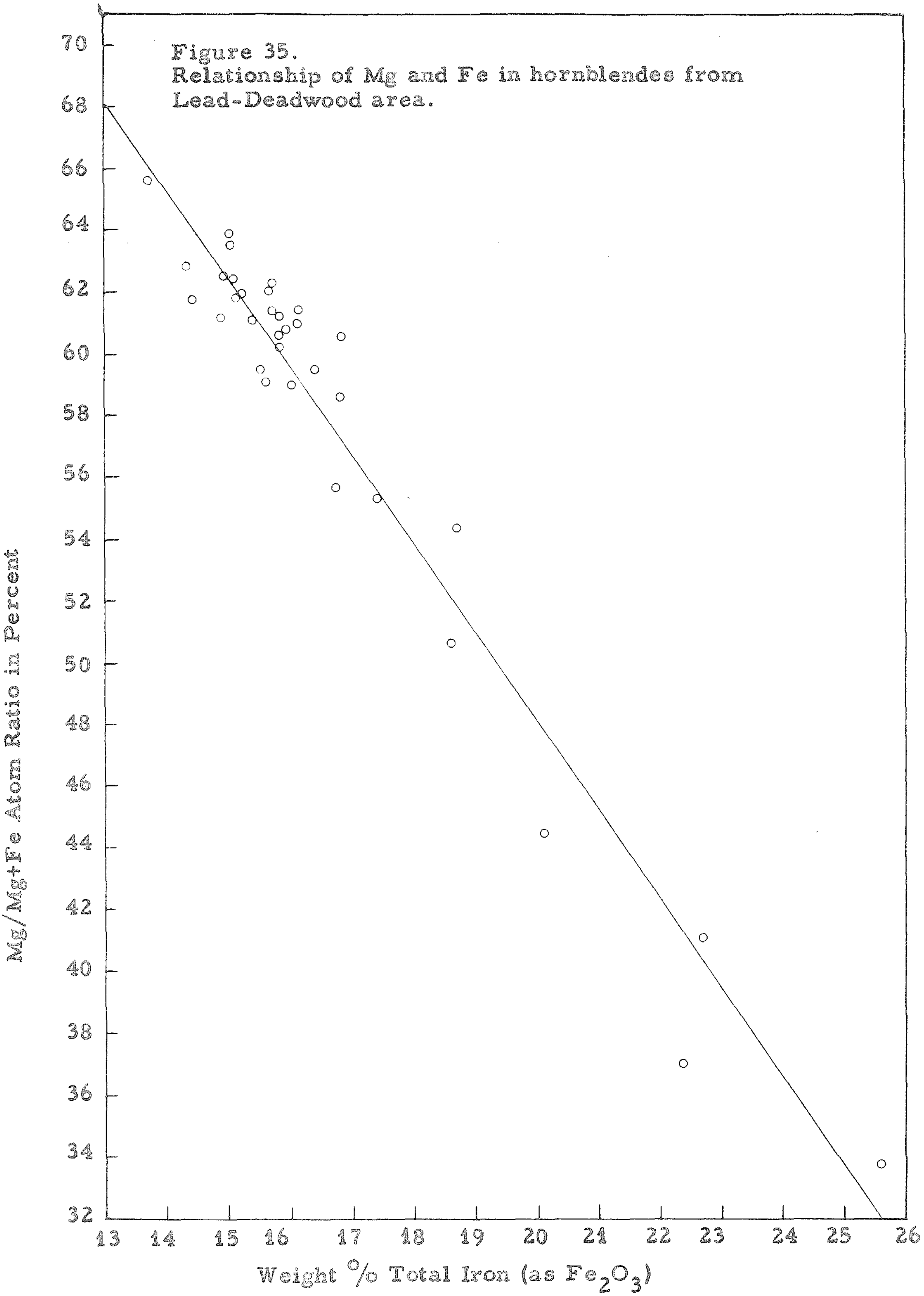


Figure 35.
Relationship of Mg and Fe in hornblendes from Lead-Deadwood area.

CHEMICAL COMPOSITIONS OF THE HORNBLENDES AND THEIR RELATIONS TO METAMORPHISM

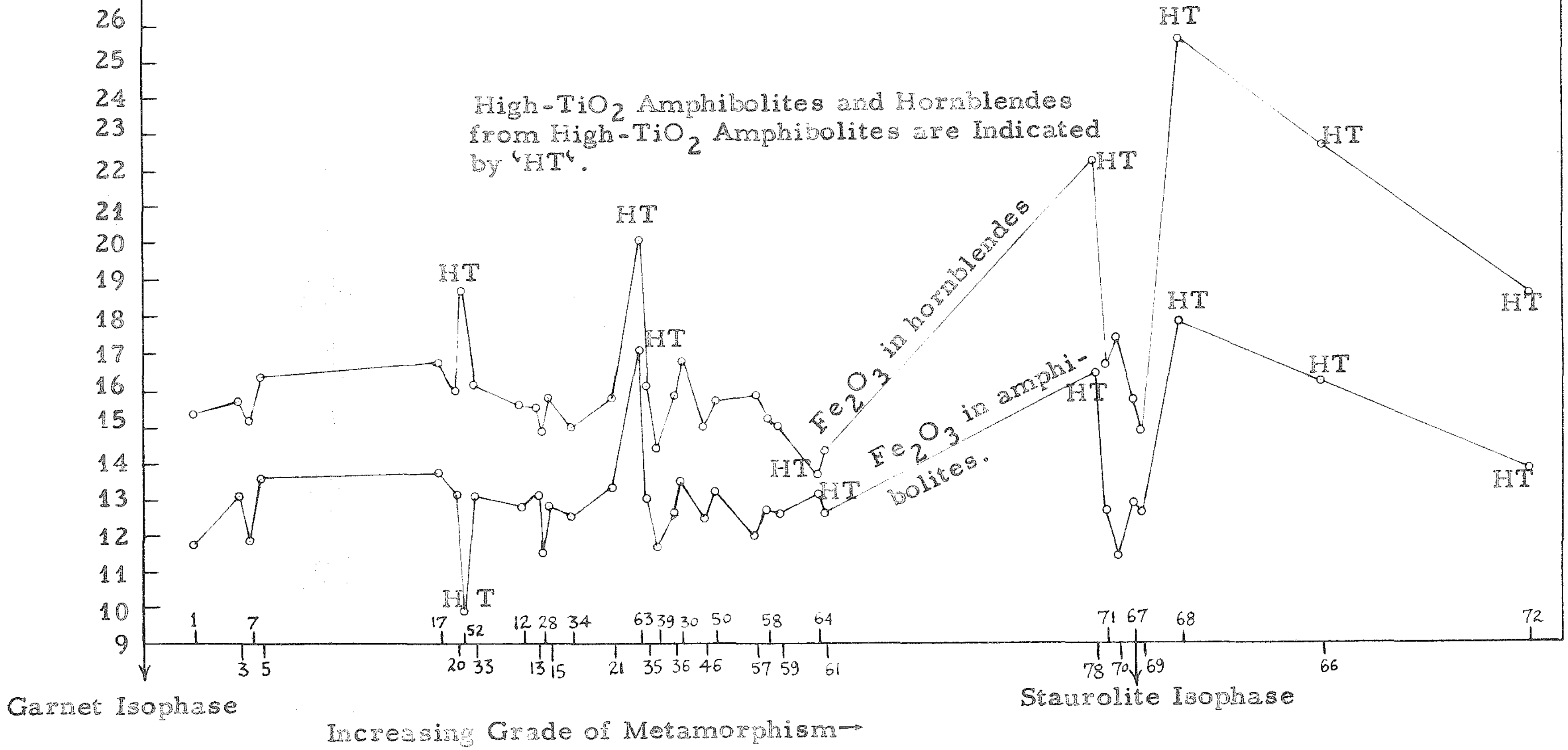
In order to study the extent to which the chemical composition of the hornblendes is affected by increasing metamorphic conditions, the chemical data from the hornblendes were plotted against the varying metamorphic ranks they represent. In figures 36 to 40 the total iron (as Fe_2O_3), TiO_2, CaO, MnO and K_2O contents of the hornblendes have been plotted against their inferred grade of metamorphism in the same way as the amphibolites in Part II. The oxides of the same elements in corresponding amphibolites have also been plotted in the figures for comparison. In the figures the points representing the 7 high-TiO_2 specimens are indicated by "HT" marked close to the points. No obvious trend in the composition of the hornblendes in either the low-TiO_2 or high-TiO_2 groups is discernible as a function of the increasing grade of metamorphism.

In order to obtain a statistical picture the 27 hornblendes from the low-TiO_2 amphibolites were divided into four sub-groups (exactly in the same way as the corresponding amphibolites, in Part II) on the basis of their distances from the garnet isophase and the means of each of the five components total iron (as Fe_2O_3), CaO, TiO_2, MnO and K_2O for each sub-group were plotted against the mean distances of the sub-groups from the garnet isophase. The four sub-groups are as follows:

Sub-group A: H-1, H-3, H-5, H-7

Sub-group B: H-13, H-14, H-15, H-17, H-20, H-28
H-33, H-34

Figure 36.
Amounts of total iron (as Fe_2O_3) in hornblendes and corresponding amphibolites plotted against grade of metamorphism.



High-TiO_2 Amphibolites and Hornblendes from High-TiO_2 Amphibolites are Indicated by 'HT'.

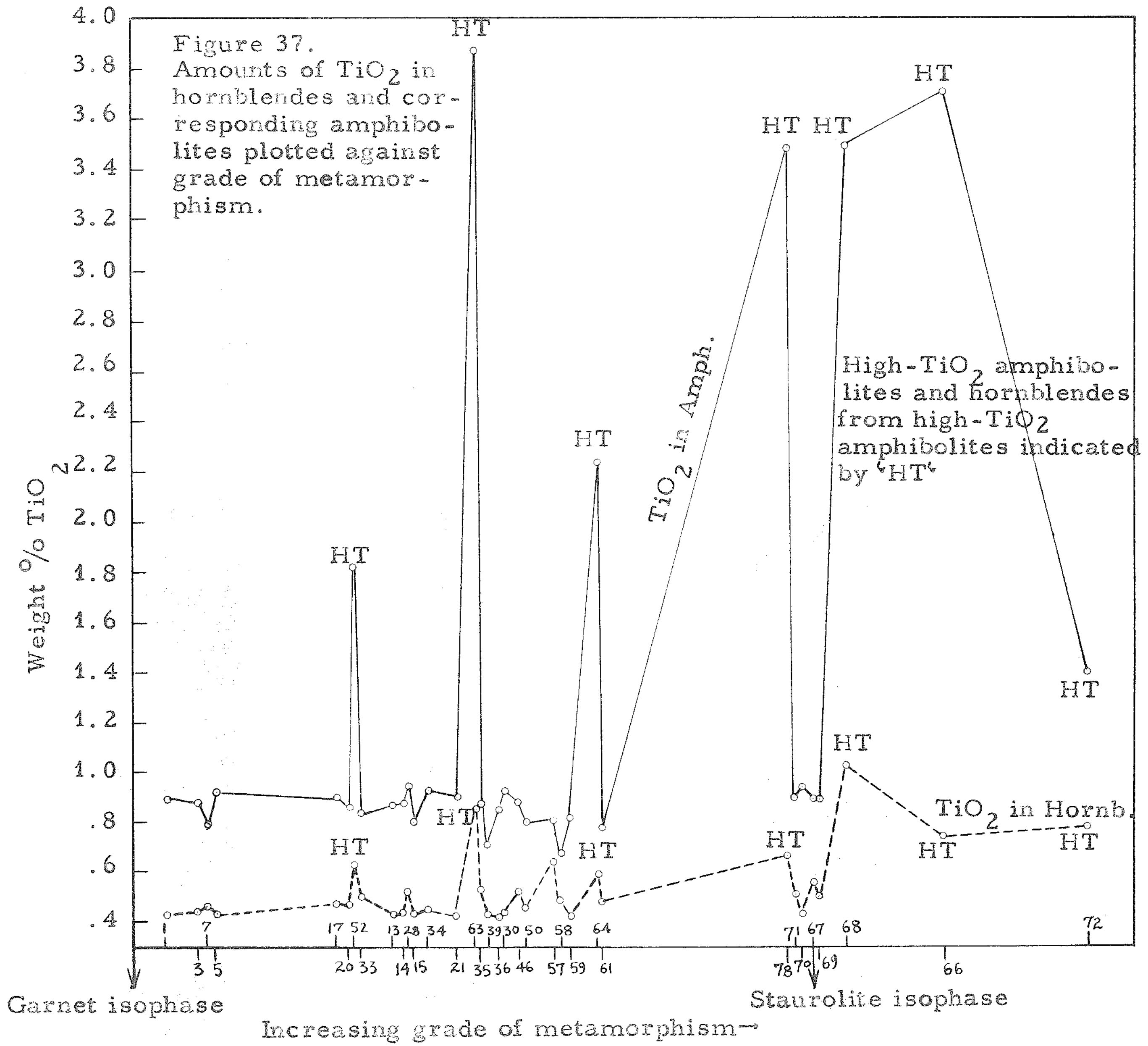
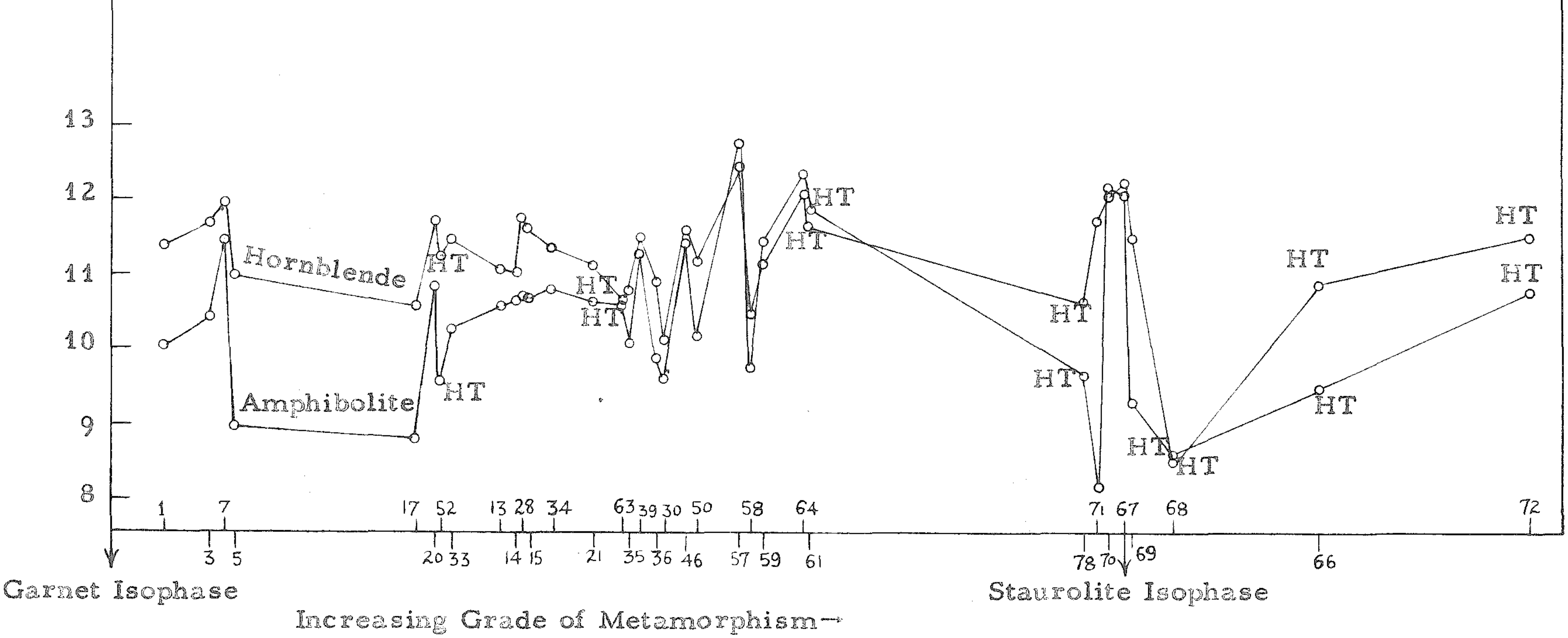


Figure 37. Amounts of TiO_2 in hornblendes and corresponding amphibolites plotted against grade of metamorphism.

Figure 38.
Amounts of CaO in hornblendes and corresponding amphibolites plotted against grade of metamorphism.



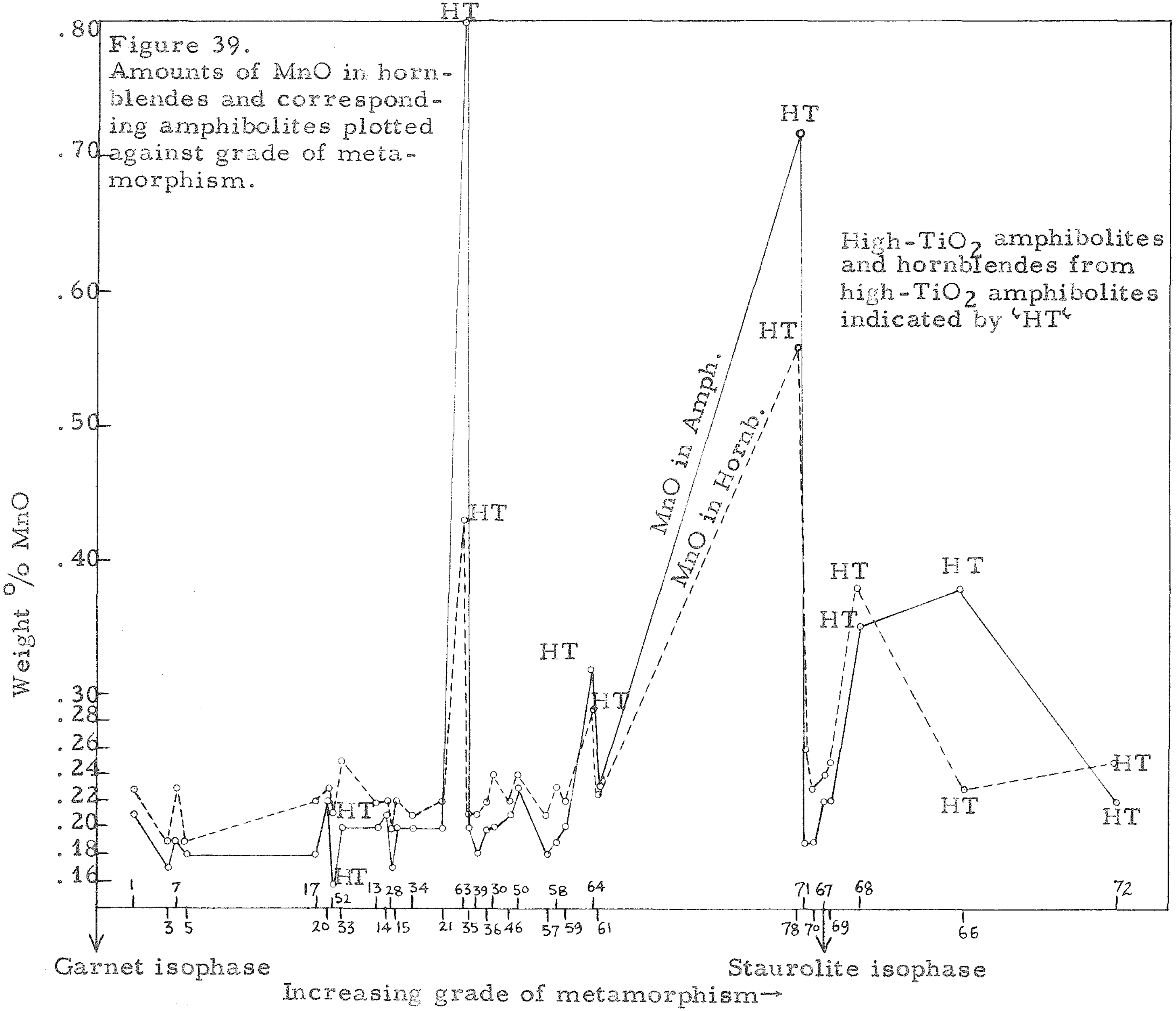


Figure 39.
Amounts of MnO in hornblendes and corresponding amphibolites plotted against grade of metamorphism.

