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Fe-Ti OXIDE MINERALS IN ANDESITE FROM THE WŻAR MOUNTAIN (PIENINY MTS.)

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Abstract. Two generations of Fe—Ti oxide minerals have been found in the younger variety of andesite from Wżar. One generation is made up of large, corroded titanomagnetite phenocrysts, a part of them being homogeneous, the other one containing inclusions of a different spinel phase. Chemical examinations have demonstrated that these are titanomaghemite inclusions. A chemical analysis performed on electron microprobe X-ray analyser has shown the complexity of maghemitization process, which is not a simple oxidation of Fe^{2+} to Fe^{3+} , but is connected with the anisotropic diffusion of cations. The untypical process of oxidation of some titanomagnetite grains only to titanomaghemite is very likely a consequence of magmatic assimilation of limestones. The second generation of Fe—Ti oxide minerals consists of idiomorphic, homogeneous, very fine (below 0.05 mm) titanomagnetite grains scattered in the groundmass.

INTRODUCTION

The petrography of the volcanic rocks of the Wżar mountain (Pieniny Mts.) was investigated by Małkowski (1921, 1958). The mountains is built of several varieties of augite-amphibolic andesites that were formed as a result of a series of intrusions.

The rock in question has been subjected to microscopic examinations in reflected light. The separated magnetic fraction has been put to X-ray and chemical analyses. In addition, a chemical analysis of Fe—Ti minerals has been performed by electron microprobe.

RESULTS

Microscopic examinations in reflected light

Microscopic examinations have shown the occurrence of two generations of Fe—Ti oxide minerals. The first one is made up of phenocrysts,

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0.05–0.3 mm in size, revealing a high degree of destruction (fractured and melted on the surface). A part of them is homogeneous, but the other part consists of two crystalline phases. The homogeneous phenocrysts and one of the phases of two-phase grains are grey with a pink tinge, with the reflectance $R = 18\%$; they are isotropic. The second phase of the diphasic grains is grey with a blue tinge, $R = 21\%$, and is isotropic as well. There is a sharp boundary between the two phases and it frequently happens that the light phase appears in the form of irregular, oval inclusions in the darker phase. The diphasic phenocrysts are shown on Phot. 1. In the light phase (with oval inclusions) there is always a tiny submicronic fissure filled with a phase of low reflectance (about 10%). The fissures become more distinct when treated with HCl 1 : 1 (Phot. 2).

On the basis of microscopic examinations it has been found that the phase with a pink tinge is titanomagnetite **, whereas that with a blue tinge — presumably titanomaghemite **. As regards the light phase, there was no certainty whether it was titanomaghemite because the microscopic images (sharp boundary between phases, oval inclusions inside the grains) were different from those described in other papers (Katsura, Kushiro 1961; Prevot *et al.* 1968; Hubicka-Ptasińska, Jasińska 1971). It could be only ascertained that it was a spinel phase, but its closer determination required an identification of the chemical composition on electron microprobe (see below).

The second generation of Fe—Ti oxide minerals consist of fine (below 0.05 mm), idiomorphic grains of titanomagnetite in the rock groundmass. They are homogeneous and are not liable to any transformations.

X-ray and chemical examinations

The results of X-ray and chemical analyses of magnetic concentrate from andesite are presented in Tables 1 and 2, respectively. The position of Fe—Ti oxides under study in the FeO—Fe₂O₃—TiO₂ ternary system is shown in Figure 1.

X-ray analysis has demonstrated the presence of spinel phase reflections only. A very weak reflection 531 has been noticed on the X-ray pattern (Tab. 1). According to O'Reilly (1968), this reflection is characteristic of $(1-x) \text{Fe}_3\text{O}_4\text{—Fe}_2\text{TiO}_4$, i.e. of titanomagnetites, and may be useful in determining x values for synthetic titanomagnetites. It is useless, on the other hand, to utilize this reflection for determining x values of natural titanomagnetites since they may contain as isomorphic substitutions various elements affecting the X-ray data in an unpredictable way.

