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# THE PIEDMONTITES OF PIEDMONT (ITALY), KAJLIDONGRI (INDIA), AND MARAMPA (SIERRA LEONE)[1]

BY

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## ABSTRACT

The piedmontites listed in the title of this paper have been examined optically, chemically, and by X-rays. The results of the examination are presented and discussed.

## CONTENTS

## INTRODUCTION

During the diamond drilling carried out at the iron mine of Marampa, Sierra Leone, a 50 cm thick sheared zone was pierced. The rock at this point was brownish red, distinctly sheared, and mainly composed of piedmontite and quartz associated with minor amounts of epidote and tremolite. This zone was situated in pyroxene-bearing gneiss, which is in places rich in the specular hematite, mined at Marampa.

The piedmontite of the drill core was kindly supplied by Dr. Bleek, the chief geologist of the Marampa mine, to V. Marmo for closer examination. In addition, piedmontite samples of Piedmont (Italy) and Central India

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[1] Received December 30, 1958.

were obtained from the mineralogical collections of the British Museum, London, by the courtesy of Dr. M. Hey.

The piedmontite samples were analysed chemically by Pentti Ojanperä, chemist of the Geological Survey of Finland.

An X-ray study of these minerals was carried out by K. J. Neuvonen in a search for superstructures among epidote minerals. The samples were optically studied under his guidance by Mr. A. I. Vorma at the Geological Survey of Finland. The diagrams for this paper were drawn by Miss Thyra Åberg.

The present paper was written largely by V. Marmo and its English kindly corrected by Mr. Paul Sjöblom, M. A.

## CHEMICAL COMPOSITION

The piedmontites were extracted from the host rocks and purified by using the Clerici solution. The products thus obtained were quite pure.

The purified material was analysed and, thereby, methodically, the common lines of an ordinary silicate analysis have been followed. Some remarks concerning the method should, however, still be made:

1. After removal of the $SiO_2$, the sulphide metals were precipitated in an acid solution by $H_2S$.
2. After the precipitation of the sesquioxides, the manganese was removed from the solution as sulphide. Nevertheless, the manganese content of the $R_2O_3$, Ca, and Mg-precipitates was also checked and the respective corrections made.
3. The total iron and titanium were determined spectrophotometrically on the basis of the color of the ferric chloride complex and the color of the titanium »tiron» complex.
4. The spectrophotometrical determination of the total manganese was carried out from a separate portion.
5. The amount of $Mn_2O_3$ was calculated according to the oxidation ability of the powdered sample. The oxidation was determined from a separate portion using the ferrous sulphate method. For this the sample powder was disintegrated with a mixture of HCl and $H_2SO_4$ in a container closed by a Bunsen valve.
6. The water was determined utilizing the Penfield tube.

The results of the chemical analyses are presented in Table 1. All three piedmontites examined fit well in the general formula: $(OH)_2(Ca, Mn^{\cdot\cdot}, Na)_4 (Al, Fe^{\cdot\cdot\cdot}, Mn^{\cdot\cdot\cdot})_6Si_6O_{24}$, but there occurs a marked variation in the ratio of $Fe^{\cdot\cdot\cdot}$ to $Mn^{\cdot\cdot\cdot}$. Furthermore, the Italian piedmontite is decidedly richer in MnO (2.0 %) than the other piedmontites examined (0.45 % and 0.51 % MnO). If, however, the total manganese content is considered, then all three samples are quite similar, containing 9.32 to 11.56 % ($MnO + Mn_2O_3$). The piedmontite of Sierra Leone is remarkable in respect to its contents of Cu (0.04 %), Pb (0.01 %), and Sn (0.01 %). Whereas the said elements are not detectable in the piedmontite from Italy by the analytical methods used. In the Indian sample, there is, however, 0.01 % Cu [1].

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[1] The occasional Cu and Pb content of piedmontites is well known from earlier studies as well. Doelter (1917) has cited two analyses of piedmontites containing still greater amounts of these metals than the piedmontites of the present paper:

1. From rhyolite of South Mountain, Pa: 0.13 % Cu—0.17 % Pb.
2. From rhyolite of Pine Mountain, Monterey, Maryland: 0.11 % Cu—0.14 % Pb.