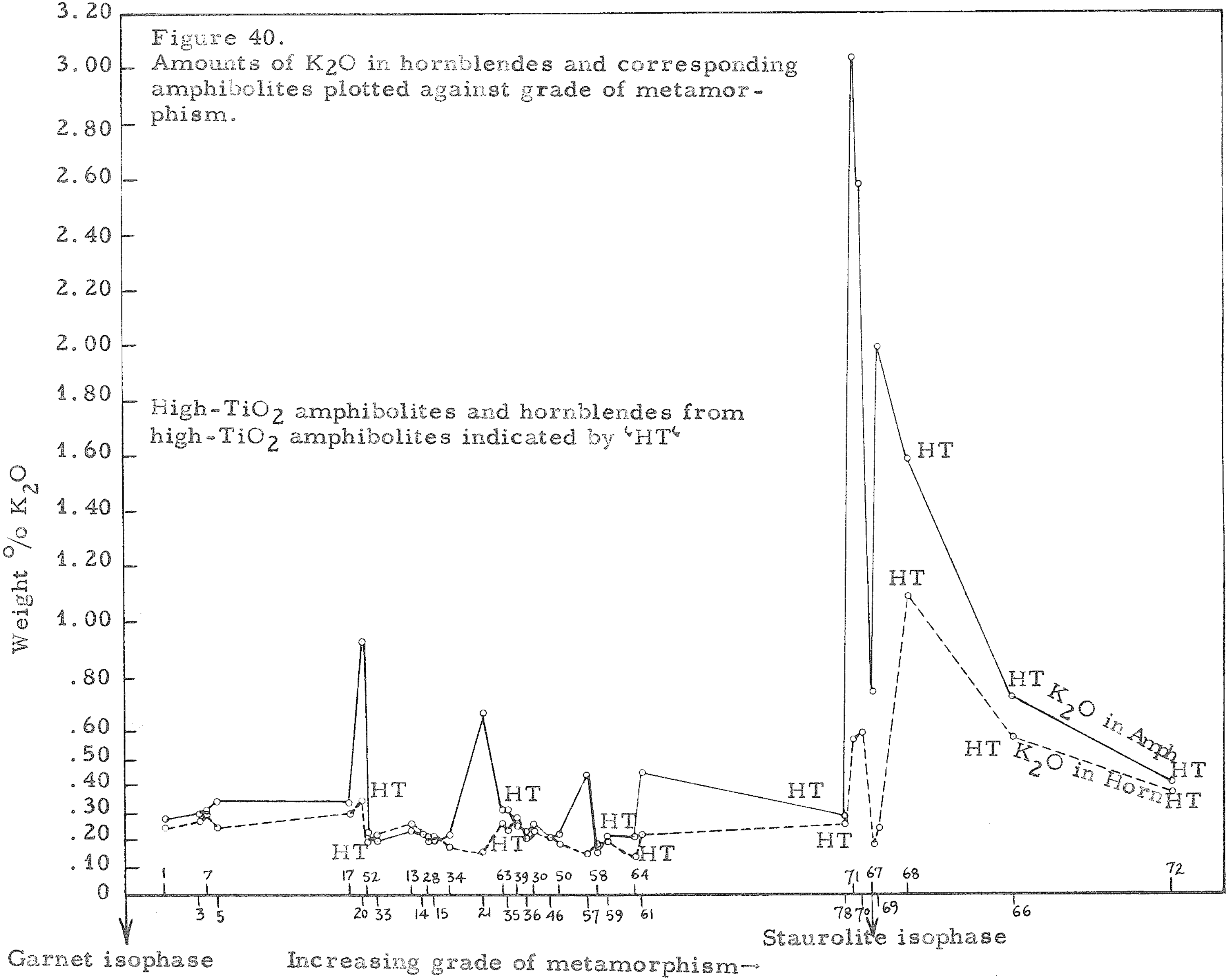


Figure 40.
Amounts of K_2O in hornblendes and corresponding amphibolites plotted against grade of metamorphism.

High-TiO_2 amphibolites and hornblendes from high-TiO_2 amphibolites indicated by 'HT'

Sub-group C: H-21, H-30, H-35, H-36, H-39, H-46,
H-50, H-57, H-58, H-59, H-61

Sub-group D: H-67, H-69, H-70, H-71

The mean values of the various components in the four sub-groups are given in Table 14 and are plotted in figures 41 and 42. In the figures the spread of the analyses in each sub-group is shown by a solid vertical line with solid circles on the line indicating individual analyses in the sub-group.

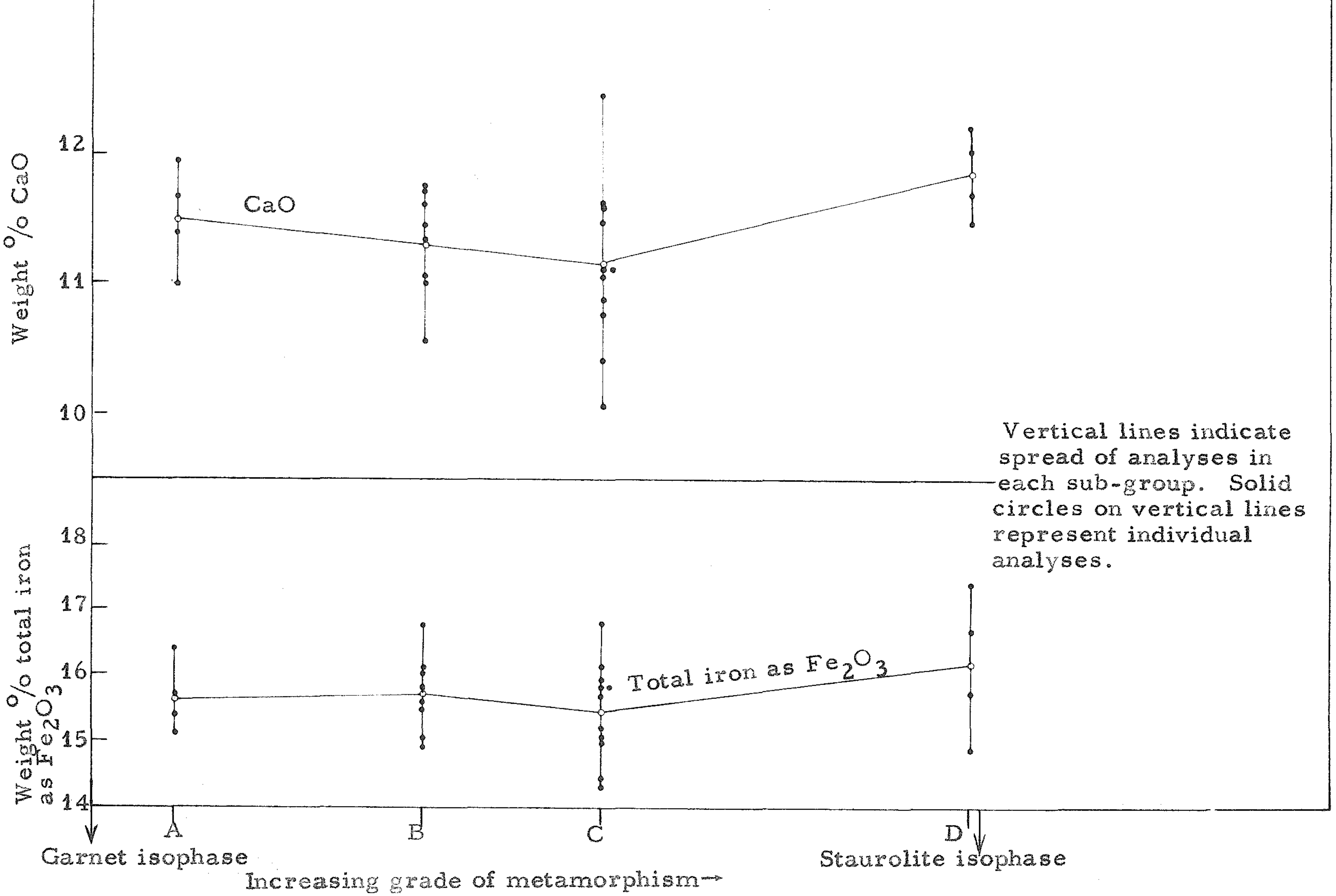
Table 14

Mean Values of Five Major and Minor Components of Hornblendes from Low-TiO_2 Amphibolites

	Total iron as Fe_2O_3	CaO	TiO_2	K_2O	MnO
Sub-group A	15.64	11.50	0.44	0.27	0.21
Sub-group B	15.71	11.32	0.46	0.24	0.22
Sub-group C	15.46	11.16	0.48	0.21	0.22
Sub-group D	16.16	11.85	0.50	0.39	0.25

It is evident that going from garnet to the staurolite isophase the abundances of the five components in the hornblendes remain remarkably constant (see figures 41 and 42). Whatever small differences are observed do not constitute any systematic trend except in cases of TiO_2 and MnO which appear to increase very slightly with increasing metamorphic rank. But even in cases of TiO_2 and MnO the overlaps of the spreads of the different sub-groups are so large that these trends can hardly be claimed as real on the basis of present data.

Figure 41.
Mean amounts of total iron (as Fe_2O_3) and CaO in hornblendes from low-TiO_2 amphibolites plotted against grade of metamorphism.



Vertical lines indicate spread of analyses in each sub-group. Solid circles on vertical lines represent individual analyses.

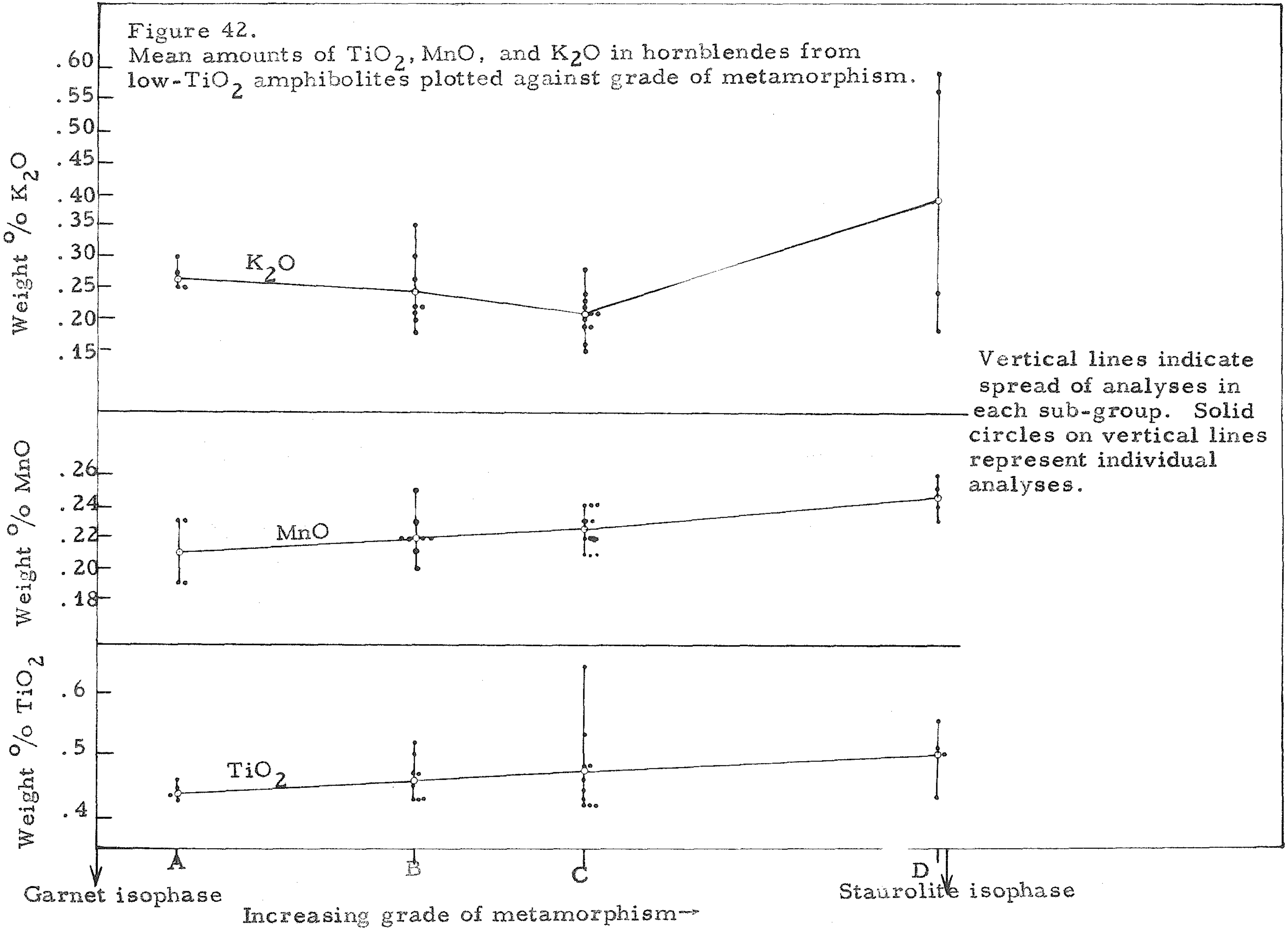


Figure 42.
Mean amounts of TiO_2, MnO, and K_2O in hornblendes from low-TiO_2 amphibolites plotted against grade of metamorphism.

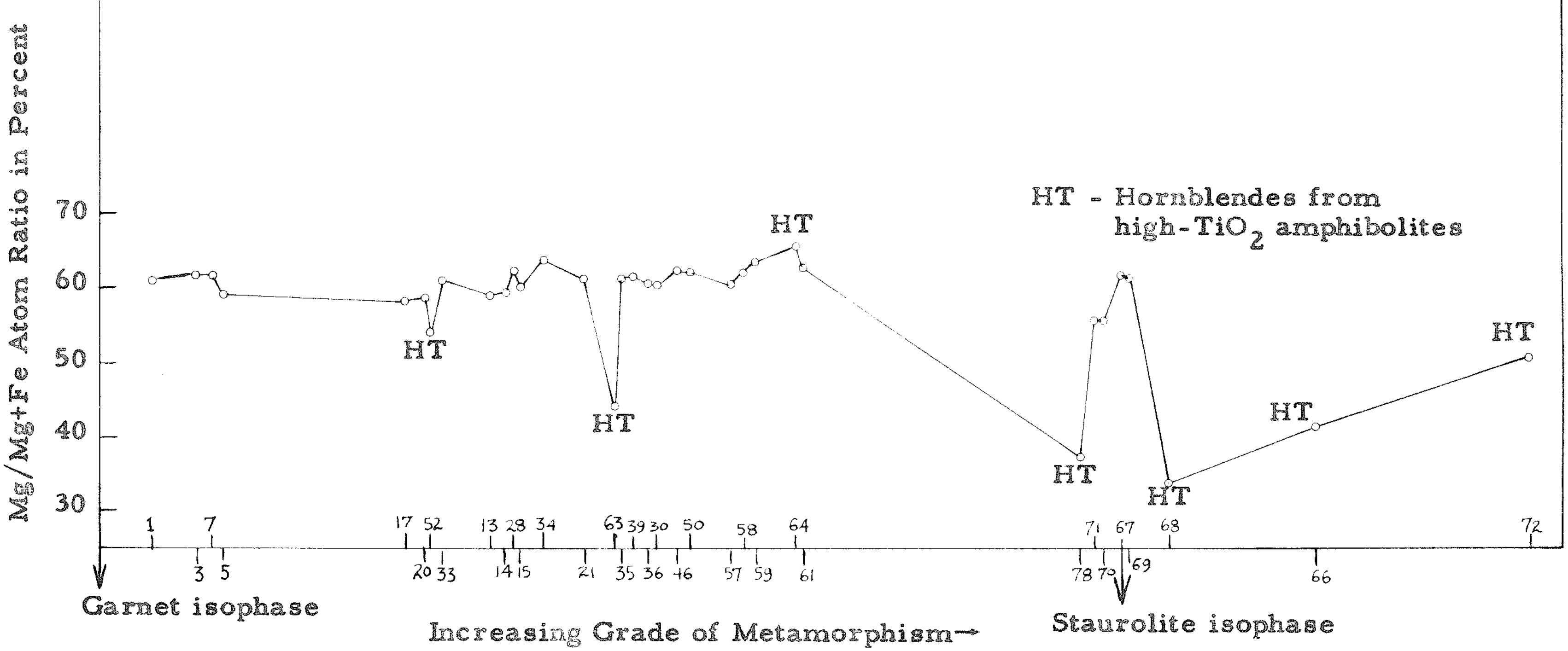
Vertical lines indicate spread of analyses in each sub-group. Solid circles on vertical lines represent individual analyses.

In figure 43 the Mg/Mg+Fe atom ratios (in percent) of the 34 hornblendes have been plotted against the grade of metamorphism (hornblendes from high-TiO_2 amphibolites are marked "HT"). Hornblende samples H-63, H-66, H-68 and H-78 are from garnetiferous amphibolites and are conspicuously low in Mg. If the hornblendes of the high-TiO_2 group (including 4 from garnetiferous ones) are excluded, then the Mg/Mg+Fe ratio of the rest of the hornblendes (from low-TiO_2 group amphibolites) seem to remain pretty much constant at about 61±% from garnet to the staurolite isophase (figure 43). Samples H-70 and H-71 have ratios slightly lower than the others in the low-TiO_2 group and come from amphibolites with considerable amounts of biotite.

In figure 44 the weight percent ratios SiO_2/Al_2O_3, K_2O/Na_2O, Fe_2O_3/FeO and TiO_2/MnO of the 12 completely analysed hornblendes have been plotted against the grade of metamorphism. No significant trends are evident. The Fe_2O_3/FeO ratio remains pretty constant throughout the sequence. The other three ratios, though show more wide fluctuations, do not show any consistent trend. The fluctuations of the SiO_2/Al_2O_3 and K_2O/Na_2O ratios and to a certain extent of the TiO_2/MnO ratio also are sympathetic. The significance of this is not very clear.

The mean concentrations and standard deviations of the various trace elements in the four sub-groups of hornblendes from low-TiO_2 amphibolites are given in Table 15. In figure 45 the mean concentrations of Co, Cr, Ni, Sc, V, Zn and Zr in the four sub-groups have been plotted against the grade of

Figure 43.
Atomic ratios of Mg/Mg+Fe in hornblendes plotted against grade of metamorphism.



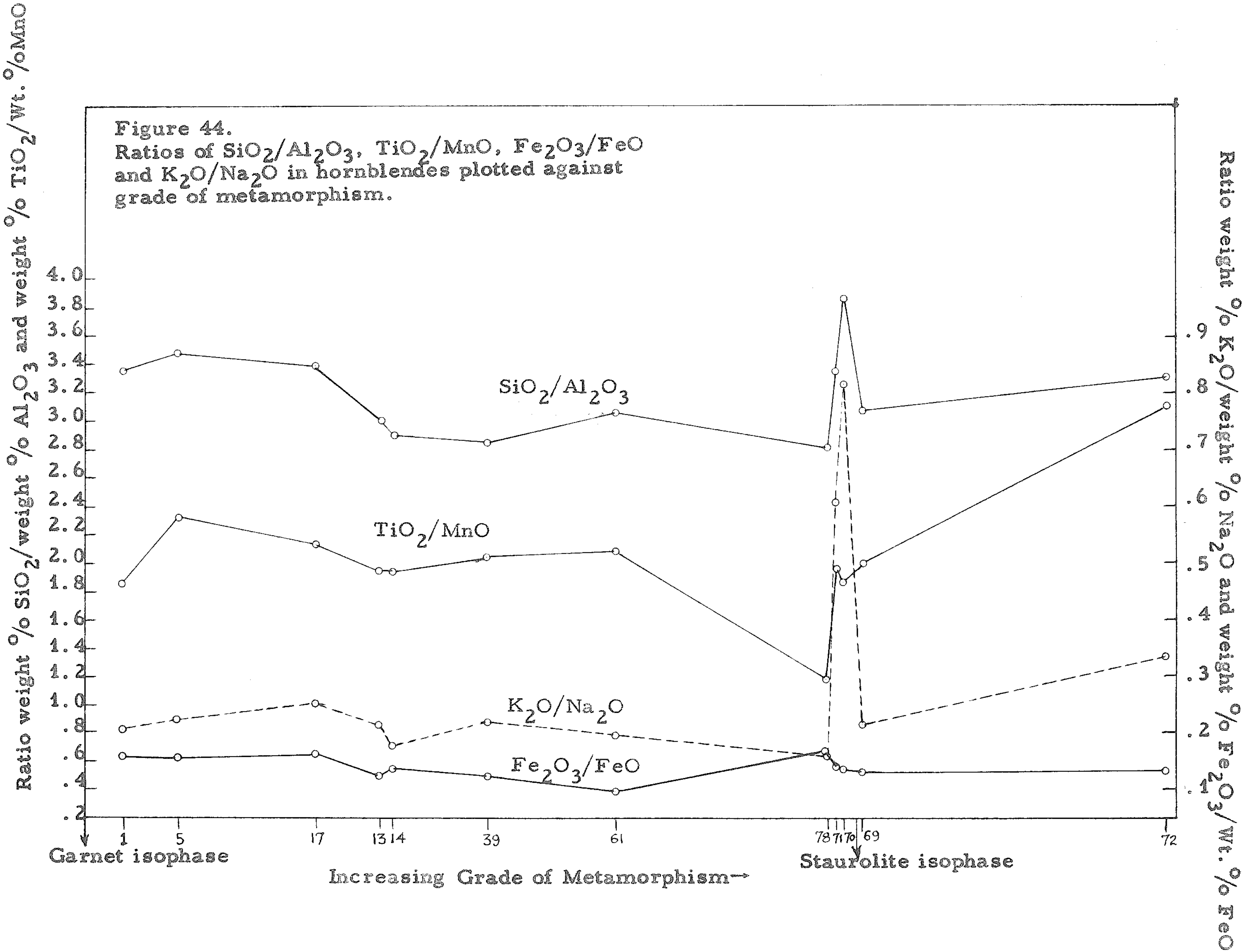


Figure 44.
Ratios of SiO_2/Al_2O_3, TiO_2/MnO, Fe_2O_3/FeO and K_2O/Na_2O in hornblendes plotted against grade of metamorphism.