The chemical analysis has shown that it is oxidized titanomagnetite that is present in the specimen studied because in the FeO—Fe₂O₃—TiO₂

* Reflectance was measured on MPV photometer with a lighting device for reflected light to Ernst Leitz-Wetzlar ORTHOLUX microscope. The measurements were made in white light („O” filter).

** For explanation of the meaning of the names „titanomagnetite” and „titanomaghemite” as used in the present paper see Hubicka-Ptasińska, Jasińska (1971).

X-ray data for magnetic concentrate

d/Å	I	hkl	d/Å	I	hkl
4,87	1	111	1,281	2	533
2,97	5	220	1,267	1	622
2,536	10	311	1,210	2	444
2,425	1	222	1,1223	2	642
2,099	5	400	1,0920	5	553 ; 731
1,715	4	422	1,0485	3	800
1,615	7	333 ; 511	0,9894	2r	660 ; 820
1,483	7	440	0,9692	4r	555 ; 751
1,419	1	531	0,9382	4r	840
1,327	2	620			

$a = 8.395 \pm 0.005 \text{ Å}$

Table 2

Chemical composition of the magnetic concentrate

Component	Weight %	Mol %
FeO	27,9	45,8
Fe ₂ O ₃	53,9	39,8
TiO ₂	9,7	14,3
Total	91,5	99,9

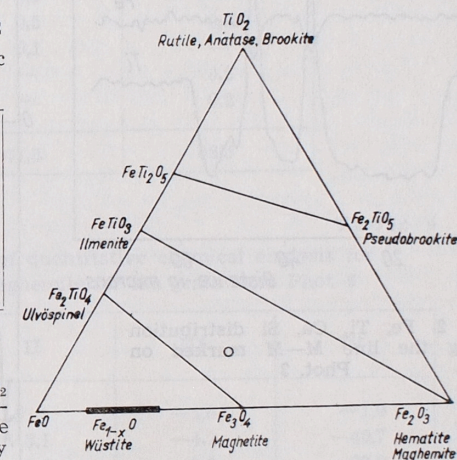


Fig. 1. Phases in the FeO—Fe₂O₃—TiO₂ system. More per cent. The circle marks the position of the magnetic concentrate under study

ternary system it is situated near the FeTiO₃—Fe₃O₄ and not near Fe₂TiO₄—Fe₃O₄ line (Fig. 1).

Electron microprobe X-ray analysis*

The analysis was performed on MS-46-Cameca apparatus with the following measurement parameters: accelerating voltage 20 kV, beam current 150 μA, sample current 15 μA. To give a conducting surface the sample was coated with a thin layer of copper. Metallic Mn, Al, Cr, Zn, Mg, Ti as well as magnetite, quartz and fluorite were used as standards.

* The analyses were performed in the Institute of Metallurgy, Academy of Mining and Metallurgy, Cracow.