The respective $Mn_2O_3$ and MnO contents of these piedmontites are: 1: 8.15 %—2.285 %; and 2: 6.85 %—1.92 %. Sn was not determined. Unfortunately, there are no optical data available for the piedmontites analysed.

*Table 1.* Chemical Composition of the Three Piedmontites
Analyst, Pentti Ojanperä

| | Piedmontite, Piedmont, Italy | | | Piedmontite, Kajlidongri, India | | | Piedmontite, Marampa, Sierra Leone | | |
|---|---|---|---|---|---|---|---|---|---|
| | wt % | cation % | Content of the Unit cell | wt % | cation % | Content of the Unit cell | wt % | cation % | Content of the Unit cell |
| $SiO_2$ .. | 37.54 | 34.33 | $2 \times \{(Ca_{1.76}\ Mn_{0.14}\ Mg_{0.01}\ Ti_{0.03}\ Na_{0.02})\ (Al_{1.88}\ Fe_{0.63}\ Mn_{0.44})\ Si_{3.01}\ O_{12.0}\ (OH)_{0.78}\}$ | 37.16 | 33.58 | $2 \times \{(Ca_{1.96}\ Mn_{0.03}\ Mg_{0.02}\ Na_{0.01})\ (Al_{1.91}\ Fe_{0.40}\ Mn\ _{0.69})\ Si_{2.95}\ O_{12.17}\ (OH)_{0.97}\}$ | 36.82 | 33.27 | $2 \times \{(Ca_{1.94}\ Mn_{0.04}\ Mg_{0.01}\ Na_{0.01})\ (Al_{1.84}\ Fe_{0.49}\ Mn_{0.67})\ Si_{2.99}\ O_{11.96}\ (OH)_{1.01}\}$ |
| $TiO_2$ . | 0.54 | 0.38 | | 0.04 | 0.03 | | 0.07 | 0.05 | |
| $Al_2O_3$ | 19.80 | 21.63 | | 19.96 | 21.26 | | 19.17 | 20.42 | |
| $Fe_2O_3$ | 10.46 | 7.30 | | 6.47 | 4.40 | | 8.03 | 5.46 | |
| $Mn_2O_3$ | 7.32 | 5.16 | | 11.11 | 7.64 | | 10.80 | 7.43 | |
| FeO .. | 0.00 | 0.00 | | 0.00 | — | | 0.00 | — | |
| MnO . | 2.00 | 1.57 | | 0.45 | 0.34 | | 0.51 | 0.39 | |
| MgO . | 0.08 | 0.11 | | 0.17 | 0.23 | | 0.04 | 0.05 | |
| CaO .. | 20.47 | 20.33 | | 22.60 | 21.88 | | 22.29 | 21.58 | |
| $Na_2O$ . | 0.13 | 0.23 | | 0.05 | 0.09 | | 0.10 | 0.17 | |
| $K_2O$ . | 0.01 | 0.01 | | 0.00 | — | | 0.00 | — | |
| $H_2O+$ | 1.46 | 8.95 | | 1.75 | 10.55 | | 1.85 | 11.15 | |
| $H_2O-$ | 0.04 | — | | 0.04 | — | | 0.04 | — | |
| CuO .. | 0.00 | — | | 0.01 | — | | 0.04 | 0.03 | |
| PbO .. | 0.00 | — | | 0.00 | — | | 0.01 | — | |
| SnO .. | 0.00 | — | | 0.00 | — | | 0.01 | — | |
| Total | 99.85 | 100.00 | | 99.81 | 100.00 | | 99.78 | 100.00 | |

## X-RAY AND OPTICAL DATA

For the optical and X-ray determinations, both the powder (the same as was used for the chemical analyses) and single crystals were used. All the respective data are compiled in Table 2. As regards the X-ray data, all the piedmontites examined for this study are quite similar. As regards the optical properties, however, remarkable variations occur. Usually, such variations have been attributed to differences in chemical composition. For the samples under consideration, this correlation is not quite clear, as will be discussed in the following pages.