Table 15

Mean Concentrations of Trace Elements in Hornblendes from Low-TiO_2 Amphibolites

	Ag		Ba		Co		Cr		Cu		Ni	
	M	S.D.	M	S.D.	M	S.D.	M	S.D.	M	S.D.	M	S.D.
Sub-group A	0.18	0.05	6.5	2	31	4	89	31	8	5	80	12
Sub-group B	0.26	0.13	10.5	5	41	16	97	26	16	12	88	19
Sub-group C	0.20	0.06	9.5	5	36	11	84	20	16	17	94	18
Sub-group D	0.21	0.08	17	16.5	51	7	102	31	6	4	103	13

	Sc		Sr		V		Zn		Zr	
	M	S.D.	M	S.D.	M	S.D.	M	S.D.	M	S.D.
Sub-group A	25.5	4.7	4.5	0.9	145	48	97	15	16.5	3
Sub-group B	26	3.4	6	1.7	197	43	118	24	21	6
Sub-group C	22.5	2	6	3.1	146	39	108	30	20.5	3
Sub-group D	32	4.5	30	41	197	33	140	36	28	6

M ≡ mean, S.D. ≡ standard deviation

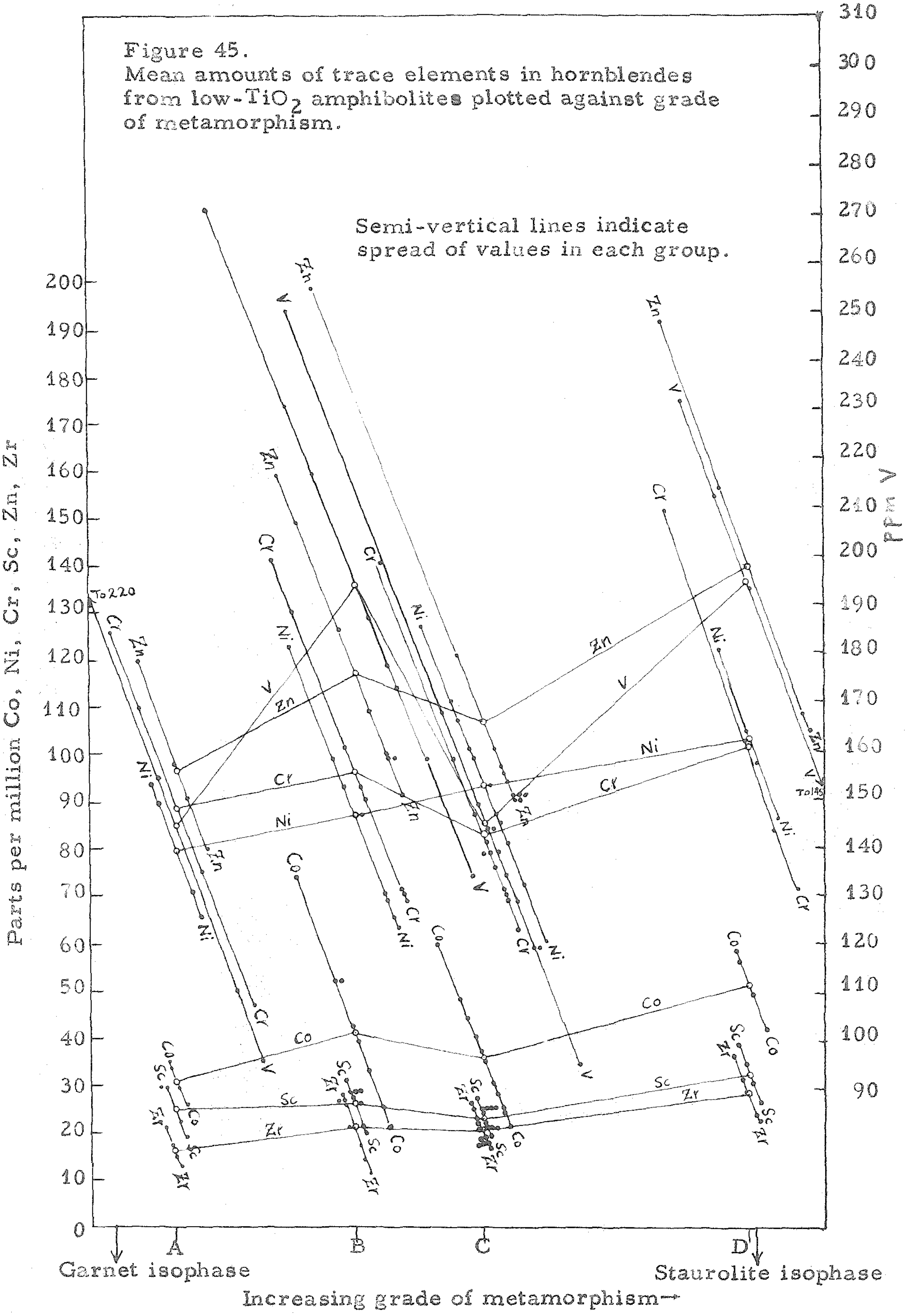


Figure 45.
Mean amounts of trace elements in hornblendes from low-TiO_2 amphibolites plotted against grade of metamorphism.

metamorphism. The semi-vertical lines indicate the spread of values in each sub-group and the solid circles on the lines indicate individual analyses in the sub-group. The mean values of Ni show a slight, consistent increase with increasing metamorphic sequence. Elements Co, Sc, Zn and Zr also show similar slight trends but these are not consistent like nickel's. The differences defining the trends are small compared to the spreads and standard deviations in the various sub-groups. On the basis of present data these trends cannot be assumed as real. But it is interesting to note that these trends are just the reverse of the weak trends shown by these elements in corresponding amphibolites.

In order to study more effectively the problem of attainment or non-attainment of chemical equilibrium and the relationship between distribution of elements and metamorphic grade, it is desirable to determine concentration ratios of judiciously chosen components in coexisting phases and to plot these ratios as a function of metamorphic sequence. This kind of approach has been applied by R. Kretz (1959) to study the problem of attainment of equilibrium in some pre-Cambrian gneisses in the Grenville subprovince. The condition for an equilibrium distribution of a component among coexisting phases is that the chemical potential is the same in all phases. This requirement is independent of the relative and absolute amounts of the phases and of the presence of other phases (thus independent of the total composition of the system). In a chemical mixture (e.g. a mineral) a relationship exists between the chemical potential of a component and its concentration. Thus, to indicate attainment of equilibrium, the distribution coefficient of a component--the relationship between atomic ratios of a component in the coexisting phases--should be the same in all specimens metamorphosed under the same physical environment. Chemical theory and experiment (Lorenz and Erbe, 1929) indicate that a distribution coefficient may be a function of temperature and pressure of crystallisation. Thus it is likely that distribution coefficient may change with metamorphic grade.

To be able to apply the above-mentioned approach in the present studies it would be necessary to isolate each mineral from the amphibolites and analyse them separately for each element capable of existing in more than one phase. Lacking such detailed analyses we can only compare the composition of the hornblendes to that of the total rocks (amphibolites). In a way it is equivalent to considering the total rock as a phase coexisting with the hornblende. This supposition of the total rock as a coexisting phase for the purpose of comparison of distribution coefficients is meaningful only when the modes of all the rocks are exactly the same. Since in the present case the modes of the amphibolites are only similar and not the same, only a crude comparison of distribution coefficients is possible. Wherever the modes are appreciably different from the average, the comparison would be less meaningful. Assuming the temperature effect on the distribution coefficient to be relatively unimportant it is expected that if the amphibolites attained chemical equilibrium, the concentration ratios would define at least a crudely smooth curve.

It is qualitatively evident from figures 36 to 40 that the concentrations of an element in the hornblendes are related to the concentrations of the same element in the corresponding amphibolites. In most cases, the higher the content of an element in the amphibolite, the higher it is in the corresponding hornblende. Figures 46 and 47 in which the Co, Ni and Cr contents of the amphibolites and hornblendes have been plotted against the metamorphic sequence, show the same general relationship although the relation is not true in each individual sample. In figures 48 to 52, total iron (as Fe_2O_3), CaO, MnO, TiO_2 and K_2O of the hornblendes have been plotted against the concentrations of the same oxides in the corresponding amphibolites. In a gross way the points in each case (except in the case of TiO_2) do fall on a smooth curve and this is believed to indicate that these amphibolites did reach chemical equilibrium. A few points which fall far from the smooth curves are in most cases found to be the ones whose modal analyses are appreciably different from the average. The widest scatter of points is found in the case of TiO_2. This is due to the fact that a major part of the TiO_2 in the rock is tied up in ilmenite and the percentwise variation in modal ilmenite in the various specimens is large compared to that of other minerals. Part of the scattering in each case may also be due to temperature effects on concentration ratios (samples included in the figures come from all parts of the garnet zone as well as from lower parts of the staurolite zone).

In figures 53 and 54 the ratios of the concentrations of total iron (as Fe_2O_3), CaO, MnO and TiO_2 in the hornblendes to

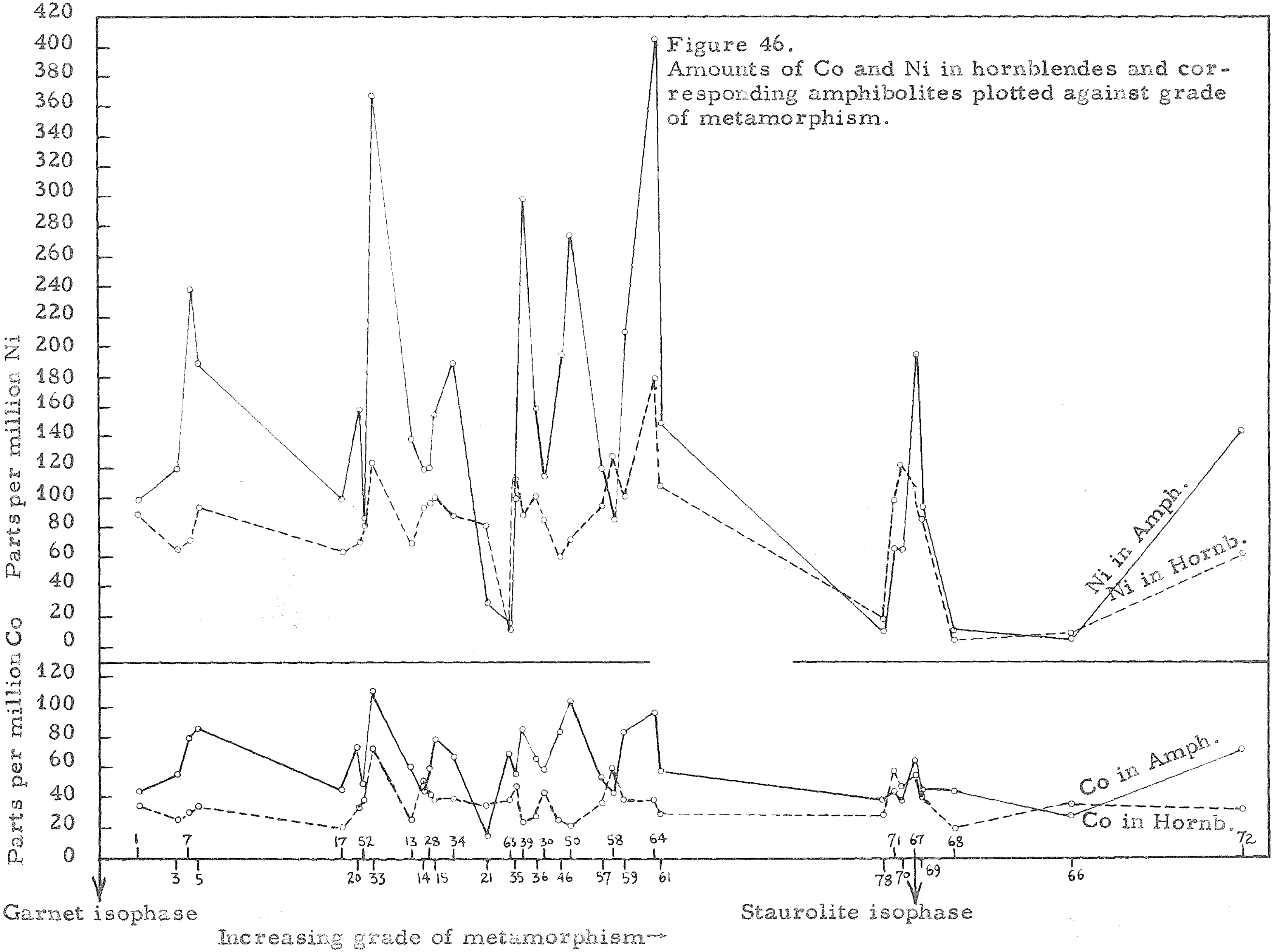
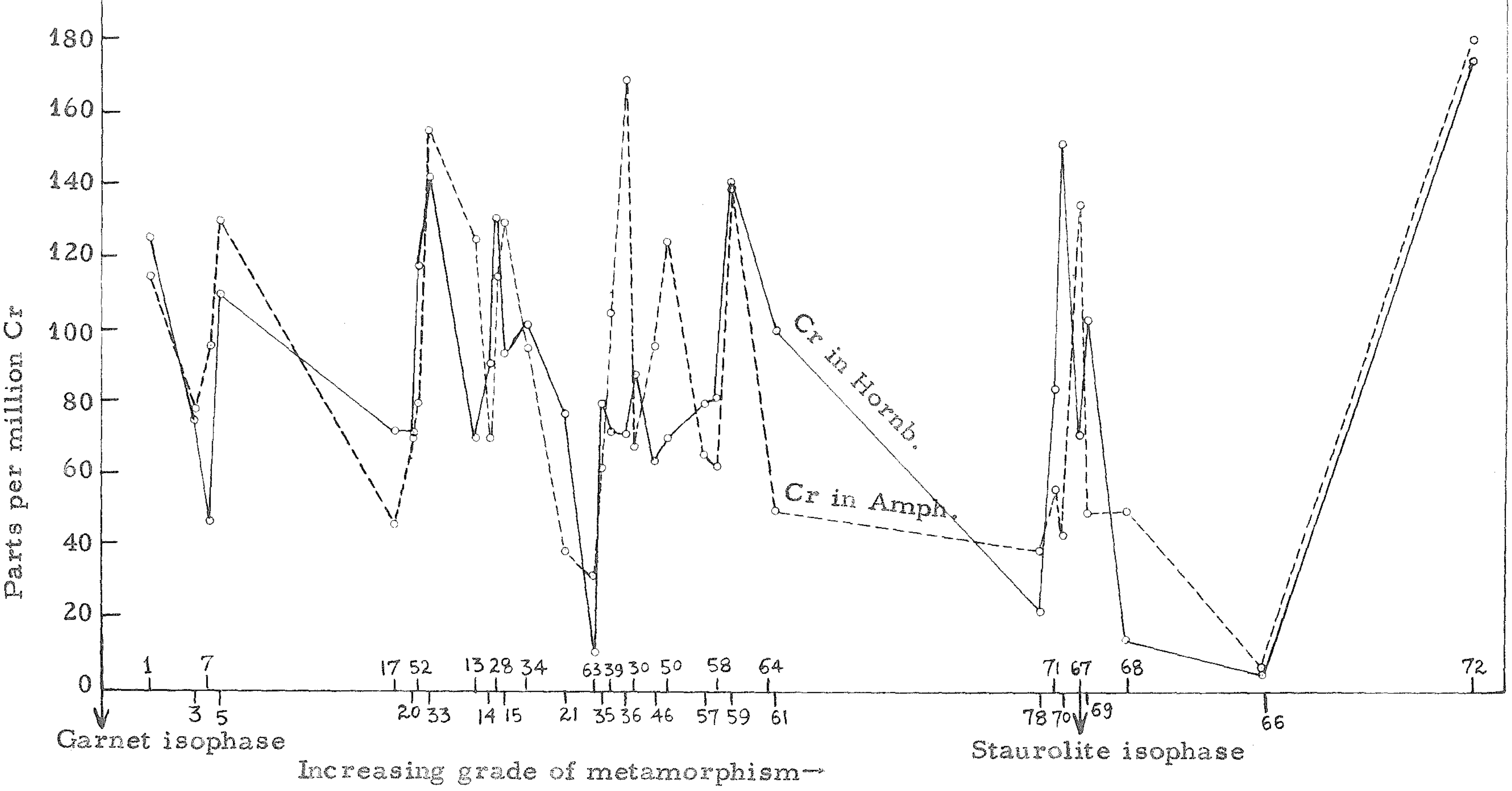


Figure 46.
Amounts of Co and Ni in hornblendes and corresponding amphibolites plotted against grade of metamorphism.

Figure 47.
Amounts of Cr in hornblendes and corresponding amphibolites plotted against grade of metamorphism.



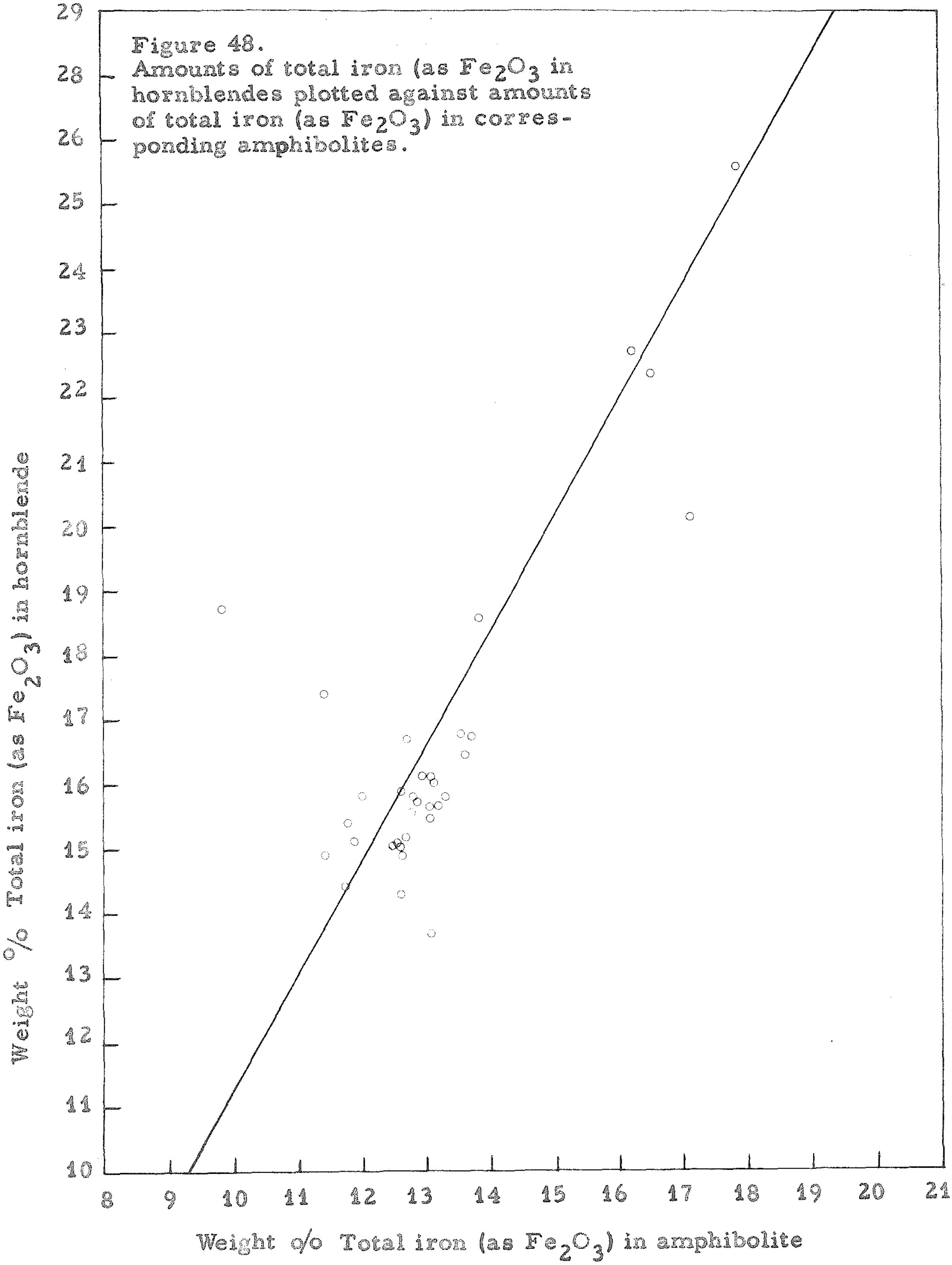


Figure 48.
Amounts of total iron (as Fe_2O_3 in hornblendes plotted against amounts of total iron (as Fe_2O_3) in corresponding amphibolites.

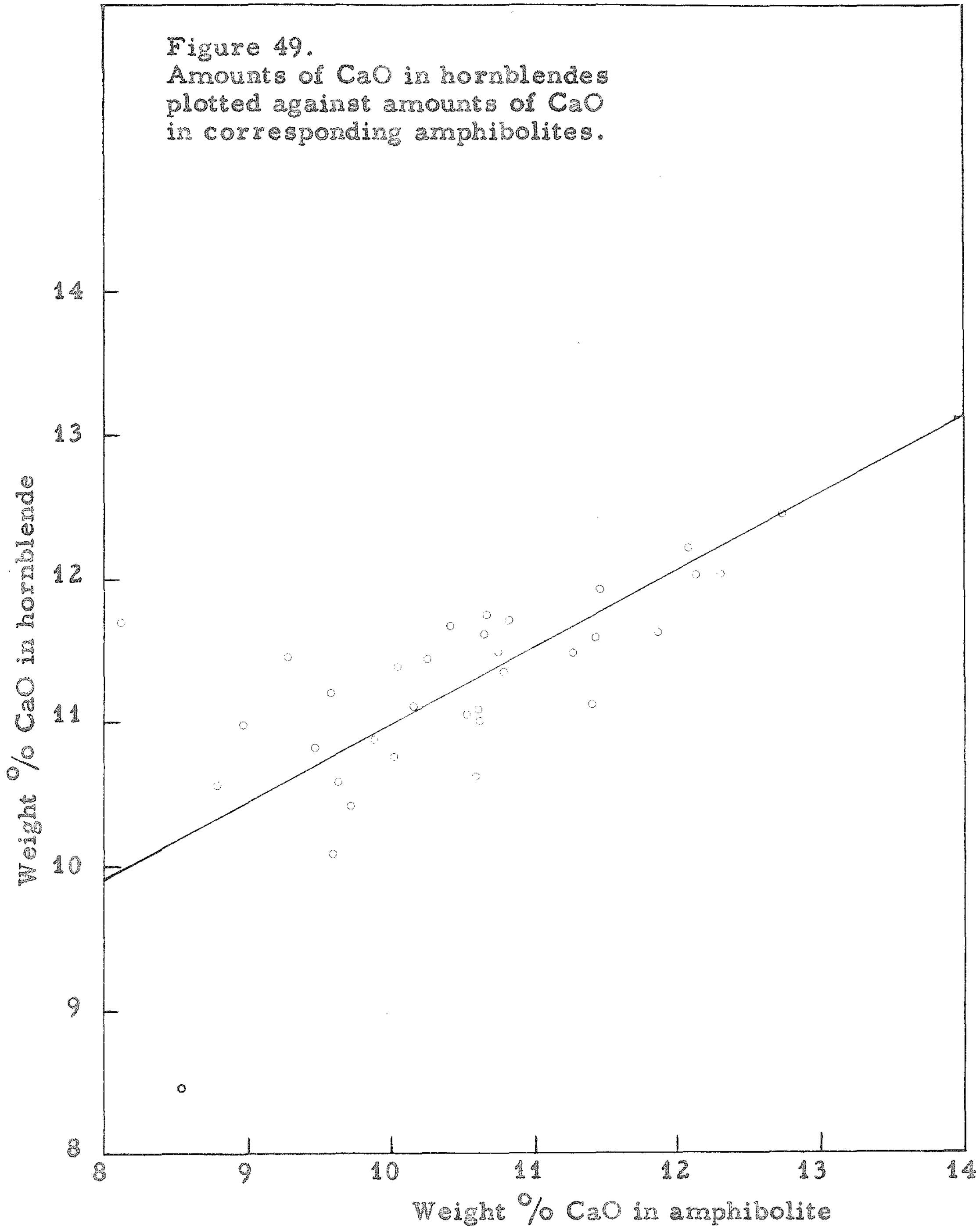


Figure 49.
Amounts of CaO in hornblendes plotted against amounts of CaO in corresponding amphibolites.