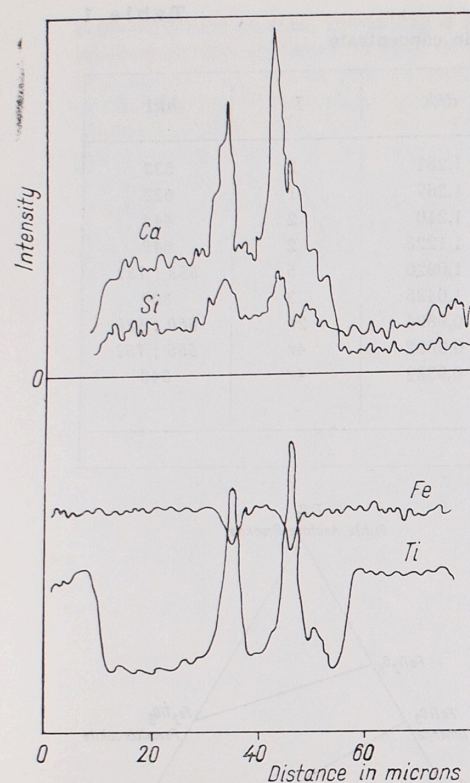


Fig. 2. Fe, Ti, Ca, Si distribution along the line M—M marked on Phot. 3

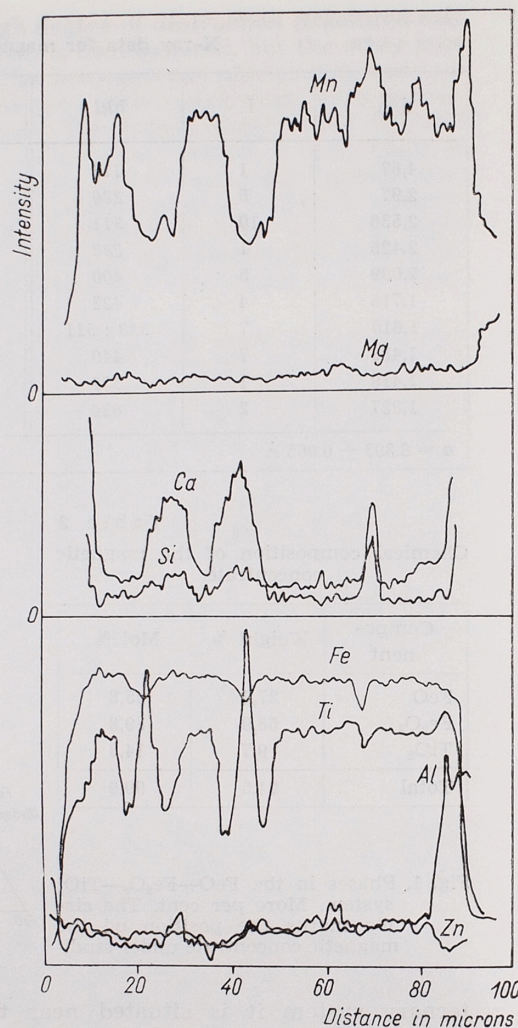


Fig. 3. Fe, Ti, Al, Zn, Mn, Mg, Ca, Si distribution along the line N—N marked on Phot. 8

In quantitative analyses, absorption corrections for Ti, Si, Al and Mg according to Philibert's formula were taken into account. Vanadium occurring in titanomagnetites was not determined because of the coincidence of the V—K α line (2.505 Å) with the Ti—K β lines ($\beta_1 = 2.514$ Å, $\beta_2 = 2.498$ Å).

Electron microprobe X-ray analyses were performed on two grains shown in Photos. 3 and 7. Their results are presented on Photos. 4—6, 8—12 and in Figs. 2, 3. Data obtained from a quantitative analysis of titanomagnetite and the light phase are given in Table 3. Their recalculations accor-

ding to the method of Prevot *et al.* (1968) are shown in Table 4. These data permitted to establish the theoretical formula of titanomagnetite

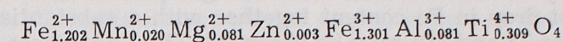


Table 5 presents a recalculation of quantitative analyses to oxide composition.

Table 3

Chemical compositions of titanomagnetite and titanomaghemite determined on electron microprobe for the grain from Phot. 6

Element	Titanomagnetite weight %	Titanomaghemite weight %
Fe	62,5	61,3
Ti	6,6	3,9
Al	1,0	0,7
Mg	0,9	—
Mn	0,5	0,2
Zn	0,1	—
Ca	—	0,2
Si	—	0,2
Total	71,6	66,5

Table 4

Recalculations of the results of quantitative chemical analysis for titanomagnetite and titanomaghemite for the grain from Phot. 6

Element	I	II	III	IV
Fe	83,4	81,8	—1,6	—1,9
Ti	10,3	6,1	—4,2	—40,7
Al	2,7	1,9	—0,8	—29,0
Mg	2,7	—	—2,7	—100,0
Mn	0,7	0,3	—0,4	—57,0
Zn	0,1	—	—0,1	—100,0
Ca	—	0,4	+0,4	—
Si	—	0,5	+0,5	—
Total	99,9	97,2	—2,7	

I — The number of cations in titanomagnetite respect to the cation sum assumed to be 100.