*Table 2.* Optical and X-ray

| Locality | [1] $\alpha$ | [1] $\beta$ | [1] $\gamma$ | $\gamma - \alpha$ | [3] $2V\gamma$ (observed) | $2V\gamma$ (calc.) |
|---|---|---|---|---|---|---|
| *Italy.* Ceres, Val di Lanzo, Val d'ala, Piedmont .......... | 1.751 (±0.002) | 1.781 (±0.002) | 1.812 (±0.002) | 0.061 | 86 ± 2° | 90.5° |
| *India.* Kajlidongri, Tabja State, State, Central India ........ | 1.742 (±0.002) | 1.767 (±0.002) | 1.805 (±0.002) | 0.063 | 81 ± 2° | 80° |
| *Sierra Leone.* Marampa Mine | 1.756 (±0.002) | 1.783 (±0.002) | 1.823 (±0.002) | 0.067 | 72 ± 3° | 80° |

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[1] Immersion method in sodium light. By Mr. A. I. Vorma.
[2] Pycnometer.
[3] On the universal stage.

## CONTENT AND DIMENSIONS OF THE UNIT CELL

The measured unit cell dimensions are given in Table 2. The axes of the cell were so chosen that the cleavage plain is parallel to (001). Weissenberg photographs calibrated with silicon powder were used for the measurements.

From the cell volume, specific gravity, and chemical analysis, the average content of the unit cell is calculated and presented in Table 1. The calculated contents agree well with the general formula of epidote. According to the structure determined by Ito (1947) for epidote, the Al and Fe (Mn) atoms occupy octahedral positions. In addition, aluminium also occupies centers of oxygen tetrahedra. Byström (Öhman, 1950) observed that in the piedmontite from Jokkmokk, Sweden, there is an excess of trivalent manganese entering the six co-ordinate positions. This same observation is true of the three piedmontites here analysed, wherein the sum of $Fe^{\cdots}$ and $Mn^{\cdots}$ per unit cell exceeds the number of the available octahedral positions. Consequently, some of these atoms must enter into other positions in the structure. In fact, there is a corresponding deficiency of Al atoms in the unit cell, so that some iron (and manganese) evidently is located in the tetrahedral positions. The distribution of these cations in the samples analysed is

Data of Three Piedmontites

| $^{2}D^{4^\circ}_{25^\circ}$ | Space group | Unit cell | | | |
|---|---|---|---|---|---|
| | | $\alpha$ and $\gamma$ | $\beta$ | Dimensions | $a_0:b_0:c_0$ |
| 3.485<br>($\pm$0.005) | $P2_1/m$ | 90° | 115.43° | $a_0$ = 8.87 Å<br>$b_0$ = 5.66 »<br>$c_0$ = 10.15 »<br>$V_0$ = 459.86 Å$^3$ | 1.568:1:1.794 |
| 3.486<br>($\pm$0.006) | $P2_1/m$ | 90° | 115.51° | $a_0$ = 8.89 Å<br>$b_0$ = 5.67 »<br>$c_0$ = 10.22 »<br>$V_0$ = 464.80 Å$^3$ | 1.568:1:1.803 |
| 3.511<br>($\pm$0.004) | $P2_1/m$ | 90° | 115.6° | $a_0$ = 8.89 Å<br>$b_0$ = 5.67 »<br>$c_0$ = 10.17 »<br>$V_0$ = 461.86 Å$^3$ | 1.568:1:1.794 |

| | |
|---|---|
| Piedmontite from Italy ................ | $(Fe_{0.56}\,Mn_{0.44})^{VI}\ (Al_{1.88}\,Fe_{0.07})^{IV}$ |
| Piedmontite from India ................ | $(Fe_{0.31}\,Mn_{0.69})^{VI}\ (Al_{1.91}\,Fe_{0.09})^{IV}$ |
| Piedmontite from Sierra Leone ......... | $(Fe_{0.33}\,Mn_{0.67})^{VI}\ (Al_{1.84}\,Fe_{0.16})^{IV}$ |