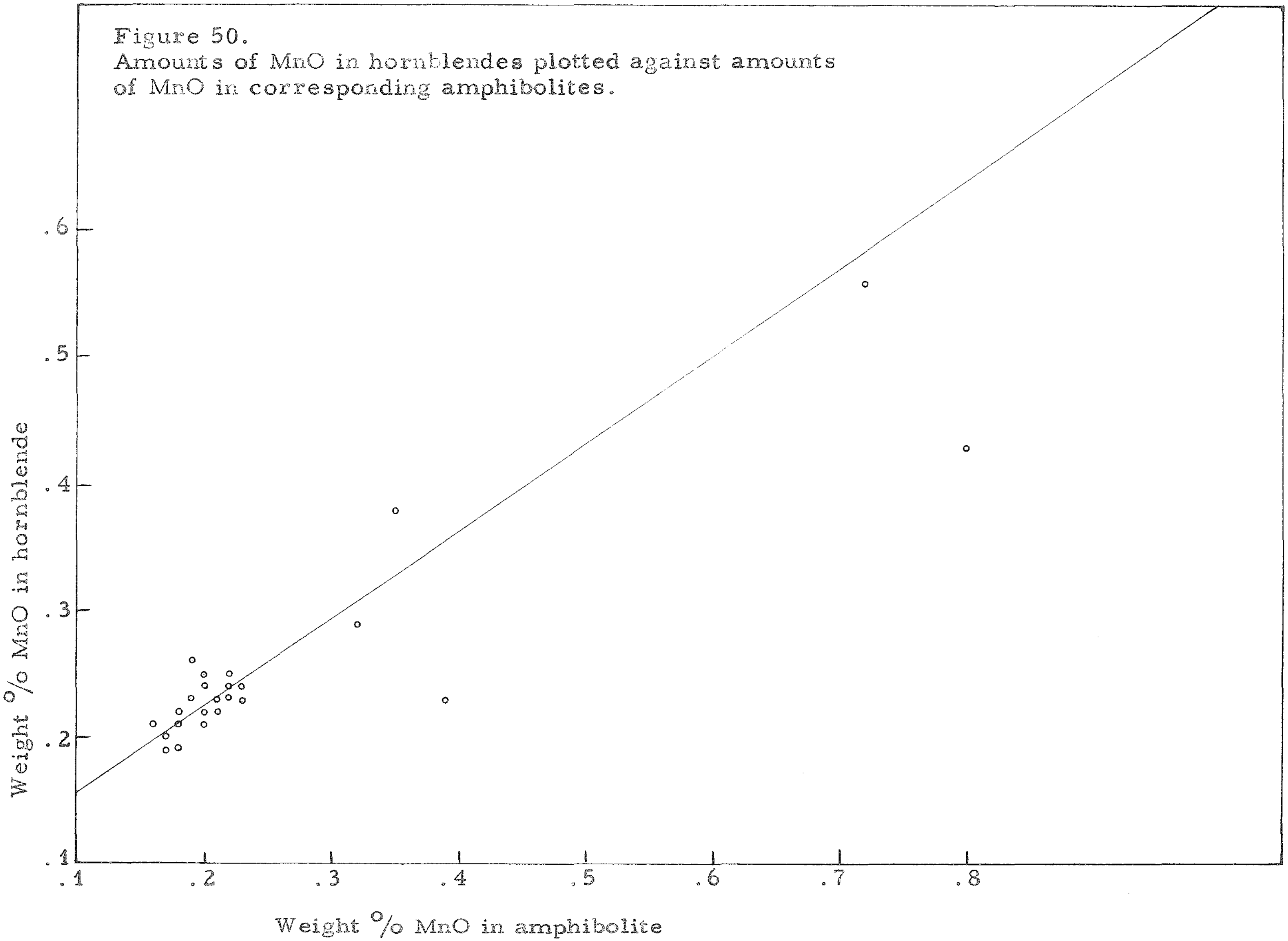


Figure 50.
Amounts of MnO in hornblendes plotted against amounts of MnO in corresponding amphibolites.

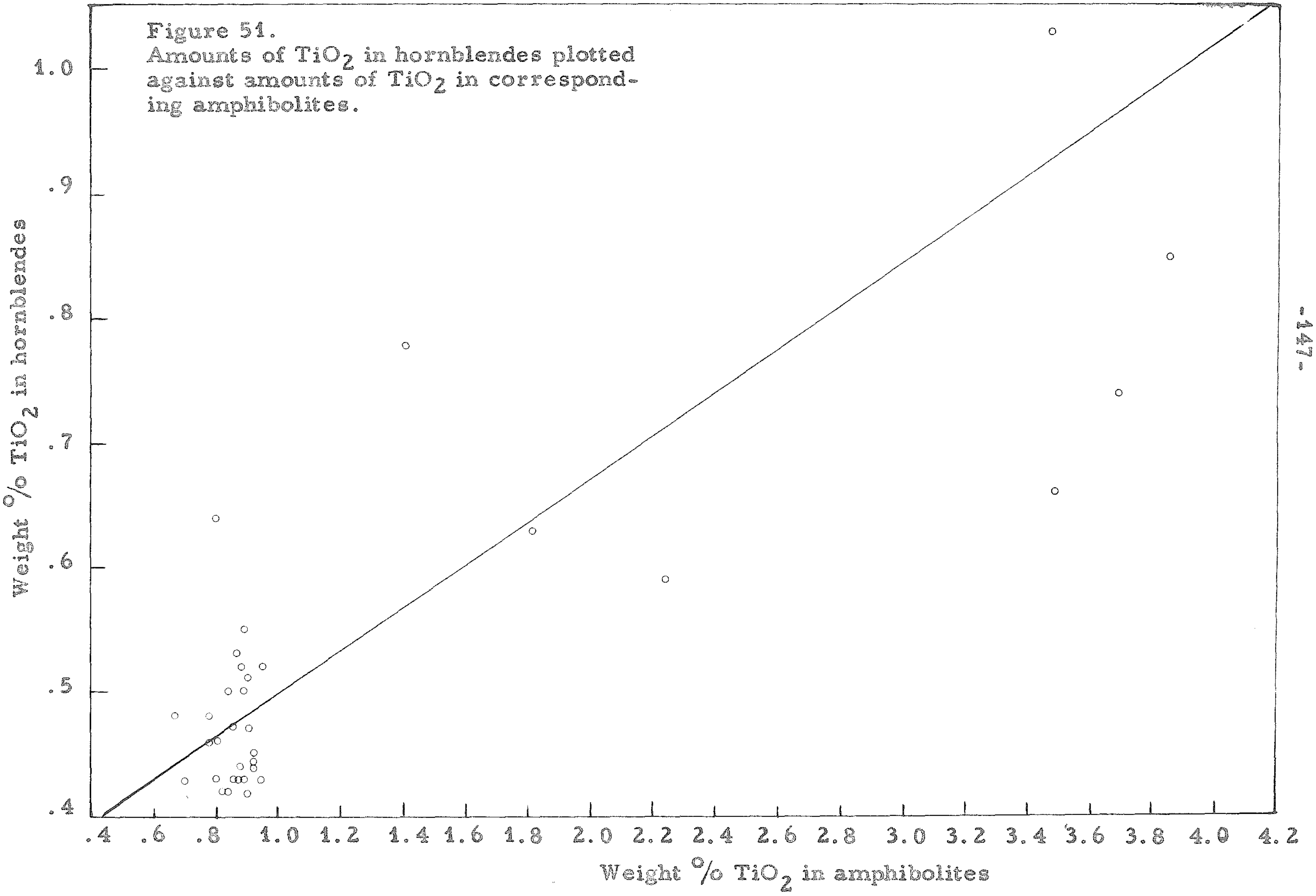


Figure 51.
Amounts of TiO_2 in hornblendes plotted against amounts of TiO_2 in corresponding amphibolites.

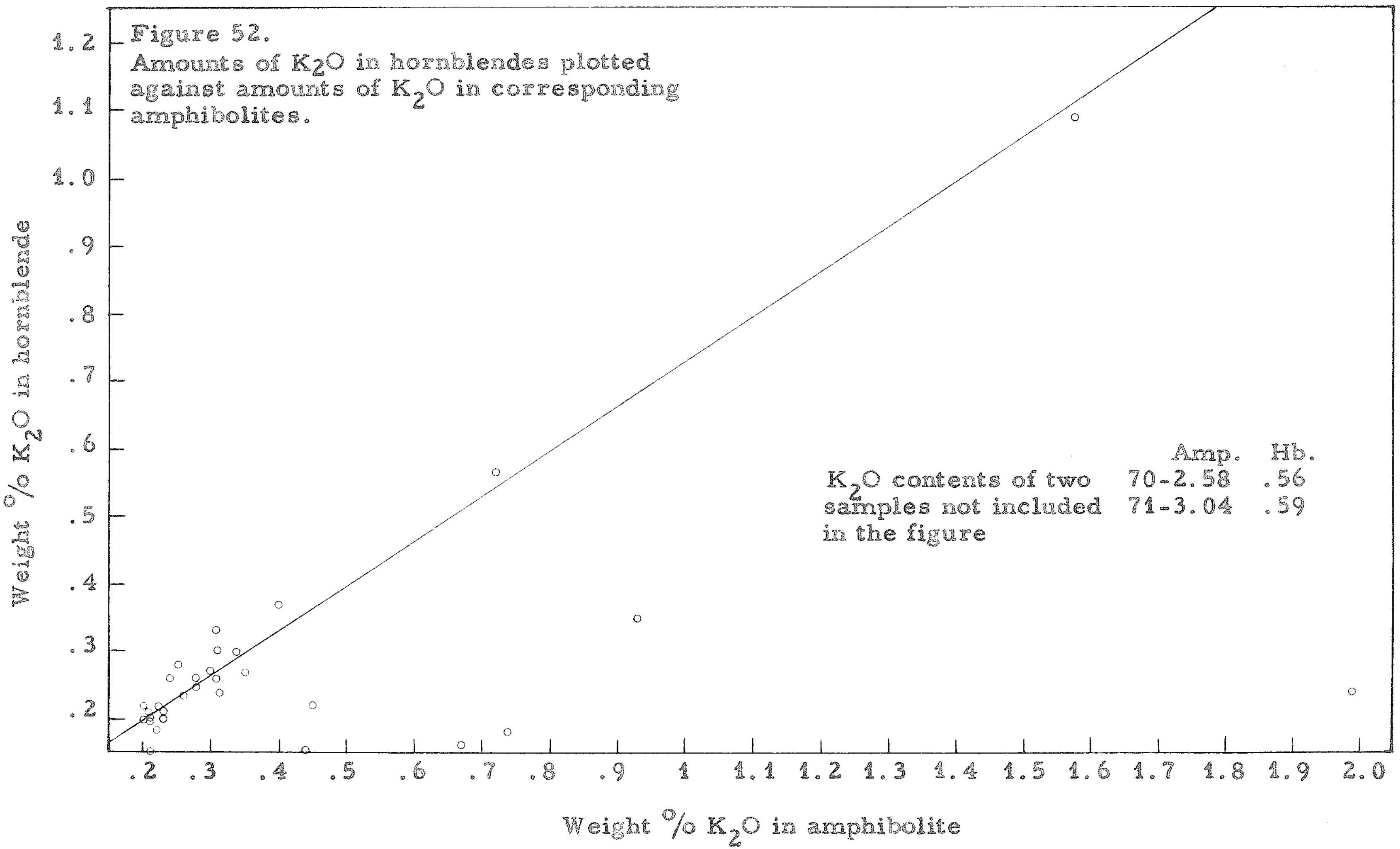
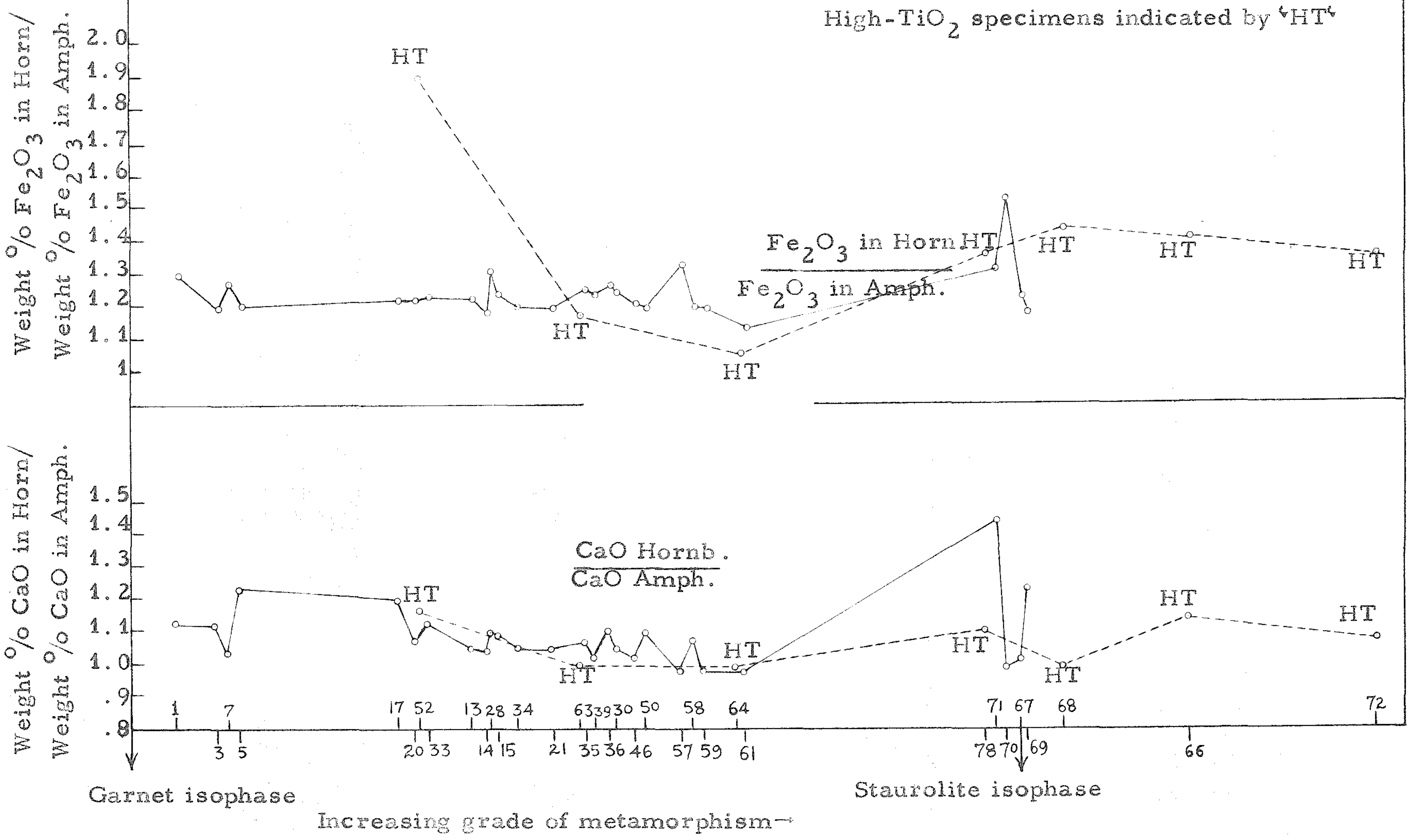


Figure 52.
Amounts of K_2O in hornblendes plotted against amounts of K_2O in corresponding amphibolites.

K_2O contents of two samples not included in the figure

	Amp.	Hb.
70	2.58	.56
71	3.04	.59

Figure 53.
Ratios of concentrations of total iron (as Fe_2O_3) and CaO in hornblendes and corresponding amphibolites plotted against grade of metamorphism.



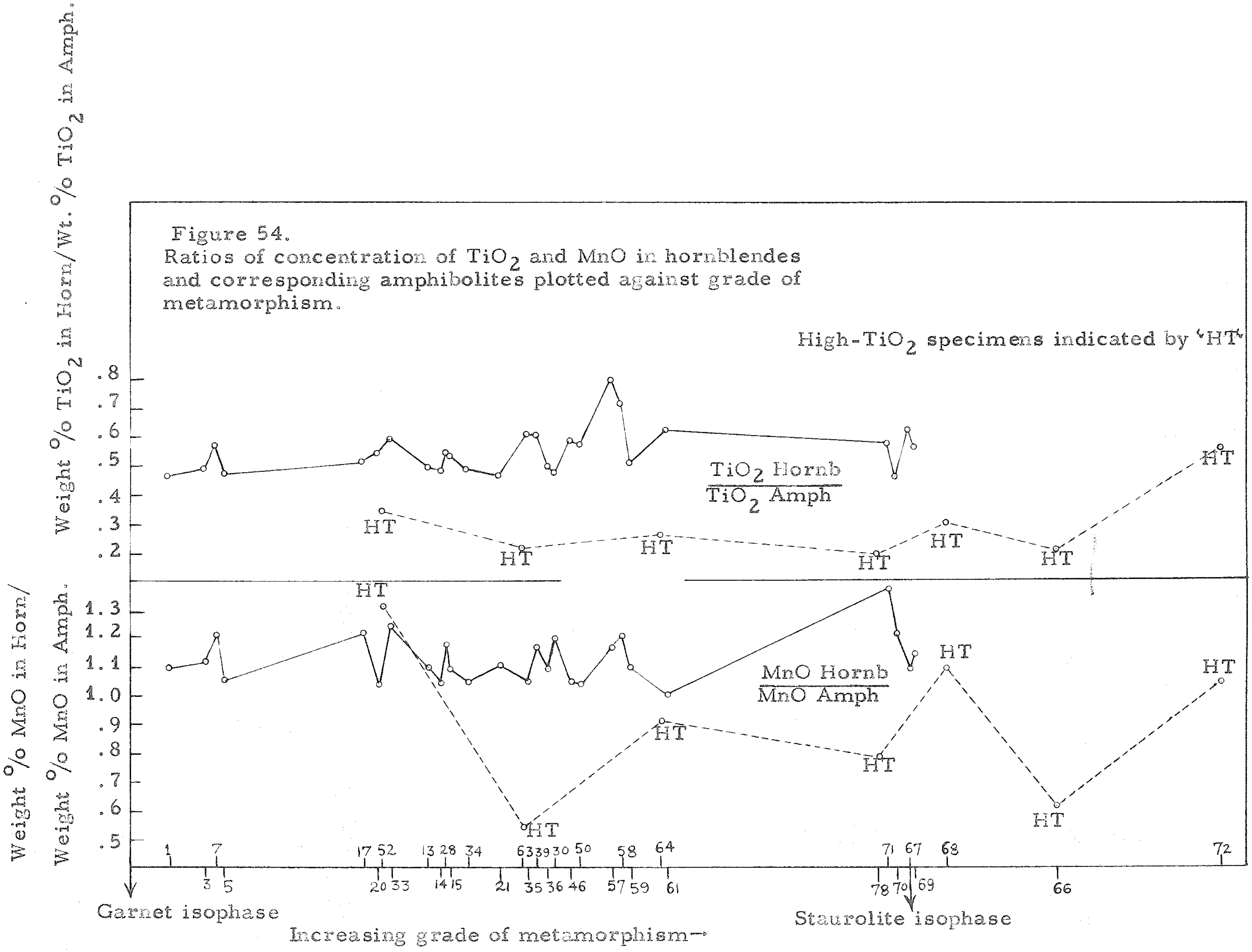


Figure 54.
Ratios of concentration of TiO_2 and MnO in hornblendes and corresponding amphibolites plotted against grade of metamorphism.

High-TiO_2 specimens indicated by 'HT' the concentrations of the same oxides in the corresponding amphibolites have been plotted against the metamorphic sequence. The samples high in TiO_2 are indicated by 'HT' in the figures. These have been plotted separately from samples low in TiO_2. As can be seen from the figures the concentration ratios do not show any trend correlatable to metamorphic rank. What fluctuations are observed appear to be random in character and the average concentration ratios seem to remain reasonably constant throughout the whole metamorphic sequence represented here. The obvious conclusion is that within the range of temperature represented by the metamorphic sequence in this area, temperature has little or no influence on the distribution coefficients (concentration ratios) of these elements among co-existing phases.

It has been mentioned earlier that if the amphibolites low in TiO_2 and their hornblendes are sub-grouped and their trace element contents averaged, the mean concentrations of Co, Cr, Ni, Sc, and Zr in the amphibolites show a slight decrease with increasing grade of metamorphism. The concentrations of the same elements in the corresponding hornblendes show a slight increase with increasing grade of metamorphism. It has also been stated earlier that on a statistical basis the present data cannot prove conclusively that these trends are true and not spurious. If the trends are true it would mean that with increasing temperature of metamorphism these elements are increasingly fractionated from the rock by hornblende. The ratios of the mean concentrations of these elements in different sub-groups of hornblendes to those in corresponding sub-groups of amphibolites are given in Table 16. The standard deviation in each ratio is also given in the table. It is quite evident from Table 16 that although the concentration ratios show trends towards increase with increasing grade of metamorphism, the standard deviations are in most cases too large to allow these trends to be considered significant.

Table 16

Ratios of the Mean Concentrations of Trace Elements in Hornblendes to Those of the Corresponding Amphibolites in Different Sub-groups of Low-TiO_2 Specimens

		Co		Cr		Ni		Sc		Zr	
		R	S.D.	R	S.D.	R	S.D.	R	S.D.	R	S.D.
Increasing Grade of Metamorphism ↓	Sub-group A	.47	.13	.85	.33	.49	.19	.77	.15	.40	.08
	Sub-group B	.61	.29	.96	.40	.52	.27	.77	.15	.55	.21
	Sub-group C	.60	.31	.93	.46	.59	.31	.75	.22	.76	.36
	Sub-group D	1.06	.26	1.43	.86	.99	.53	1.10	.31	1.08	.72

R = conc. in hornb/conc. in Amph.   S.D. = standard deviation

OPTICAL PROPERTIES OF HORNBLENDES

Optical properties were determined on seven selected samples of hornblende. Two of these (H-1, H-5) are from the lowest part of the garnet zone, two (H-14, H-61) are from the middle part of the garnet zone and one (H-78) is from the highest part of the garnet zone. The remaining two hornblendes (H-69, H-72) are from the staurolite zone.