II — The number of cations in titanomaghemite related to the sum of cations in the initial phase (titanomagnetite) assumed to be 100.

III — Difference between columns II and I (II—I).

IV — Relative change in the percentage of cation content in relation to the content given in column I.

From linear analyses of the two grains (Figs. 2 and 3) it appears that, upon the entry of electron beam into the light phase with a higher reflectance, a slight drop in Fe content together with a substantial decrease in the quantity of Ti and Mn may be observed. The light phase also contains Ca and Si so, compared to the darker phase, it is richer in light elements (Ca, Si) and poorer in the heavy ones (Fe, Ti, Mn). In the centre of the light phase, where submicronic fissures were observed under the microscope in reflected light, a marked increase in Ti concentration can be ascertained. The maximum of Ti content coincides with that of Ca and Si

Table 5

Theoretical oxide composition of titanomagnetite and oxide composition of titanomaghemite determined on electron microprobe for the grain from Phot. 6

Component	Titanomagnetite Weight %	Titanomaghemite Weight %
FeO	38,6	—
Fe ₂ O ₃	46,4	87,4
TiO ₂	11,0	1,3
Al ₂ O ₃	1,9	1,3
MgO	1,5	—
MnO	0,6	0,3
ZnO	0,1	—
CaO	—	0,3
SiO ₂	—	0,2
Total	100,1	96,4

contents. It is impossible however to determine the quantitative composition of the phase rich in Ti, Ca and Si, which always appears in the centre of the light phase, as its width is below 1 μ m so that an accurate determination of its chemical composition is beyond the capacity of an electron microprobe. It is only possible to determine its approximate composition basing on linear analyses (Tab. 6). Recalculations of quantitative analyses (Tab. 5) have shown a deficiency of cations in the light phase in relation to titanomagnetite. It seems therefore reasonable to assume that the light phase is titanomaghemite. This hypothesis is further confirmed by titanomagnetite oxidation ascertained on the basis of chemical analyses of magnetic concentrate (Fig. 1). The mechanism of titanomagnetite oxidation to titanomaghemite in the sample under study is different from that observed in teschenites (Hubicka-Ptasińska, Jasińska 1971) as well as from that described by Prevot *et al.* (1968) in andesites from St. Clement (France). It seems that maghemitization in the Wzar andesites proceeded due to the diffusion of titanium from titanomagnetite to an indefinite phase enriched in Ti, Ca and Si that is always situated in the centre of titanomaghemite grains. To make the process of maghemitization quite clear, it is necessary to consider it against the background of the origin

Table 6

Approximate chemical composition of the phase enriched in Ti, Ca, Si determined on electron microprobe for the grain from Phot. 6

Element	Weight %
Fe	56,8
Ti	8,0
Al	0,3
Mn	0,2
Ca	0,3
Si	0,5
Total	66,1

of the volcanic rocks of the Wzar mountain. Magmatic assimilation of limestones has been recorded in the Wzar andesites (Małkowski 1958; Gumowska 1967). The assimilation played a specific role in the youngest intrusion of Wzar (Gumowska 1967), which is represented by the specimen under study. It was most likely magma rich in calcium and oxygen that penetrated into the fissures of the previously crystallized grains of titanomagnetite since in the magma assimilating limestones an increase in oxygen pressure can be expected. This pressure in magmatic melts is determined by the dissociation of either H₂O or CO₂ (Buddington, Lindsley 1964). Upon cooling, the state of equilibrium between the magma and crystalline phases became stabilized due to the crystallization of minerals from the melt. On the other hand, the silicate phase enriched in calcium and oxygen, which had crystallized earlier in titanomagnetite fissures, had no contact with liquid magma and was probably unstable at lower temperatures. It is feasible that titanium cations diffused to this phase from titanomagnetite, but what silicate phase resulted is not exactly known. It is conceivable that it consists of submicronic sphene inclusions. Those parts of titanomagnetite from which titanium had diffused were transformed into titanomaghemite. The vacancies in the defect spinel structure of titanomaghemite are partly occupied by Ca²⁺ and Si⁴⁺. On the plots of linear distribution of elements, a gradual increase in Ca and Si concentration is visible as the electron beam approaches the phase with the maximum Ti, Ca, Si content. Iron oxidation, accompanying the diffusion of titanium, was due either to oxygen supplied by the occluded silicate phase or to the reaction of oxidation-reduction, which resulted in Fe²⁺ oxidizing to Fe³⁺ and Ti⁴⁺ being reduced to Ti³⁺. Ti³⁺ cation could have entered the silicate phase, a possibility of its occurrence in silicate minerals having been demonstrated (Burns 1970).