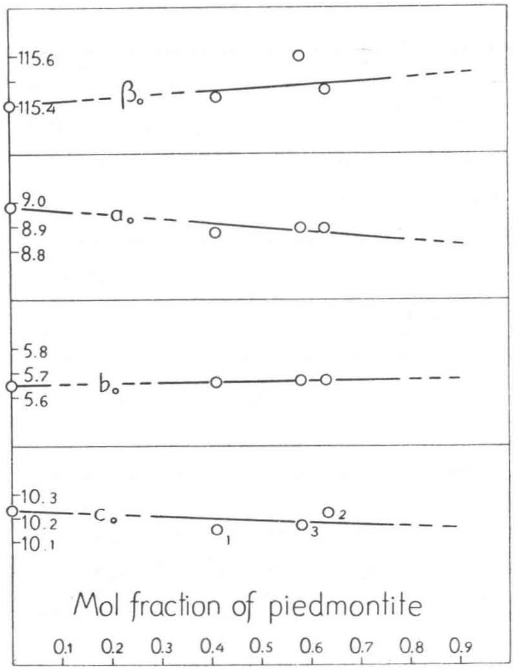
If it is assumed that in pure clinozoisite, pistacite, and piedmontite, the octahedral position is occupied by Al, Fe, and Mn, respectively, the analysed piedmontite samples may be held as solid solutions of pistacite and piedmontite. The mol fraction of the piedmontite end member in the mineral is given by the cation ratio

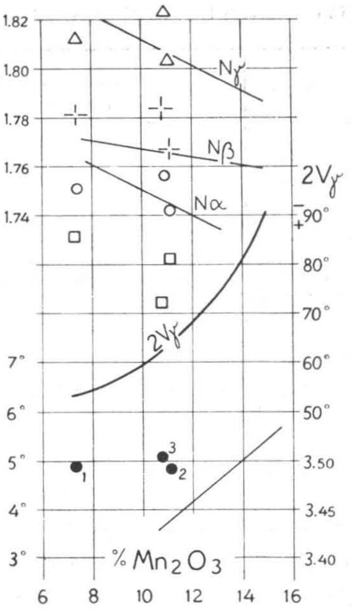
$$\frac{\mathrm{Mn}^{\cdots}}{\mathrm{Fe}^{\cdots}+\mathrm{Mn}^{\cdots}}.$$

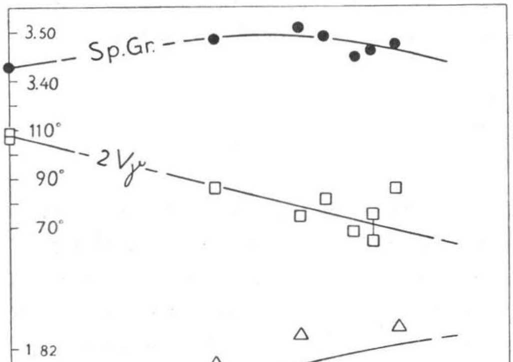
In Fig. 1 the unit cell dimensions are plotted against mol fraction of piedmontite in the samples analysed. A straight line connects the measured values to those given for pistacite by Ito (1947). The dimensions measured from piedmontite from Jokkmokk by Byström (Ödman, 1950) do not agree with the values now measured. This might be caused by a different choice of $a_0$ and $c_0$ axes. The dimensions of the Italian piedmontite tend to be low, which might be due to a high amount of $\mathrm{Mn}^{\cdot\cdot}$ in this mineral.

### OPTIC AXIAL ANGLE

According to Short (1933), when $Mn_2O_3$ and $Fe_2O_3$ are present in approximately equal quantities, the mineral piedmontite is optically positive, and it should have $2V\gamma$ between 50° and 60°. When the manganese content grows, the optical axial angle will rapidly increase. In Fig. 2, his curve of







↖ Fig. 1. Unit cell dimensions in the pistacite (HCa$_2$FeAl$_2$Si$_3$O$_{13}$)-piedmontite (HCa$_2$MnAl$_2$Si$_3$O$_{13}$) series.

Numbers in the diagram refer to the samples studied as follows: (1) Italy, (2) India, (3) Sierra Leone, (4) Långban, (5) Tunaberg, and (6) Shadow Lake.

↑ Fig. 2. The refractive indices, optical axial angle, and the specific gravity of the samples analysed on the diagram of Short (1933).