The indices of refraction were determined on -150+200 mesh mineral grains in sodium light with oils graduated on .002 intervals. The extinction angle in each case was measured on the grain showing the highest interference color in a thin section.

Samples H-72 and H-78 have much stronger color than the other hornblendes in the group.

The optical properties of the hornblendes together with some relevant features of their chemical compositions are detailed in Table 17. There seems to be no simple correlation between chemical composition and optical properties of the hornblendes except that in a general way the iron-rich hornblendes show deeper color than the iron-poor hornblendes. Similar lack of obvious correlations of optics and composition is implicit in most modern studies (Deer, 1938; Buddington and Leonard, 1953; Larsen and Draisen, 1950) and has been noted specifically by C. G. Engel (1959).

Table 17

Optical Properties and Some Compositional Features of Seven Hornblendes

Sample No.		Extinction Angle	FeO/MgO (Mol. Prop.)	Fe_2O_3/FeO (Mol. Prop.)	$\frac{\text{Wt. \% } K_2O}{\text{Wt. \% } Na_2O}$	Ti^{4+} ions per molecule	Mn^{2+} ions per molecule	Al^{3+} ions at tetrahedral site-per molecule
H-1	1.659	18°	.591	.071	.208	.044	.026	1.409
H-5	1.659	18°	.634	.072	.223	.053	.026	1.392
H-14	1.661	17°	.641	.063	.180	.044	.026	1.539
H-61	1.658	21°	.569	.042	.196	.052	.026	1.475
H-69	1.658	17°	.603	.060	.214	.052	.035	1.474
H-72	1.666	20°	.924	.058	.336	.089	.035	1.469
H-78	1.677	21°	1.584	.074	.160	.073	.073	1.539

Sample No.	Pleochroism X	Y	Z
H-1	pale greenish yellow	green	bluish green
H-5	pale greenish yellow	green	bluish green
H-14	pale yellow green	yellow green	bluish green
H-61	yellowish green	green	bluish green
H-69	greenish yellow	green	bluish green
H-72	greenish yellow	olive	dark green
H-78	pale green	dark olive	dark bluish green

X-RAY DIFFRACTION STUDIES

Introduction

The biggest obstacle to elaborate geochemical studies on minerals is the enormity of time and expense involved in obtaining a large number of analyses by the wet method. To overcome this, attempts have been made to determine chemical composition indirectly by finding and measuring easily determinable physical properties that may be related to composition.

Numerous attempts have been made to relate optical properties of minerals to composition. The relation of optical properties, especially refractive indices, to composition in plagioclases is well known. But in minerals of more complex composition (e.g. micas, pyroxenes, amphiboles) with complicated substitution relationships, the relation of optical properties to composition is much more complex and useful relations are difficult to ascertain. Winchell and Winchell (1951) give curves and diagrams showing changes in optical properties with changes in composition for these minerals. These, at best, are useful in giving a rough approximation of composition. But in determining compositional variations within a species or between closely related species, these are either useless or of very questionable value.

Over the last decade several workers attempted to employ certain structural parameters, quickly determinable by x-ray diffractometric methods, for the determination of mineral compositions. Claisse (1950), Goodyear and Duffin (1954, 1955), J. V. Smith (1956), J. R. Smith and Yoder (1956) and others have discussed the determination of composition of plagioclases by x-ray powder diffraction patterns. Hess (1952) in his studies on orthopyroxenes found a general correlation of unit cell dimensions with ion substitution and composition. Gower (1955) claimed that the iron-magnesium ratio in biotites may be determined to about 5% or better accuracy by measuring the ratio of the intensities of the 004 to 005 reflections. There is no report in the literature regarding similar studies on hornblendes; so an attempt was made to apply similar approaches in the determination of the composition of hornblendes.

In hornblendes two different approaches were tried to relate structure to composition, namely, (1) intensities of certain chosen reflections as these may reflect composition, and (2) unit cell dimensions as indicative of composition.

Indexing of Reflections

The indexing of reflections in the hornblende diffraction patterns was done in an empirical way. An actinolite powder pattern was first indexed carefully and the hornblende patterns were indexed by comparison with it. Warren (1930, p. 494) in his single crystal work with monoclinic amphiboles found that the rotation photographs of tremolite, kupfferite, actinolite and hornblende "are practically identical, spot for spot, in both position and intensity". The reason that an actinolite and not a hornblende was first indexed as a standard reference was that precise lattice parameters for an actinolite was available from a recent work of Zussman (1955, p. 302) and it was thought that it would be much easier to index an actinolite pattern on the basis of these parameters than a hornblende whose parameters, though very similar, might not quite be the same as those of actinolite.

The sample of actinolite used as the standard reference came from the Geology Division collection. It had a very fine needle-like habit. A -100 mesh fraction of this sample was ground for two hours in a mechanical grinder. The resulting pulp showed no discreet grains under a powerful binocular microscope and was used for powder work.

The powder work was done with a Norelco gieger counter x-ray diffractometer using nickel filtered Cu radiation at 40 kv and 15 ma, scanning speed $\frac{1}{2}^{\circ}$/minute, chart speed $\frac{1}{2}$ inch/minute, time constant 8 seconds, divergent slit 1°, receiving slit .006 inch and scatter slit 1°.

In order to obtain results of requisite accuracy the upper surface of the sample must be a flat, smooth plane. Slight curvature introduces considerable error. The powdered samples were packed in a rectangular cavity (2 c.m. x 1.5 c.m. x 2 m.m.) in an aluminum holder. The powders were pressed down on a glass slide put below the aluminum holder such that the smooth surface of the powder pack in contact with the glass plate coincided with the surface plane of the aluminum holder. The glass slide was gently slid off the powder pack before it was put in the diffractometer. With careful packing the peak locations are easily reproducible to within 0.02 degree 2θ, more often, to within 0.01 degree 2θ. All diffraction work was done at a room temperature of 72°F.

Two powder patterns of the actinolite sample were obtained; in one the sample was mixed with an internal standard of spectroscopically pure NaCl (Pattern I) and in the other case no internal standard was used (Pattern II). The 2θ region covered was from 110° to 8°.

The 'd' spacings of six strong reflections from NaCl were read off from pattern I and compared with the 'd' values given for these reflections by Swanson and Fuyat (1953, p. 43). The necessary corrections in 'd' and in corresponding 2θ were calculated (see Table 18). Another appreciably strong NaCl reflection, in the higher 2θ region, was partially overlapped by an actinolite reflection and thus could not be read accurately.

Table 18

Instrumental Corrections in 'd' and 2θ Values

Obtained from Using NaCl as an Internal Standard

hkl	Relative Intensity	dÅ	Read dÅ	Correction dÅ	Correction 2θ
111	13	3.258	?		
200	100	2.821	2.825	-.004	+0.05
220	55	1.994	1.9968	-.0028	+0.07
222	15	1.628	1.6302	-.0022	+0.08
400	6	1.410	1.4116	-.0016	+0.08
420	11	1.261	1.2622	-.0012	+0.08
422	7	1.1515	1.1524	-.0009	+0.08

In his pioneering work on tremolite Warren (1929, p. 53) listed 32 lattice planes giving reflections with intensities estimated as weak to medium (W-M), medium (M), medium to strong

(M-S), strong (S) and very strong (VS). These are listed in column 1 of Table 19. Column 1 also includes a number of additional structural planes of hko type which, in actinolite, give appreciably high structure amplitudes as listed by Zussman (1955, p. 307). Two planes, $56\bar{1}$ and $16\bar{3}$, are also included in column 1. Inasmuch as the ASTM card on actinolite indicates these also give reflections of relatively high intensity. Column 2 shows the 'd' spacings calculated from the lattice parameters ($a = 9.89Å$, $b = 18.14Å$, $c = 5.31Å$, $\beta = 105^{\circ}48'$) obtained by Zussman (1955, p. 302) for an actinolite. Columns 3 and 4 show the calculated and observed structure amplitudes respectively for some hko type reflections of the same actinolite by Zussman. Columns 5 and 6 show the calculated structure amplitudes and observed intensities respectively of some reflections from a tremolite (Warren, B. E., 1929, p. 53). The 'd' values of all observable reflections in powder pattern I and II are listed in columns 7 and 12 respectively, according to the best possible correspondence between these and the 'd' values calculated from actinolite parameters given by Zussman. Two reflections in pattern I (330 and 370) were interfered with by reflections from NaCl and could not be read. Reflections $20\bar{2}$ in pattern I and $10\bar{1}$ in pattern II were not properly resolved from adjoining reflections, and reflection 3,11,0 in pattern I is so low in intensity that it could not be distinguished from the background. The 'd' values from patterns I and II are practically identical considering the limits of error in measurement and similar corrections were applied

Table 19

Comparison of the ‘d’ spacings of Various Lattice Planes of the ‘Standard’ Actinolite with Those of Zussman’s Actinolite

1 hkl	2 dÅ calculated from Zussman’s cell	3 F(Calc.) Zussman	4 F(obs.) Zussman	5 F(Calc.) Warren	6 I (est.) Warren	7 dÅ(I) This work	8 Correction Å	9 Corrected dÅ(I) This work	10 Recalculated dÅ This work	11 Difference of dÅ(I) from Recalculated dÅ	12 dÅ(II) This work	13 Corrected dÅ(II) This work	14 Difference of dÅ(II) from Recalculated dÅ	15 Possible error Å	16 Peak Height in inches I	17 Peak Height in inches II
020	9.074	-60	63	-46	W-M	9.098	-.045	9.053	9.058	-.005	9.092	9.047	-.011	±.018	2.0	2.2
110	8.427	88	85	24	W-M	8.450	-.037	8.413	8.414	-.001	8.448	8.411	-.003	±.015	10.1	11.5
$10\bar{1}$	5.121			-46	W-M	5.123	-.015	5.108	5.110	-.002	?	?		±.006	1.0	?
130	5.105	31	38	62	W-M	5.110	-.015	5.095	5.096	-.001	5.110	5.095	-.001	±.006	1.2	1.8
Unidentified						4.897	-.013	4.884			4.897	4.884		±.005	1.4	1.4
200	4.759	-21	19	-54	W-M	4.764	-.012	4.752	4.751	+.001	4.763	4.751	.000	±.005	1.1	1.5
040	4.535	-92	104	-87	M	4.538	-.011	4.527	4.529	-.002	4.536	4.525	-.004	±.0045	2.7	2.5
220	4.214	-40	38	-40	W-M	4.215	-.009	4.206	4.207	-.001	4.213	4.204	-.003	±.0038	2.2	4.1
Unidentified						3.883	-.008	3.875			3.882	3.874		±.0027	1.0	1.2
$23\bar{1}$	3.383			-154	S	3.389	-.006	3.383	3.386	-.003	3.388	3.382	-.004	±.0026	2.7	3.4
240	3.283	108	110	83	M-S	3.281	-.006	3.275	3.278	-.003	3.279	3.273	-.005	±.0024	4.4	6.1
310	3.125	177	149	132	S	3.126	-.005	3.121	3.120	+.001	3.125	3.120	.000	±.0021	11.0	11.8
$32\bar{1}$	2.933			136	S	2.945	-.005	2.940	2.941	-.001	2.943	2.938	-.003	±.0019	2.6	4.0
330	2.809	-70	69	-59	M	-	-.004	-	2.805	-	2.808	2.804	-.001	±.0017	-	4.8
$\bar{2}3\bar{1}$	2.750			-123	M-S	2.736	-.004	2.732	2.732	.000	2.735	2.731	-.001	±.0016	2.4	2.6
$25\bar{1}$	2.711			264	VS	2.711	-.004	2.707	2.711	-.004	2.710	2.706	-.005	±.0016	5.5	7.0
$16\bar{1}$	2.603			162	VS	2.599	-.004	2.595	2.599	-.004	2.598	2.594	-.005	±.0014	1.6	2.0
$20\bar{2}$	2.560			-146	S	?	-.004	-	2.556	-	2.558	2.554	-.002	±.0014	-	0.8
002	2.555			265	VS	2.538	-.004	2.534	2.534	.000	2.538	2.534	.000	±.0014	2.6	2.2
350	2.388	-58	67	-111	M	2.385	-.003	2.382	2.384	-.002	2.384	2.381	-.003	±.0012	0.9	1.5
400	2.380	29	33	-14	V-W	2.380	-.003	2.377	2.376	+.001	2.379	2.376	.000	±.0012	0.7	1.1
$\bar{2}5\bar{1}$	2.352			228	S	2.341	-.003	2.338	2.339	-.001	2.340	2.337	-.002	±.0012	2.2	3.0
321						2.324	-.003	2.321	2.320	+.001	2.323	2.320	-.000	±.0012	1.6	1.9
$31\bar{2}$	2.304			34	V-W	2.303	-.003	2.300	2.305	-.005	2.303	2.300	-.005	±.0012	1.0	1.1
Unidentified						2.279	-.003	2.276			2.279	2.276		±.0011	0.8	0.8
$36\bar{1}$	2.164			152	S	2.164	-.003	2.161	2.165	-.004	2.164	2.161	-.005	±.0010	2.8	3.1
$40\bar{2}$	2.040			255	VS	2.047	-.003	2.044	2.044	-.000	2.046	2.043	-.001	±.0008	0.8	1.1
$\bar{2}0\bar{2}$	2.032			134	S	2.018	-.003	2.015	2.014	+.001	2.018	2.015	+.001	±.0008	1.6	2.1

Table 19 (Cont'd)

Comparison of the 'd' Spacings of Various Lattice Planes of the 'Standard' Actinolite with Those of Zussman's Actinolite

1 hkl	2 dÅ calculated from Zussman's cell	3 F(Calc.) Zussman	4 F(obs.) Zussman	5 F(Calc.) Warren	6 I(est.) Warren	7 dÅ(I) This work	8 Correction Å	9 Corrected dÅ(I) This work	10 Recalculated dÅ This work	11 Difference of dÅ(I) from Recalculated dÅ	12 dÅ(II) This work	13 Corrected dÅ(II) This work	14 Difference of dÅ(II) from Recalculated dÅ	15 Possible error dÅ	16 Peak Height in inches I	17 Peak Height in inches II
370	2.007	80	80			-	-.003	-	2.004	-	2.003	2.000	-.004	±.0008	-	1.3
510	1.8929	-90	72			1.8922	-.0028	1.8894	1.8898	-.0004	1.8922	1.8894	-.0004	±.0007	1.2	2.5
0,10,0	1.8142	103	96			1.8144	-.0028	1.8116	1.8116	.0000	1.8142	1.8114	-.0002	±.0007	0.8	1.4
550	1.6854	-16	10			1.6851	-.0023	1.6828	1.6828	.0000	1.6851	1.6828	.0000	±.0006	0.5	0.7
$56\bar{1}$	1.6490					1.6515	-.0023	1.6492	1.6506	-.0014	1.6512	1.6489	.0017	±.0006	1.8	2.5
480	1.6414	-108	95			1.6392	-.0022	1.6370	1.6390	-.0020	1.6392	1.6370	-.0020	±.0006	0.8	1.3
1,11,0	1.6249	150	177			1.6195	-.0022	1.6173	1.6227	-.0054	1.6193	1.6171	-.0056	±.0005	1.0	0.9
600	1.5862	129	118	176	S	1.5855	-.0020	1.5835	1.5835	.0000	1.5855	1.5835	.0000	±.0005	0.9	1.3
$60\bar{2}$	1.5499			182	S	1.5568	-.0020	1.5548	1.5543	+.0005	1.5569	1.5549	+.0006	±.0005	0.5	0.7
$\bar{4}0\bar{2}$	1.5439			174	S	1.5333	-.0020	1.5313	1.5311	+.0002	1.5332	1.5312	+.0001	±.0004	0.8	1.0
$16\bar{3}$	1.5221			206	S	?	-.0020		1.5151		?			±.0004		
0,12,0	1.5117	232	227			1.5118	-.0019	1.5099	1.5097	+.0002	1.5118	1.5099	+.0002	±.0004	0.6	0.6
3,11,0	1.4632	119	107			?	-.0018	?	1.4612		1.4671	1.4653	-.0041	±.0004	?	0.6
$\bar{5}6\bar{1}$	1.4437					1.4387	-.0017	1.4370	1.4372	-.0002	1.4387	1.4370	-.0002	±.0004	1.7	3.2
Unidentified						1.3654	-.0015	1.3639			1.3653	1.3638		±.0003	0.9	1.1
Unidentified						1.3554	-.0015	1.3539			1.3552	1.3537		±.0003	0.7	0.9
Unidentified						1.3356	-.0014	1.3342			1.3355	1.3341		±.0003	0.6	0.9
Unidentified						1.3092	-.0013	1.3079			1.3091	1.3078		±.0002	0.5	1.2
Unidentified						1.2950	-.0013	1.2937			1.2950	1.2937		±.0002	0.6	0.8
$40\bar{4}$	1.2800			172	S											
004	1.2774			176	S											
$80\bar{2}$	1.2121			-22	M											
800	1.1896	138	119	106	S											
$60\bar{4}$	1.1611			140	S											
$\bar{4}0\bar{4}$	1.0160			144	S											

to both groups. Corrections listed in column 8 were obtained from Table 18 except in the case of low 2θ (large 'd') region for which no data from NaCl were available. For the low 2θ region the corrections in 'd' were applied by assuming a +0.05 degree shift in 2θ value. The corrected 'd' values for patterns I and II are given in columns 9 and 13 respectively. Assuming the 'd' values for reflections 002; $23\bar{1}$; 0,10,0 and 600 given in column 9 to be correct, a new set of lattice parameters for the actinolite were calculated. These are shown below with Zussman's values for comparison.

This work	Zussman (1955, p. 302)
$a = 9.903$	$a = 9.89$
$b = 18.116$	$b = 18.14$
$c = 5.282$	$c = 5.31$
$\beta = 106^\circ 23'$	$\beta = 105^\circ 48'$

On the basis of these new parameters 'd' spacings of all the reflections were recalculated and are shown in column 10. The differences of corrected 'd' values of columns 9 and 13 from these recalculated 'd'-values are given in columns 11 and 14. Assuming a maximum error of 0.02 degree 2θ in reading the peak locations in the patterns, the corresponding possible errors in 'd' values are shown in column 15. Columns 16 and 17 show the peak heights in inches for patterns I and II respectively. The peak heights in pattern I are somewhat lower because of dilution with NaCl internal standard. A comparison of the peak intensities in both the patterns with the estimated intensities and structure amplitudes of Warren (columns 6 and 5) and Zussman (columns 4 and 3) shows that there is a high degree of preferred orientation in the powder packs. The c axis (the needle axis) and particularly the 110 cleavage plane of the crystals lie preferentially parallel to the plane of the powder pack. As a result the reflections from planes parallel to 'c' have greatly enhanced intensities. Several higher order reflections from planes parallel to 'b' which are listed by Warren as 'strong' from single crystal work, could not be satisfactorily distinguished from 'background' in the powder patterns--all these reflections lying beyond 75° 2θ, a region where the peak intensities are usually very low.

The correspondence of the corrected 'd' values of columns 9 and 13 with the recalculated 'd' values (column 10) for the actinolite of this work is considered to be reasonably good. It should be pointed out here that though the 'd' values match well, there are anomalies in the intensities of some reflections. On a relative basis there is no general agreement between the intensities obtained from powder patterns and the intensities obtained by Warren and Zussman from single crystal work. Preferred orientation may possibly be a factor causing this disagreement. But it is hard to account for the fact that 110 is disproportionately stronger than 330, which is a somewhat stronger reflection according to Warren. It is also hard to understand why in the powder patterns $\bar{2}0\bar{2}$ shows as a stronger reflection than $40\bar{2}$, while $40\bar{2}$ is actually a much stronger reflection than $\bar{2}0\bar{2}$ and both lie in the same general 2θ region. In spite of such unexplained intensity anomalies the indexing of the actinolite pattern was accepted as correct and the powder patterns from the hornblendes were indexed by comparison with it.

Reflection Intensity Studies

By far the most important substitution of cations in hornblendes is the replacement of Mg by Fe in the octahedral site. This substitution may be a simple replacement of Mg by Fe^{2+} or part of the paired substitution $Mg^{VI}Si^{IV}$ by $Fe^{3+VI}Al^{IV}$. The other important substitution is the replacement of Si by Al in the tetrahedral site which is a part of the paired substitutions either $NaAl^{IV}$ for Si^{IV} or $Al^{VI}Al^{IV}$ (or $Fe^{3+VI}Al^{IV}$) for $Mg^{VI}Si^{IV}$. Any other substitution noted in the present study is minor.

A comparison of atomic scattering factors of these exchangeable ions over any $\sin\theta/\lambda$ region makes it clear that any difference between the intensities of any reflection from two different specimens in the hornblende solid solution series would be mainly caused by the difference of the extent of Mg-Fe substitution between the two specimens. Iron has a scattering factor more than twice as large as that of magnesium. The atomic scattering factors of Mg, Al and Si are very similar and as a result substitution of Mg^{VI} by Al^{VI} or Si^{IV} by Al^{IV} does not cause any material difference in structure amplitudes and reflection intensities (provided the atomic coordinates do not change). Any difference between samples in the extent of Na and/or K substitution in the "vacant site" will be a source of difference in intensity but the total contribution to the structure amplitude by these atoms is small compared to the contribution by Mg-Fe. Besides, the extent of the substitutions of Na and/or K in the specimens studied in this work is pretty much the same in all samples. Other minor substitutions encountered in the present study are Ti and Mn for Mg in the octahedral site and Fe^{2+}, Na and Mn^{2+} for Ca in the calcium site. The effect on intensity caused by the substitution of Mg by Mn or Ti is very similar to the effect caused by the substitution of Mg by Fe. This is because of similarities in atomic scattering factors of Fe, Mn and Ti. But the total concentration of Mn and Ti or differences of their concentrations between samples in the hornblendes studied by the author is so small that they do not make any material difference in the structure amplitudes. The same holds true for the substitutions at the calcium site.

As a result of the above considerations it was felt that studies of the intensity of some suitable reflections might lead to the development of a simple diffractometric method for the estimation of Mg-Fe content in hornblendes. Since Mg and Fe atoms in the hornblende cell lie in layers parallel to the 100 plane and since their absolute contribution to intensity is thus maximum in the h00 type reflections, it was decided to investigate the intensities of h00 type reflections as a function of Mg-Fe content in some hornblendes of known composition.

In order to obtain some idea of the expected intensity differences caused by the variation of Mg-Fe content, structure amplitudes of six h00 reflections (h = 2 through 12) were calculated for 2 hornblendes of known composition. These were chosen from the 12 hornblendes which were completely analysed. One of them, H-61, has the highest amount of Mg and lowest amount of Fe among the twelve; the other, H-72, contains the second lowest amount of Mg and second highest amount of Fe in the group. These two samples represent almost the extreme cases of variation of Mg-Fe content encountered in the present study of 34 hornblendes. To get some idea of the extreme variations in intensity that are theoretically possible with complete substitution of Mg by Fe, structure amplitudes of the above mentioned reflections were also calculated for an ideal tremolite $[Ca_2Mg_5Si_8O_{22}(OH)_2]$ and an ideal ferrotremolite $[Ca_2Fe_5Si_8O_{22}(OH)_2]$.

The atomic coordinates used for all structure amplitude calculations are those given by Zussman (1955, p. 302) for an actinolite. The tetrahedral Si and Al atoms were assumed to be equally distributed between the two possible positions. Atomic scattering factors for the various elements used in the calculations are from the following sources: F, O, Ca and Na from Berghuis et al. (1955, p. 479); Al, Ti, K, Si and Mg from James and Brindley (1931, p. 104) and Mn and Fe from Thomas and Umeda (1957, p. 295-296). Values for Cos2 hx were obtained from tables by Buerger (1941). An example of the calculations involved is given in Table 20. The structure amplitudes of the various h00 reflections from H-61, H-72, tremolite and ferrotremolite are given in Table 21. Table 21 also shows the intensities of the various reflections calculated from structure amplitudes according to the following relationship:

$$\text{I(Intensity)} = F^2 \cdot \frac{1+\cos^2 2\theta}{\sin 2\theta} \cdot \frac{1}{\sin\theta} \cdot K$$

where $\frac{1+\cos^2 2\theta}{\sin 2\theta} \cdot \frac{1}{\sin\theta}$ is the combined Lorenz and Polarization

Table 20

An Example of the Calculation of Structure Amplitude Sample H-61 (Hornblende)

h00		n	x	f	nf	Cos2πhx	nfCos2πhx
200	O_1	8	.117	7.18	57.44	.100	5.74
	O_2	8	.120	7.18	57.44	.063	3.62
	O_3	3.966	.112	7.18	28.48	.163	4.64
	F_3	.034	.112	8.14	0.28	.163	0.05
	O_4	8	.362	7.18	57.44	-.163	-9.36
	O_5	8	.350	7.18	57.44	-.309	-17.75
	O_6	8	.340	7.18	57.44	-.426	-24.47
	O_7	4	.335	7.18	28.72	-.482	-13.84
	Mg	5.052	.000	10.4	52.54	1.000	52.54
	Fe	2.776	.000	23.5	65.24	1.000	65.24
	Al	2.068	.000	10.88	22.50	1.000	22.50
	Ti	0.104	.000	19.1	1.99	1.000	1.99
	Mn	-	.000	22.52	-	1.000	-
	Ca	3.606	.000	17.17	61.92	1.000	61.92
	Fe	0.342	.000	23.5	8.04	1.000	8.04
	Mn	0.052	.000	22.52	1.17	1.000	1.17
	Si_1	6.525	.280	11.28	73.60	-.930	-68.45
	Si_2	6.525	.288	11.28	73.60	-.888	-65.30
	Al_1	1.475	.280	10.88	16.05	-.930	-14.93
	Al_2	1.475	.288	10.88	16.05	-.888	-14.25
	Na	0.628	.000	9.68	6.08	1.000	6.08
	K	0.070	.000	16.36	1.15	1.000	1.15
	Ca	0.018	.000	17.17	.31	1.000	.31
							F = 6.64

h00 - Miller indices

n - number of atoms per cell

x - atomic coordinate

f - atomic scattering factor

Table 21

Calculated Structure Amplitudes and Intensities of h00 Type Reflections from Hornblende Samples H-61 and H-72

Indices of Planes		200	400	600	800	10,00	12,00
Structure Amplitude	H-61	6.6	55.4	176.9	177.7	121.5	14.0
	H-72	18.5	65.6	185.1	184.8	128.1	20.2
Intensity	H-61	16	252	973	508	210	8
	H-72	125	352	1066	550	233	16
Structure Amplitude	Tremolite	-43	17	143	148	96	-6
	Ferrotremolite	88	125	234	227	168	54

Structural Formulae

H-61: $\{Na_{.314}, K_{.035}, Ca_{.009}\}\{Ca_{1.803}, Fe^{2+}_{.171}, Mn^{2+}_{.026}\}\{Mg_{2.526}, Fe^{2+}_{1.266}, Al_{1.034}, Fe^{3+}_{.122}, Ti_{.052}\}\{Si_{6.525}, Al_{1.475}\}$
$\{O_{22.154}, OH_{1.829}, F_{.017}\}$

H-72: $\{Na_{.167}, K_{.071}\}\{Ca_{1.822}, Na_{.153}, Mn_{.025}\}\{Mg_{1.999}, Fe^{2+}_{1.848}, Al_{.841}, Fe^{2+}_{.213}, Ti_{.089}, Mn_{.010}\}\{Si_{6.531}, Al_{1.469}\}\{O_{21.849}, OH_{2.133}, F_{.018}\}$

Tremolite: $Ca_2 \; Mg_5 \; Si_8 \{O_{22}, OH_2\}$

Ferrotremolite: $Ca_2 \; Fe_5 \; Si_8 \{O_{22}, OH_2\}$

factor for powder patterns and where the intensity is obtained in arbitrary units by setting the proportionality constant K equal to 0.01. One possible loop-hole in the theoretical intensity calculation is the assumption that the atomic coordinates are unaffected by the substitution of Mg by Fe. Actually the $a \sin\beta$ dimension of the unit cell increases with increasing Fe-substitution (see later under 'unit cell dimension studies'). Assuming this increase in $a \sin\beta$ to be caused entirely by the larger size of the Fe-ion, the change in the atomic coordinates of the Si, Al^{IV}, O, OH and F ions can be calculated. Taking the difference in $a \sin\beta$ between samples H-61 and H-72 (from figure 55) to be 0.02 Å, new coordinates for the above-mentioned ions in H-72 were calculated. Using these new atomic coordinates the structure amplitudes and intensities of h00 type reflections from H-72 were recalculated. These new values together with the old ones calculated on the basis of atomic coordinates used for H-61, are given below.

Sample H-72

		200	400	600	800	10,00	12,00
Old	F	18.5	65.6	185.1	184.8	128.1	20.2
	I	125	352	1066	550	233	16
New	F	18.2	63	188.5	184.5	127.5	17.0
	I	121	326	1105	548	231	11

It seems clear that though the change of atomic coordinates with Fe-substitution partially compensates (except in the case of 600) the increase in intensity, the compensation is only of a very minor nature.

It can be seen from Table 21 that the variation from 1.388 iron atoms per molecule in the octahedral site in H-61 to 2.061 iron atoms per molecule in H-72 results in a percent increase in intensities of the various reflections as follows: 200, 681; 400, 40; 600, 9.5; 800, 8; 10,00, 11 and 12,00, 100. Thus the intensity gain due to Fe-substitution in reflection 200 is very much more pronounced relative to the intensity gains in the other reflections of the group. It was therefore felt that the intensity ratio of 200 to 600, 800 or 10,00 might give at least semiquantitative information about the extent of Fe-substitution in hornblendes.

Several powder patterns of samples H-61 and H-72 were obtained to check the above idea. The powders used were extremely fine prepared by grinding -100 mesh size grains in a mechanical grinder for two hours. The instrumental set-up was the same as that for the actinolite described earlier except that in several runs a divergent slit of 4° was used instead of 1° to improve intensity and scanning speeds of 1/4°/minute or 1/8°/minute were used to obtain better resolution of the reflections. It was found that even with a divergent slit of 4° the 800, 10,00 and 12,00 reflections were too low in intensity to be definitely identified in the powder patterns. Reflections 200, 400 and 600 could be definitely identified with 600 having the highest intensity. Reflection 200 showed a symmetrical peak but in the case of 400 and 600, though the peak locations could be ascertained without much confusion, the peaks were asymmetrical due to interference from neighbouring reflections. This was true under even the best obtainable instrumental conditions for maximum resolution.

Besides, the height of the peaks and the area under the peaks were so limited that certain likely variations in the choice of the background made considerable differences percentwise in the measurements of peak height or area under the peak. Under these circumstances intensity measurements were considered to be too imprecise to be useful. To improve the precision of background determination and to obtain better resolution, Fe radiation was tried instead of Cu radiation. But with Fe radiation the peak intensities declined too much to balance the other improvements and the situation was not any better than with Cu radiation.

To get some idea of the expected increase in peak height (in inches) of reflection 200 for about 700% increase in calculated intensity from H-61 to H-72, some rough calculations were made. It was found that the expected increase in peak height is of the order of 0.2 inch. Considering the accuracy of the estimation of peak heights that is possible under the circumstances described earlier, it is not possible to make precise measurements of differences of this magnitude. In reflections 400, 600, 800, 10,00 and 12,00 the differences are much smaller and cannot be measured. The peak heights of the h00 type reflections from samples H-61 and H-72 are pretty much the same. Powder patterns of H-78 and H-61--which are respectively the most iron-rich and iron-poor hornblendes available among the 12 completely analysed--were also compared with the view of finding any other type of reflection which may have major intensity differences that can be measured more accurately. The results, given in Table 22, show that there is none.

Unit Cell Dimension Studies

Unit cell parameters $a\sin\beta$, b and $c\sin\beta$ for six hornblendes were determined. These six, chosen from among the twelve hornblendes completely analysed represent approximately the widest variation in composition encountered in the present studies.

$a\sin\beta$ was determined from reflection 600, b from 0,10,0 and $c\sin\beta$ from 002. Sample preparation and experimental procedures were the same as described earlier for actinolite except that a divergent slit of 4° was used instead of 1° and a scanning speed of $1/8^\circ$/minute was used for better intensity and resolution respectively. The three reflections were scanned four times, each time with a different powder pack of the same sample, and the values were averaged. In preparing each powder pack extreme care was taken to make the powder surface as flat as possible and in plane with the surface of the holder, thus making the geometrical condition between packs as reproducible as possible. It was found that peak locations from different packs of the same sample could be reproduced within 0.02 degree 2θ in most cases. Since the samples had to be saved for other work, no internal standards were used to avoid contamination. But spectroscopically pure NaCl was run under identical experimental conditions and the observed d-values of the reflections from it were compared with the corresponding values of

Table 22

Comparison of the Various Peak Heights of an Iron-rich Hornblende (H-78) with Those of an Iron-poor (H-61) Hornblende (In Inches)

hkl	H-78	H-61	hkl	H-78	H-61
020	0.5	0.8	002	1.6	1.8
110	7.8	8.1	350	0.7	0.7
130	0.6	0.5	400	0.9	0.8
200	0.9	0.7	$\bar{2}5\bar{1}$	1.7	1.9
040	1.1	1.1	321	1.1	1.3
220	0.6	0.8	$31\bar{2}$	0.8	0.8
$23\bar{1}$	1.8	2.0	$36\bar{1}$	1.4	1.6
240	2.4	2.6	$40\bar{2}$	0.8	0.8
310	8.2	8.8	$\bar{2}0\bar{2}$	1.3	1.3
$32\bar{1}$	2.0	2.2	510	0.7	0.8
330	2.0	2.1	0,10,0	0.9	0.8
$\bar{2}3\bar{1}$	1.7	1.7	$56\bar{1}$	1.3	1.6
$25\bar{1}$	3.6	3.5	600	1.3	1.3
$16\bar{1}$	1.5	1.5	$\bar{5}6\bar{1}$	1.6	1.6

Structural Formulae

$$\begin{aligned}\text{H-78}\ &\{\mathrm{Na}_{.447}, \mathrm{K}_{.054}\}\{\mathrm{Ca}_{1.717}, \mathrm{Fe}^{2+}_{.185}, \mathrm{Mn}_{.073}, \mathrm{Na}_{.025}\}\{\mathrm{Fe}^{2+}_{2.032}, \mathrm{Mg}_{1.399}, \mathrm{Al}_{1.169},\\ &\mathrm{Fe}^{3+}_{.327}, \mathrm{Ti}_{.073}\}\{\mathrm{Si}_{6.461}, \mathrm{Al}_{1.539}\}\{\mathrm{O}_{22.574}, \mathrm{OH}_{1.417}, \mathrm{F}_{.009}\}\end{aligned}$$

$$\begin{aligned}\text{H-61}\ &\{\mathrm{Na}_{.314}, \mathrm{K}_{.035}, \mathrm{Ca}_{.009}\}\{\mathrm{Ca}_{1.803}, \mathrm{Fe}^{2+}_{.171}, \mathrm{Mn}_{.026}\}\{\mathrm{Mg}_{2.526}, \mathrm{Fe}^{2+}_{1.266}, \mathrm{Al}_{1.034},\\ &\mathrm{Fe}^{3+}_{.122}, \mathrm{Ti}_{.052}\}\{\mathrm{Mg}_{6.525}, \mathrm{Al}_{1.475}\}\{\mathrm{O}_{22.154}, \mathrm{OH}_{1.829}, \mathrm{F}_{.017}\}\end{aligned}$$

NaCl given by Swanson and Fuyat (1953, p. 43) to calculate the instrumental error. Averaging results from three different runs of NaCl the total instrumental correction in d in the 2θ regions of 600, 0,10,0 and 002 reflections from hornblende were calculated as -0.0020 Å, -0.0029 Å and -0.004 Å respectively. The corresponding corrections for the $a \sin\beta$, b and $c \sin\beta$ values were thus -0.012 Å, -0.029 Å and -0.008 Å respectively. The corrected cell dimensions and their averages are given in Table 23. Table 23 also shows the number of octahedral Fe^{2+} ions, octahedral $(Al^{3+}+Fe^{3+})$ ions and tetrahedral Al^{3+} ions per unit cell of the six hornblendes. Assuming a maximum error of ±0.02 degree in 2θ values, the possible errors in $a \sin\beta$, b and $c \sin\beta$ were calculated as ±0.003 Å, ±0.007 and ±0.003 Å respectively.

H. H. Hess (1952, p. 176-177) in his studies of the changes in unit cell dimensions as a function of ion substitutions in orthopyroxenes of the Bushveld type, found that in samples with approximately the same R_2O_3 weight percent the substitution of Fe^{2+} for Mg^{2+} in the structure "results in a regular increase in the size of all three dimensions, a, b and c, but is comparatively smaller for c than for the other two." He further found that b decreases regularly with the substitution of the smaller Al^{3+} or other R^{3+} ions for Mg^{2+}. The c dimension, though somewhat affected by small amounts of R_2O_3, remains effectively constant after R_2O_3 reaches a value around 2 3/4 percent by weight. Hess also found that "the substitution of the larger Al^{3+} ion for the

Table 23

Unit Cell Dimensions of Six Hornblendes

Sample No.	$a \sin\beta$ Å	mean $a \sin\beta$ Å	b Å	mean b Å	$c \sin\beta$ Å	mean $c \sin\beta$ Å	Octahedral Fe^{2+} per unit cell	Octahedral $(Al^{3+}+Fe^{3+})$ per unit cell	Tetrahedral Al^{3+} per unit cell
	9.500		18.064		5.104				
H-1	9.498	9.500	18.060	18.063	5.102	5.105	2.714	2.224	2.818
	9.501		18.065		5.106				
	9.501		18.064		5.106				
	9.515		18.041		5.098				
H-5	9.517	9.515	18.043	18.040	5.102	5.101	2.780	2.164	2.780
	9.513		18.039		5.101				
	9.515		18.037		5.102				
	9.512		18.024		5.096				
H-61	9.511	9.511	18.029	18.028	5.096	5.097	2.532	2.312	2.950
	9.510		18.029		5.098				
	9.510		18.025		5.098				
	9.508		18.087		5.100				
H-70	9.505	9.508	18.085	18.088	5.096	5.099	3.310	2.110	2.452
	9.509		18.090		5.100				
	9.505		18.083		5.098				

Table 23 (Cont'd)

Sample No.	$a \sin\beta$ Å	mean $a \sin\beta$ Å	b Å	mean b Å	$c \sin\beta$ Å	mean $c \sin\beta$ Å	Octahedral Fe^{2+} per unit cell	Octahedral $(Al^{3+}+Fe^{3+})$ per unit cell	Tetrahedral Al^{3+} per unit cell
	9.523		18.087		5.108				
H-72	9.519	9.522	18.085	18.088	5.105	5.107	3.696	2.108	2.938
	9.523		18.091		5.108				
	9.521		18.089		5.106				
	9.536		18.046		5.111				
H-78	9.534	9.536	18.048	18.049	5.108	5.110	4.064	2.992	3.078
	9.538		18.052		5.111				
	9.535		18.049		5.109				

Assuming a possible error of ± 0.02 degree in 2θ values possible error in $a \sin\beta$ is ± 0.003 Å, in b is ± 0.007 Å and in $c \sin\beta$ is ± 0.003 Å.

smaller Si^{4+} ion at first increases the length of the $-SiO_3$ chains but larger amounts of Al^{3+} possibly cause the $-SiO_3$ chains to zigzag in the (010) plane. Zigzag in this plane is further suggested by the lack of change of 'a', though the Mg^{2+} ions are being replaced by smaller Al^{3+} ions and the conspicuous contraction of 'b'."

In a qualitative way, Hess's conclusions were also found to be true in the present study on hornblendes. Assuming that 'β' for all the six hornblendes is very much the same, the 'c' dimensions of all six are practically the same within the limits of error. In figure 55 octahedral Fe^{2+} plus tetrahedral Al^{3+} ions per unit cell has been plotted against the $a \sin\beta$ value of the corresponding cell. Assuming that 'b' increases with substitution of Fe^{2+} for Mg^{2+} and decreases with substitution of Al^{3+} or Fe^{3+} for Mg^{2+}, in figure 56, the ratio of octahedral Fe^{2+} to octahedral $(Al^{3+}+Fe^{3+})$ ions per unit cell has been plotted against 'b' value of the corresponding cell. The trends indicate that Hess's conclusions are probably qualitatively true in the case of hornblendes also. In figure 57 $a \sin\beta$ and 'b' have been plotted against metamorphic rank (in terms of distances of the sample locations from garnet isophase). There is no correlation.

It is admitted that the number of samples studied are too small to justify any definite conclusion. Besides, there is a certain amount of unreliability in the data for no internal standard was used.

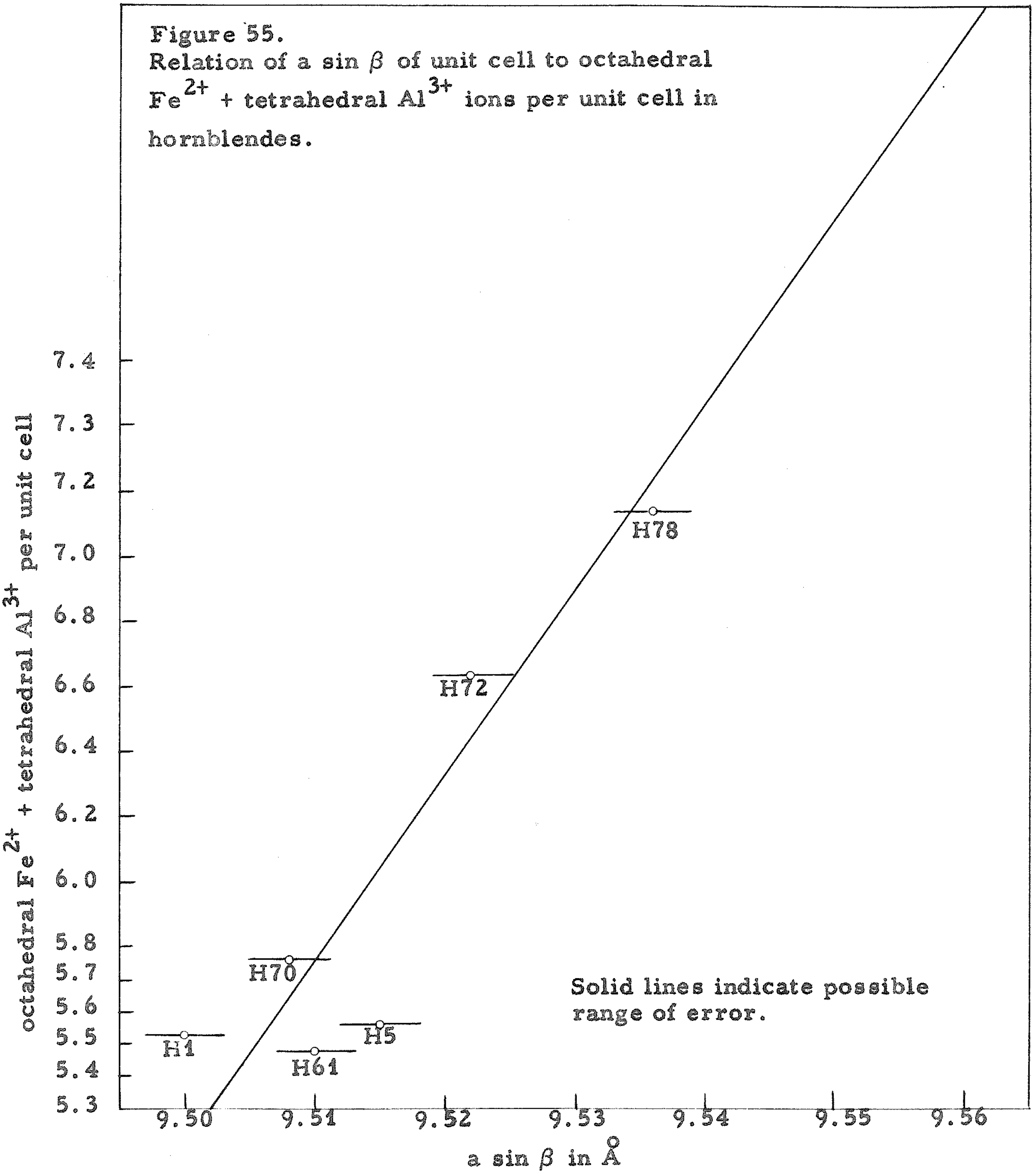


Figure 55.
Relation of a sin β of unit cell to octahedral Fe^{2+} + tetrahedral Al^{3+} ions per unit cell in hornblendes.