○ = $\alpha$, + = $\beta$, △ = $\gamma$, □ = 2V, and ● = Sp. gr. The sample numbers the same as in Fig. 1.

← Fig. 3. Variation of the specific gravity and optic properties in the pistacite (HCa$_2$FeAl$_2$Si$_3$O$_{13}$)-piedmontite (HCa$_2$MnAl$_2$Si$_3$O$_{13}$) series.

○ = $\alpha$, + = $\beta$, △ = $\gamma$, □ = 2V, and ● = Sp. gr. The sample numbers the same as in Fig. 1.

2V is reproduced. If the values of the piedmontites discussed in the present paper are plotted on the same graph, there appears a marked discrepancy between the new values and the curve of Short. There the relationship between 2V and the $Mn_2O_3$-per cent is exactly opposite: The decreasing optical angle is irregularly parallel to the increase of the $Mn_2O_3$-content.

For the common epidotes, a relationship between 2V and the $Fe_2O_3$-content has been suggested by Winchell (1951). The 2V-values measured for the now analysed samples, however, do not agree with this curve either. In Fig. 3 the measured 2V-values are plotted against the mol fraction of piedmontite. The optical axial angle around $\gamma$ decreases together with the increasing tenor of the manganese. The optic axis measured by Short (1933) for piedmontite from Shadow Lake, California, is plotted in the same diagram and fits well the curve drawn. The 2V measured by Malmqvist (1929) for piedmontites from Långban and Tunaberg, Sweden, agree also fairly well with the curve in the diagram. The sample from Långban is exceedingly rich in manganese and does not strictly belong to the piedmontite-pistacite series, which might explain the high value of $2V\gamma$ of the mineral.

## REFRACTIVE INDICES

According to Winchell (1951), the refractive indices of the epidote increase together with the iron content of the mineral. From the data given by Larsen and Berman (1934) Short deduced that »it is very probable that Ng and Np curves converge with an increase of $Mn_2O_3$ but not enough data are available to justify a definite statement». In Fig. 2, the curves of Short are reproduced and the values of piedmontites treated in the present paper are inserted in the graph. There the Sierra Leonean piedmontite clearly stands out from the curves proposed by Short. The piedmontites of Italy and India, on the other hand, fit the curves of Short quite well.

In Fig. 3 the refractive indices are plotted against the mol fraction of piedmontite, including the values of pure pistacite and those of the two Swedish samples of Malmqvist (1929) as well as those of Shadow Lake (Short, 1933). The distribution of the plots is quite uniform in the graph for all the refractive indices, $\alpha$, $\beta$, and $\gamma$. The values of the samples from Italy, Sierra Leone, and Långban are high and the indices of the samples from India, Tunaberg, and Shadow Lake are all low. It is notable that no such tendency could be seen in the variation of the optic angle.

## SPECIFIC GRAVITY

The highest value for the specific gravity of the piedmontites cited by Winchell is 3.47 (6.43 % $Fe_2O_3$ and 22 % ($Mn_2O_3$ + MnO)). Short reported a value of 3.55 (approx. 14.5 % $Mn_2O_3$); Larsen and Berman gave a value of 3.47.

For the piedmontites of Italy, India, and Sierra Leone, the specific gravitites are: 3.485 (10.46 % $Fe_2O_3$ and 9.32 % ($Mn_2O_3$ + MnO)); 3.486 (6.47 % $Fe_2O_3$ and 11.56 % ($Mn_2O_3$ + MnO)); and 3.511 (8.03 % $Fe_2O_3$ and 11.31 % ($Mn_2O_3$ + MnO)). According to Short, the specific gravity increases together with the $Mn_2O_3$-content. This tendency, although not very convincing, appears in the piedmontites dealt with in the present paper, too (Fig. 2). According to Winchell, the specific gravity of epidotes increases with the content of $Fe_2O_3$. Consequently, a more evident parallelity between the specific gravity and the total of ($Fe_2O_3$ + $Mn_2O_3$ + MnO) should be expected. The piedmontites of Italy, India, and Sierra Leone are in good agreement with such an assumption. Likewise, when plotted against the mol fraction of piedmontite, a good mutual agreement is found, as seen in Fig. 3. The values of the piedmontite samples from Shadow Lake, Tunaberg, and Långban harmonize well together with those now measured.