Solid lines indicate possible range of error.

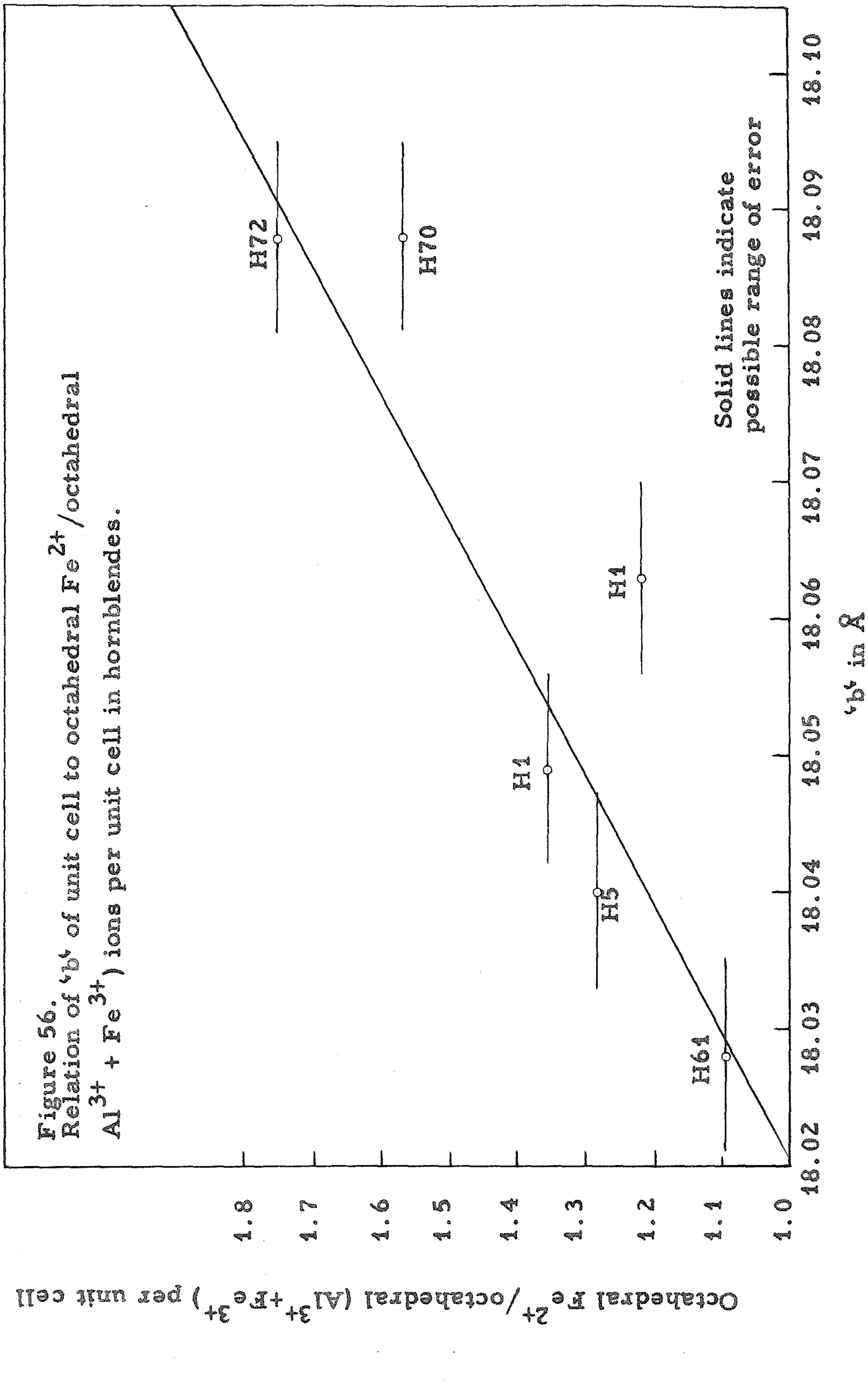


Figure 56.
Relation of 'b' of unit cell to octahedral Fe^{2+}/octahedral $Al^{3+} + Fe^{3+}$) ions per unit cell in hornblendes.

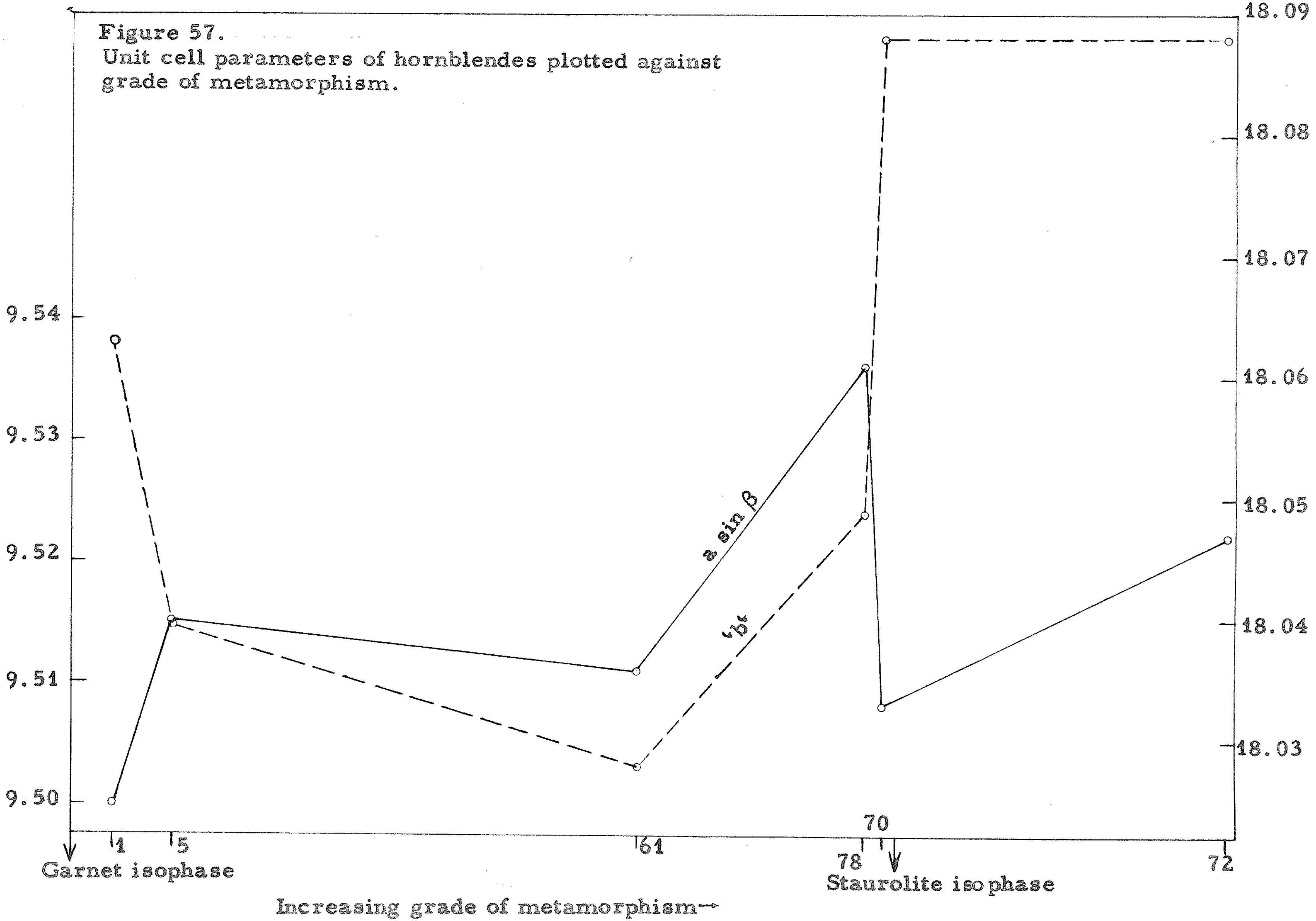


Figure 57.
Unit cell parameters of hornblendes plotted against grade of metamorphism.

SPECIFIC GRAVITY OF THE HORNBLENDES

Specific gravities of 10 out of the 12 completely analysed hornblendes were determined by the pycnometer method. Ten c.c. pycnometers and 8 to 10 gms of mineral sample (-150+200 mesh) was used in each case. The medium used were quadruple-distilled water to which a trace of detergent (Aerosol) was added as a wetting agent. Specific gravities of this medium and of the hornblendes were determined. The values for hornblende were multiplied by the specific gravity of the medium to convert them to specific gravities with respect to water. All gravity measurements were made at 24°C. Before drying and weighing the liquid filled pycnometers were kept for 3 hours in a thermostat controlled water bath maintained at a constant temperature of 24°C. The specific gravity values being reported are with respect to water at 24°C and no temperature correction has been made.

The biggest potential source of error in the determinations is the incomplete wetting of the grains and hence the incomplete removal of airbubbles trapped between the grains and on the grain surfaces. To minimise this error as far as practicable, the wetting was carried out under suction with frequent agitation of the contents of the pycnometer.

The specific gravity values are given in Table 24. From the substitutions known to be possible in the hornblende molecule, it can be predicted that the greatest effect on specific gravity would be that due to the substitution of heavy ions such as Fe^{2+}, Fe^{3+} and Ti^{4+} in the octahedral site in place of much lighter Mg^{2+} ion. Replacement of either Mg^{2+} at the octahedral site or Si^{4+} at the tetrahedral site by Al would have little effect in so far

Table 24

Specific Gravities, Atomic Constitutions and Unit Cell Volumes of Selected Hornblendes

Sample	Sp. Gravity	Fe+Ti+Mn ions per unit cell	(Fe+Ti+Mn+Ca+K+Na) ions per unit cell	$V \sin\beta$ unit cell volume · $\sin\beta$ Å^3	$100 \frac{\text{Fe+Ti+Mn per cell}}{V \sin\beta}$
H-78	3.281	5.380	9.866	879.51	.612
H-72	3.214	4.370	8.796	879.60	.497
H-70	3.209	3.996	8.434	876.93	.456
H-71	3.201	3.880	8.306		
H-13	3.192	3.574	7.854		
H-14	3.191	3.550	7.748		
H-1	3.191	3.502	7.826	876.01	.400
H-69	3.189	3.436	7.728		
H-39	3.186	3.274	7.646		
H-61	3.184	3.274	7.596	873.95	.375

as changing the weight of the molecule. Substitution of Fe^{2+} and Mn^{2+} for Ca^{2+} would increase while substitution of Na^{1+} for Ca^{2+} would decrease the specific gravity. The extent to which the vacant site is occupied by the alkali atoms would also influence the specific gravity to a certain extent. Figure 58 in which the specific gravities have been plotted against the total (Fe+Ti+Mn) ions per unit cell, shows how specific gravity increases with heavy metal ion content. Figure 59 in which the specific gravities have been plotted against the total (Fe+Ti+Mn+Ca+K+Na) ions per unit cell shows the same kind of relationship.

In Table 24 unit cell volumes (as volume x sin β) for five of the hornblendes are also given. Assuming that β is the same for all, the largest volume (H-72) is about 0.64% larger than the smallest volume (H-61). With constant composition the specific gravity of a hornblende will change from 3.20 to 3.18 with this increase in cell volume. Assuming β unchanged, it is highly probable that cell volume increases with increasing substitution of Fe^{2+} for Mg^{2+} and Al^{3+} for Si^{4+} and decreases with increasing substitution of (Al^{3+}, Fe^{3+}) for Mg^{2+} (see unit cell dimension studies). Thus, unless high Fe^{2+} is accompanied by high (Al^{3+}, Fe^{3+}) at the octahedral site, increase in specific gravity due to increase in Fe content would be partly compensated by the simultaneous increase in cell volume. In figure 60 specific gravity has been plotted against 100 [Fe+Ti+Mn per unit cell/volume of unit cell x sinβ]. The curve is essentially linear except for the point for H-78.

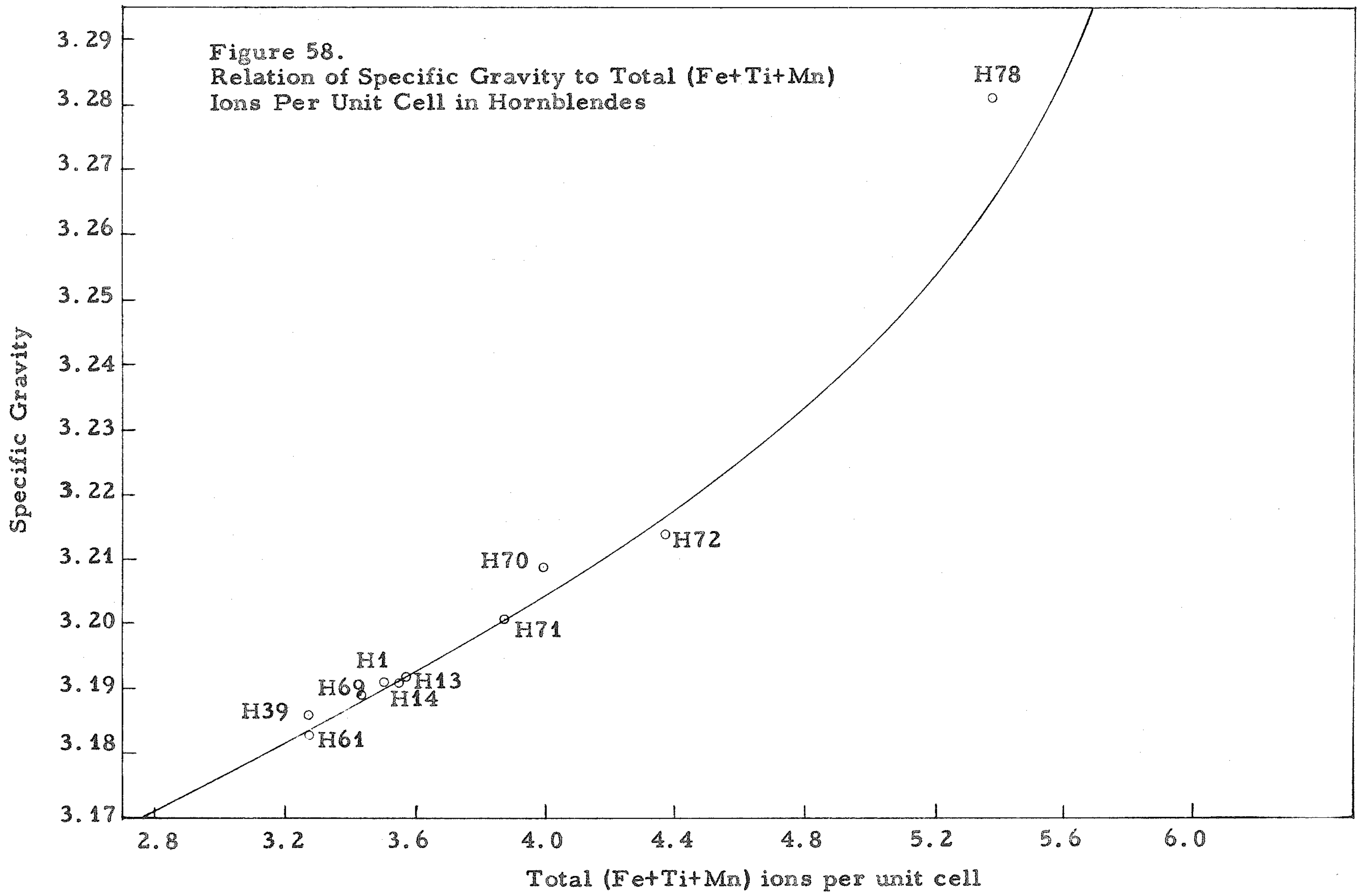


Figure 58.
Relation of Specific Gravity to Total (Fe+Ti+Mn) Ions Per Unit Cell in Hornblendes

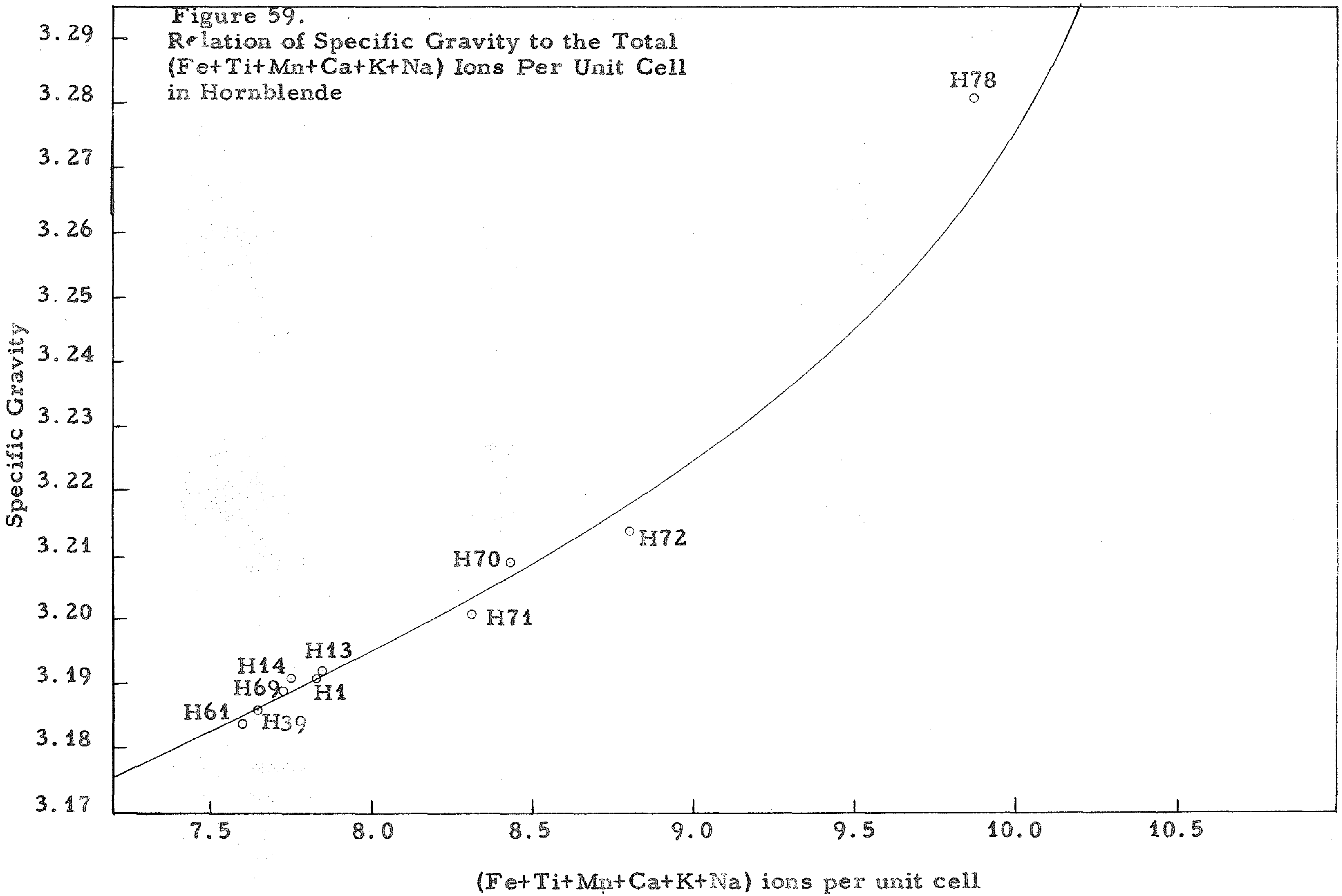


Figure 59.
Relation of Specific Gravity to the Total (Fe+Ti+Mn+Ca+K+Na) Ions Per Unit Cell in Hornblende

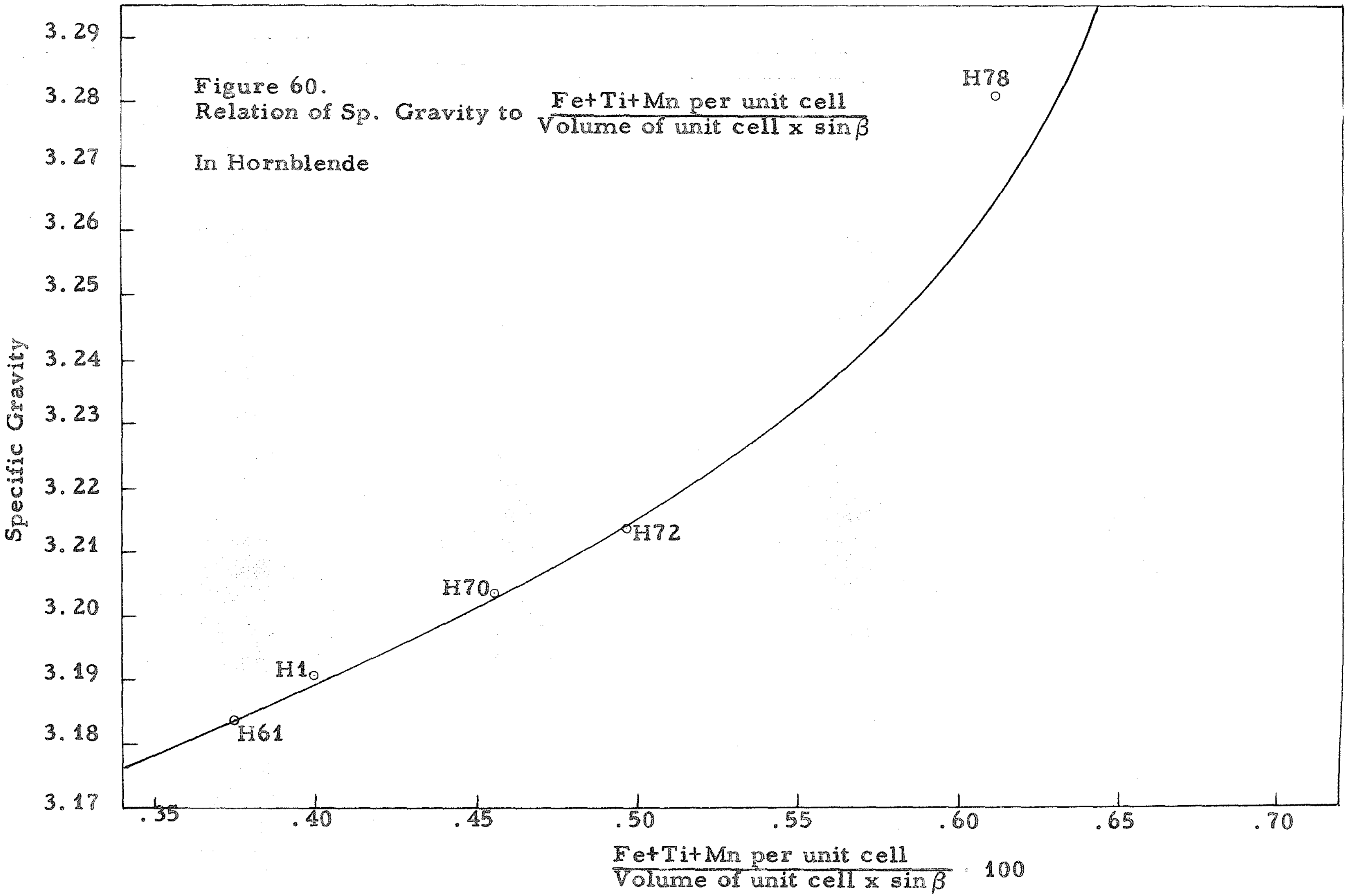


Figure 60.
Relation of Sp. Gravity to $\frac{\text{Fe+Ti+Mn per unit cell}}{\text{Volume of unit cell x sin}\,\beta}$

In Hornblende

The practice of reporting value of specific gravity of minerals up to the third or fourth decimal point is probably not very meaningful unless there is reason to believe that the mineral sample is absolutely pure or at least the nature and content of the impurity is very accurately known so that necessary corrections can be made. For example, an impurity of 1% (by volume) of andesine of specific gravity 2.670 in a mineral sample of hornblende of specific gravity 3.200 would diminish the specific gravity of the hornblende by 0.17% i.e. by 0.005. A similar 1% ilmenite impurity would increase the specific gravity by about 0.46% i.e. by about 0.015. All the hornblende samples for which specific gravity is being reported here have about 0.5% to 1.5% plagioclase impurity in them. All except H-72 and H-78 have 0.3% or less ilmenite impurity. Sample H-72 has about 0.5% ilmenite impurity and the ilmenite impurity in sample H-78 is about 1 to 1.5%. The error in specific gravity value for H-78 is, therefore, relatively higher than in other samples. No correction for impurity has been made in the specific gravity values reported here (Table 24).

PART IV

PLAGIOCLASES

PLAGIOCLASES

Concentrates of plagioclase were obtained from the six amphibolites A-1, A-5, A-14, A-61, A-72 and A-78. The fractions of light colored minerals in the amphibolites obtained from treatment with tetra-bromo-ethane were cycled in the Franz magnetic separator to purify the plagioclase samples. These plagioclase samples are indicated by the same numbers as the corresponding amphibolites with a prefix 'F' to indicate plagioclase instead of 'A' which indicates amphibolite. The plagioclases were used for refractive index determination and x-ray diffractometric work. Two of these plagioclases (F-1, F-4) are from the lowest part of the garnet zone, two (F-14, F-61) are from the middle part of the garnet zone and one (F-78) is from the uppermost part of the garnet zone. The remaining sample (F-72) is from the staurolite zone.

Refractive index ($N_x^{\prime}$) of the plagioclases was determined on (010) or (001) cleavage flakes using sodium light and oils graduated on .002 intervals. In the refractive index range encountered, $N_x^{\prime}$ on (010) and on (001) flakes is the same for all practical purposes (Tsuboi, 1923, Plate I) and so no attempt was made to distinguish the two types of cleavage flakes. The compositions of the plagioclases reflected by their refractive indices, were read off Tsuboi's curve (Tsuboi, 1923, Plate I) and are listed in Table 25.

The angular separations between (131) and ($1\bar{3}1$) reflections in the diffraction patterns of the same six plagioclases were determined and are also listed in Table 25. The instrumental set-up and experimental procedures for these determinations

Table 25

Angular Separations Between (131) and ($1\bar{3}1$) Reflections, Refractive Indices and Compositions of Six Plagioclases

Sample No.	2θ (131)	2θ ($1\bar{3}1$)	Angular Separation	Average Angular Separation	N_x' on (010), (001)	An Content from Tsuboi's Curve	$\frac{CaO}{CaO+Na_2O}$ (mol. prop.) in co-existing hornblendes
F-1	31.42	29.73	1.69	1.69	1.546	An 37	.914
	31.43	29.74	1.69				
	31.43	29.74	1.69				
F-5	31.44	29.76	1.68	1.68	1.546	An 37	.915
	31.43	29.75	1.68				
	31.42	29.74	1.68				
F-14	31.40	29.67	1.73	1.73	1.550	An 42.5	.907
	31.40	29.68	1.72				
	31.40	29.67	1.73				
F-61	31.44	29.58	1.86	1.86	1.554	An 50	.920
	31.43	29.58	1.85				
	31.44	29.58	1.86				
F-72	31.40	29.69	1.71	1.70	1.549	An 42	.919
	31.40	29.70	1.70				
	31.39	29.70	1.69				

Table 25 (Cont'd)

Sample No.	2θ (131)	2θ $(1\bar{3}1)$	Angular Separation	Average Angular Separation	N_x' on (010), (001)	An Content from Tsuboi's Curve	$\frac{CaO}{CaO+Na_2O}$ (mol. prop.) in co-existing hornblendes
F-78	31.38	29.78	1.60	1.60	1.542	An 28	.879
	31.40	29.80	1.60				
	31.38	29.78	1.60				

F-72 and F-78 are from high-TiO_2 amphibolites; others from low-TiO_2 amphibolites.

F-78 is from garnetiferous amphibolite; others from non-garnetiferous amphibolites.

were the same as that described in connection with unit cell dimension studies in hornblendes although the relevant 2θ regions scanned were of course different. Each sample was scanned three times and the separations averaged.

On the basis of their anorthite-contents F-78 should be described as oligoclase and the others as andesine. It is a common experience that plagioclases of higher metamorphic rank are more anorthitic than plagioclases of lower rank. In the present case, however, the two plagioclases from the higher grade (F-72, F-78) are less anorthitic than the other four from lower grades (F-1, F-5, F-14, F-61) even though in the latter four the anorthite-content increases systematically with grade of metamorphism. One possible explanation may be that the two plagioclases F-72 and F-78 from the higher grade did not reach equilibrium compositions. In a simple system involving only plagioclase, temperature alone determines the Ca-Na ratio of the stable phase. In a more complex system, (e.g. amphibolite) the composition of the stable plagioclase would be determined not only by the temperature but also by the nature and composition of all those co-existing phases in which these two components can enter. One way to check attainment of equilibrium or not is to plot concentrations of a common component between co-existing phases and compare the distribution coefficients among the various co-existing pairs. But this approach is often complicated by the fact that the distribution coefficient is a function of temperature and sometimes also depends on the concentrations of other elements in one of the co-existing phases. If correlations of these types go undetected then the significance of a distribution diagram with respect to attainment of equilibrium may very easily be misinterpreted.

In figure 61 the An-contents (mol. %) of the six plagioclases have been plotted against the Ca/CaO+Na_2O (mol. prop.) of co-existing hornblendes. The points obviously do not fall on any simple curve and the number of samples are too small to justify a serious attempt to interpret the distribution. Points for samples 1 and 5 (lowest part of garnet zone) fall closer to the point for sample 72 (staurolite zone) than to the points for samples 14 and 61 (middle part of garnet zone) and it is obvious that if equilibrium was reached the scatter cannot be explained simply on the basis of temperature. It is possible that part of the irregularity in distribution is due to the fact that the distributions are influenced by variable amounts of another element-- a correlation that has not been detected.

Several workers have used reflection separations in plagioclase for determinative purposes. Claisse (1950) after studying reflection separations in eight natural plagioclases of various origins, concluded that a plagioclase composition can be determined to an accuracy of 1% An with the use of his curves, regardless of the origin of the sample. Goodyear and Duffin (1954) subsequently measured the same reflection separations measured by Claisse, using different samples; their data indicate that Claisse's curves are incorrect, and should not be used for determinative purposes. Later studies of a large number of natural plagioclases of various origins by Smith and Yoder (1956,

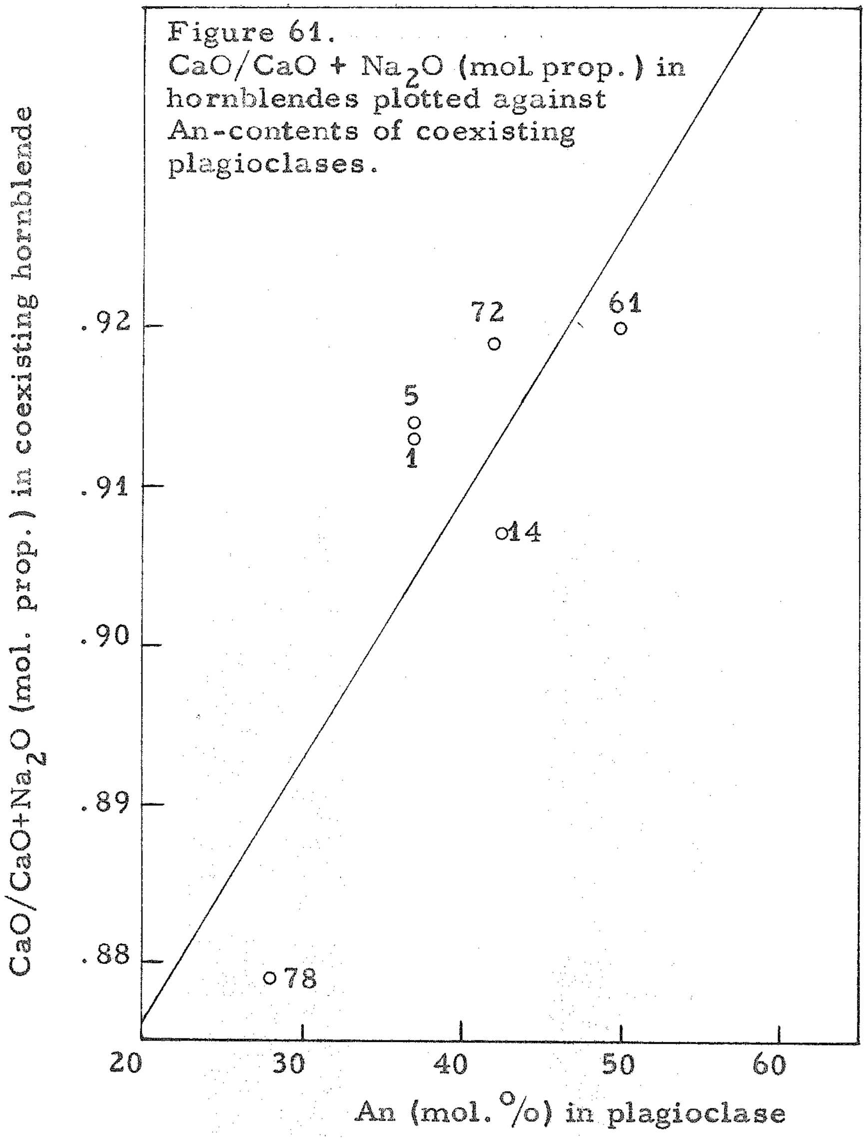


Figure 61.
CaO/CaO + Na_2O (mol. prop.) in hornblendes plotted against An-contents of coexisting plagioclases.

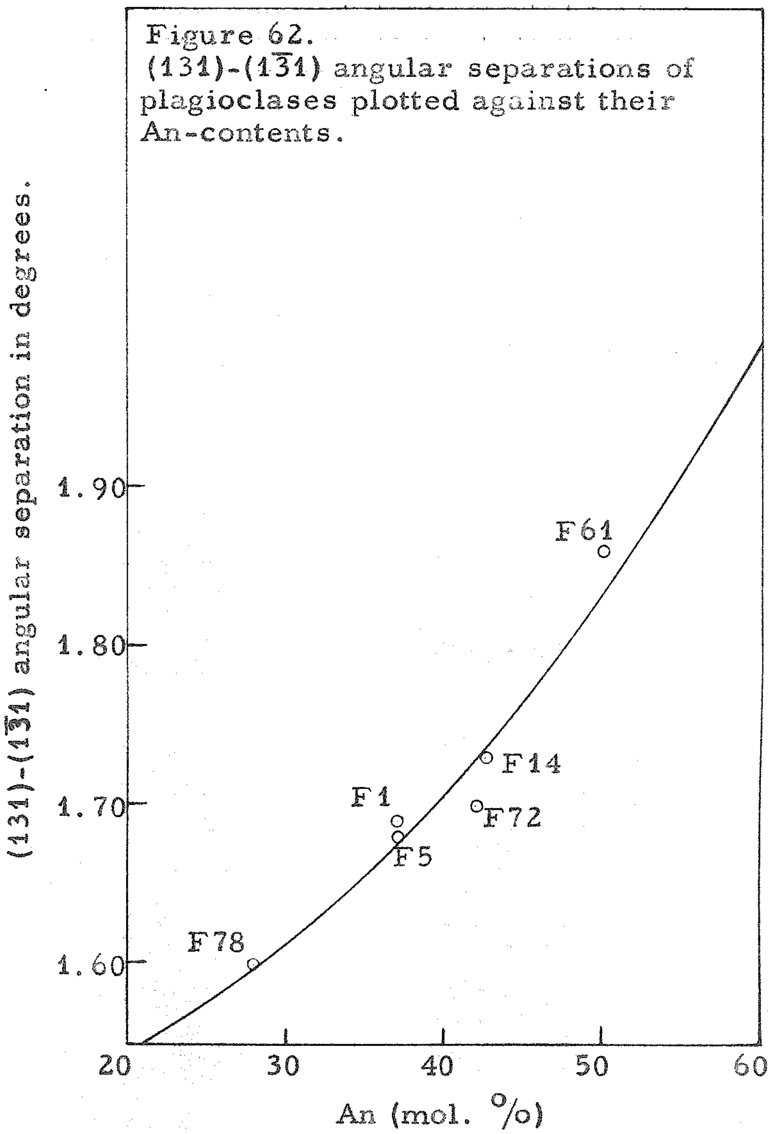


Figure 62.
(131)-(1$\bar{3}$1) angular separations of plagioclases plotted against their An-contents.

p. 645-646) show that the reflection separations of all natural plagioclases do not belong to a unique high-temperature and a unique low-temperature series. These workers recognised, however, that a curve could be determined that plots separation of given reflections against composition in any suite of plagioclases of closely similar origins and thermal histories. Such a curve could be used for determinations of composition of other plagioclases from the same suite.

The angular separations between the (131) and ($1\bar{3}1$) reflections in x-ray diffractometer patterns of 6 plagioclases from the Lead-Deadwood area were measured. A plot of the angular separations of these plagioclases against their compositions (determined optically) shows a good correlation (figure 62).

SUMMARY AND CONCLUSIONS

Some of the amphibolites in the Lead-Deadwood area showing relict gabbroic and diabasic texture (A-16, A-18, A-23, A-26, A-27, A-31, A-32, A-49, A-52, A-54) are definitely ortho-amphibolites. Some minor occurrences of hornblende-bearing rocks (A-37, A-51, A-53) which are mineralogically quite different from typical amphibolites have field relations highly suggestive of a meta-sedimentary origin. The remaining majority of the amphibolites are of ambiguous origin. The 34 amphibolites that have been analysed chemically can be divided into two broad groups on chemical basis, suitably called the high-TiO_2 group (7 specimens) and the low-TiO_2 group (27 specimens). One specimen (A-52) of the high-TiO_2 group is also considered to be definitely an ortho-amphibolite on the basis of its relict texture. If the chemical similarity between this and the rest of the high-TiO_2 group is considered as a reasonable basis for correlation then the whole high-TiO_2 group of amphibolites may be of meta-igneous origin. On the basis of relict texture no member of the low-TiO_2 group belongs to the group of definite ortho-amphibolites and none are from the outcrops of hornblende-bearing rocks where field relations are suggestive of meta-sedimentary origin. The 'average' TiO_2 content of known para-amphibolites is significantly lower than the 'average' TiO_2 content of known ortho-amphibolites; but in view of the known variability of TiO_2 in basic igneous rocks it is doubtful if TiO_2-content can serve as a sure criterion to distinguish ortho- from para-amphibolites. The average TiO_2 content of the low-TiO_2 group is not impossibly low for gabbros and diabases. If both groups are ortho-amphibolites, the two groups possibly represent two separate suites of intrusions or differentiated fractions of one intrusive magma.

The concentrations of five major and minor components total iron (as Fe_2O_3), CaO, TiO_2, K_2O, MnO in the amphibolites do not show any consistent trends correlatable with the intensity of metamorphism. The average concentration of each of these oxides remains practically constant throughout the metamorphic sequence. The concentrations of the trace elements also do not show any significant trend with metamorphic rank. Mean concentrations of Co, Cr, Cu, Ni, Sc, Sr, V and Zr show a very slight decrease with increasing intensity of metamorphism but these trends cannot be definitely established on the basis of a stringent statistical analysis of the present data.

The metamorphism of amphibolites in the Lead-Deadwood area is thus essentially isochemical throughout the range of conditions represented by the appearance of successively the garnet and the staurolite isophases in the enclosing meta-sediments. This conclusion is similar to Shaw's (1956) who worked with pelitic rocks. One major limitation of the present study is that within the range of conditions represented by metamorphism here, no great mineralogic changes involving drastic phase transformations occur in the suite of rocks studied. Whether or not significant changes in the bulk composition of amphibolite may occur when its constituent minerals are involved in such drastic transformations, cannot thus be concluded from the present study. C. G. Engel and A. E. J. Engel (1958) studied the progressive metamorphism of amphibolite interlayers in the major paragneiss of the northwest Adirondack Mountains, New York. They report that in spite of marked and systematic mineralogical changes represented by the appearance of successively the clino- and orthopyroxenes with increasing rank of metamorphism, the chemical composition of the amphibolites varies little from that of a typical basalt even at the highest temperature of metamorphism represented there. In contrast lesser changes in mineralogical composition in the enclosing major paragneiss are accompanied by large changes in bulk composition (Engel, A. E. J. and Engel, C. G., 1958). It seems likely that the susceptibility of a rock to chemical change in response to progressive metamorphism, is critically related to its bulk composition. It seems probable that in examples of this type, progressive metamorphism is essentially a process of progressive "basification" with the basification being more obvious in rocks initially enriched in alkalis and silica. It may also be pointed out here that even in rocks susceptible to significant chemical changes in response to progressive metamorphism, the establishment of a chemical gradient possibly occurs only beyond some critical threshold conditions. Before these conditions are attained mobility of elements probably remains too low to make the chemical gradient conspicuous. It is interesting to note in this connection that excepting H_2O and CO_2 the mineralogic and chemical trends found by A. E. J. Engel and C. G. Engel (1958, fig. 4, p. 1394) in the Adirondack paragneiss do not show any linear relationship with metamorphic rank. The major part of the changes defining the trends occur only at relatively high grades of metamorphism. At the lower and middle grades the changes are very small or absent. Shaw (1956) studied the progressive metamorphism of the pelitic Littleton formation and found its metamorphism to be essentially isochemical. Presumably the metamorphic conditions in the Littleton formation never attained the critical threshold values beyond which matter becomes mobile enough to make a chemical gradient conspicuous.

The concentrations of five major and minor components total iron (as Fe_2O_3), CaO, TiO_2, K_2O and MnO and the ratios Mg/Mg+Fe, SiO_2/Al_2O_3, TiO_2/MnO, K_2O/Na_2O and Fe_2O_3/FeO in the constituent hornblendes do not show any significant correlation with intensity of metamorphism and the average values of these remain reasonably constant throughout the range of metamorphism represented. The concentrations of the trace elements in the hornblendes likewise do not show any significant trend with metamorphic rank. The mean concentrations of Co, Cr, Ni, Sc and Zr show a very slight increase with increasing metamorphism. This is opposite the slight trends shown by these elements in amphibolites; but these trends cannot be definitely established on the basis of present data. If they are real, it would mean that with increasing temperature of metamorphism these elements (Co, Cr, Ni, Sc, Zr) are increasingly fractionated from the rock by hornblende.

The concentrations of the major, minor and trace elements in the hornblendes seem to be closely related to the concentrations of the same elements in the corresponding amphibolites. The ratios of concentrations of major and minor elements between hornblendes and the corresponding amphibolites do not show any significant change with the metamorphic sequence. The distribution characteristics of the major and minor elements between hornblende and amphibolite crudely suggest that most of the rocks under study represent equilibrium assemblages.

The optical properties of the hornblendes do not show any simple correlation with composition except that iron-rich hornblendes are of deeper color than iron-poor hornblendes.

There is some evidence to show that in hornblende the substitution of Fe^{2+} for Mg^{2+} in the octahedral site and the substitution of Al^{3+} for Si^{4+} in the tetrahedral site, increases the dimension of 'a' of the unit cell. Substitution of Fe^{2+} for Mg^{2+} in the octahedral site increases the size of 'b' while the substitution of Fe^{3+} or Al^{3+} for Mg^{2+} in the octahedral site results in a decrease in the size of 'b'. The 'c' dimension of the unit cell seems to be very little affected by these substitutions.

The specific gravity of the hornblendes shows a direct correlation with composition.

The composition of the plagioclases shows a good correlation with the angular separation between (131) and $(1\bar{3}1)$ reflections.

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