## DISCUSSION

The somewhat surprising feature revealed by the present study is that the optic properties of the piedmontites of Italy, India, and Sierra Leone do not follow the chemical composition, as they should do in the light of the curves of Short and Winchell. These deviations may be well understood: in the composition of the piedmontites, there are too many factors affecting the optic properties of these minerals. If the epidote proper is concerned, $Al_2O_3$ and $Fe_2O_3$ may be taken as the only variable constituents of the mineral. Therefore, in the series indicated by the end members of $HCa_2Al_3Si_3O_{13}$ and $HCa_2FeAl_2Si_3O_{13}$, a distict correlation between the chemical composition, the respective optical properties, and the specific gravity can be found. The diagram of Winchell (1951) mainly represents this series. The same would probably work for the hypothetical series between the end members of $HCa_2Al_3Si_3O_{13}$ and $HCa_2MnAl_2Si_3O_{13}$ as well. By means of the samples analysed, an approximative correlation between the chemical composition and unit cell dimensions, optical properties, and specific gravity was evaluated and presented in Figs. 1 and 3 for the series pistacite-piedmontite ($HCa_2FeAl_2Si_3O_{13}$—$HCa_2MnAl_2Si_3O_{13}$). The curves in the diagrams are drawn to agree with all the points plotted, although some of the samples considered do not strictly belong to the pistacite-piedmontite series. Members of this series should have the cation ratio Al: ($Fe^{\cdots}$ + $Mn^{\cdots}$) = 2, but the samples from Långban (4) and Sierra Leone (3) deviate greatly from this requirement, having too high a content of iron and manganese. This fact explains the high indices measured in these samples. In the same manner the indices are high in the Italian piedmontite because of the deviation from the series owing to the high $Mn^{\cdot\cdot}$ content. The series is evidently best represented by the samples from India (2), Tunaberg (5) and Shadow Lake (6).

In addition to the chemical composition, the optical properties might be affected by differences in the mutual distribution of the atoms in the structure of the mineral, caused by contrasts in the thermal prehistory. No superstructures were detected in any of the piedmontites examined. Consequently, possible structural dissimilarities cannot be of the order-disorder type. The distribution of the atoms Al, Fe, and Mn in the six and four co-ordination positions in the structure offers, however, many more possibilities. Only more elaborate x-ray studies would give information about such differences in the minerals considered.

According to the structural requirements the formula of the epidote minerals is taken as $HCa_2$ (Al, Fe, Mn) $Al_2Si_3O_{13}$. This gives at least two aluminium atoms per formula or four per unit cell. As mentioned earlier, however, this postulation does not hold and types with an excess of $Fe^{\cdot\cdot\cdot}$ ($\pm$ $Mn^{\cdot\cdot\cdot}$) exist. Consequently, end members of the type $HCa_2Fe_2AlSi_3O_{13}$ or $HCa_2Fe_3Si_3O_{13}$ have to be accepted. Both these formulas have been used. The use of the latter formula, however, is not justified either from a structural or chemical point of view. The end members $HCa_2Al_2AlSi_3O_{13}$, $HCa_2Fe_2AlSi_3O_{13}$, and $HCa_2AlSi_3O_{13}$ were not applied in this discussion since only a small part of the atoms Fe and Mn could be assumed to occupy tedrahedral positions in the minerals analysed. Accepting more aluminium-rich end members, it was possible to handle the specimens as representatives of the binary system pistacite-piedmontite, instead of a more complex ternary system including clinozoisite as one of the end members.

Compiling iron and manganese, the properties of the analyzed piedmontites could be demonstrated in the series clinozoisite—mangano-pistacite, ($HCa_2(Fe, Mn)_2AlSi_3O_{13}$). Thereby it appears that the effect of iron and manganese upon the optical properties is not similar, however. Therefore the authors wanted to use the new data measured to trace the variation of the properties in the series pistacite-piedmontite, e. g., to ascertain the difference between the effects of iron and manganese. It is hoped, that when more data is available, the variation can be explored in greater detail, to provide a basis for the preparation of a diagram of the ternary system as well.

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