The above explanation of maghemitization in titanomagnetite phenocrysts of the sample studied is a concept the quantitative formulation of which is impossible so long as the quantitative chemical composition of the phase enriched in Ti, Ca and Si is not exactly known.

CONCLUSIONS

The investigations performed have permitted to draw the following conclusions:

1. In the analysed variety of the Wzar andesite, Fe—Ti oxides form a titanomagnetite-titanomaghemite assemblage.
2. Titanomagnetite oxidation to titanomaghemite proceeded under specific conditions and it is difficult to judge whether it was a low-temperature oxidation as postulated by Ozima and Larson (1970). According to these authors, rocks containing titanomaghemite are unfit for palaeomagnetic examinations as titanomaghemites reveal secondary magnetization. This problem therefore may be of importance when interpreting palaeomagnetic investigations of the Wzar andesites.
3. Titanomagnetite maghemitization is not based on a simple oxidation

of Fe^{2+} to Fe^{3+} but is a far more complex process connected in the first place with anisotropic diffusion of cations (Ti, Mn, Ca, Si).

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 PRÉVOT M., REMONDE M., CAYEA E. G., 1968: Étude de la transformation d'une titanomagnetite en titanomaghemite dans roche volcanique. *Bull. Soc. Fr. Mineral. Crist.* 91, 65.

Maria HUBICKA-PTASIŃSKA

TLENKOWE MINERAŁY Fe-Ti Z ANDEZYTU Z GÓRY WŻAR (PIENINY)

Streszczenie

W młodszej odmianie andezytu z Wżaru zauważono dwie generacje tlenkowych minerałów Fe—Ti. Jedną stanowią skorodowane, duże pryzmaty tytanomagnetytu. Część z nich jest jednorodna, a część zawiera wtrącenia innej fazy spinelowej. Badaniami chemicznymi stwierdzono, że są to wtrącenia tytanomaghemitu. Analiza chemiczna wykonana na mikroanalizatorze rentgenowskim wykazała złożoność procesu maghemityzacji, który nie polega na prostym utlenieniu Fe^{2+} do Fe^{3+} , lecz jest związany z różnokierunkową dyfuzją kationów. Nietypowy obraz utlenienia tylko niektórych ziarn tytanomagnetytu do tytanomaghemitu jest przypuszczalnie następstwem asymilacji wapieni przez magmę. Drugą generację tlenkowych minerałów Fe—Ti stanowią idiomorficzne, jednorodne, bardzo drobne (poniżej 0,05 mm) wydzieliska tytanomagnetytu w cieście skalnym.

OBJASNIENIA FIGUR

- Fig. 1. Fazy w układzie $\text{FeO}-\text{Fe}_2\text{O}_3-\text{TiO}_2$. Procenty molowe. Kółkiem oznaczono położenie analizowanego koncentratu magnetycznego
 Fig. 2. Rozmieszczenie Fe, Ti, Ca, Si wzdłuż linii M—M zaznaczonej na fot. 3
 Fig. 3. Rozmieszczenie Fe, Ti, Al, Zn, Mn, Mg, Ca, Si wzdłuż linii N—N zaznaczonej na fot. 8

Мария ГУБИЦКА ПТАСИНЬСКА

ОКИСЛЫ Fe-Ti В АНДЕЗИТЕ ГОРЫ ВЖАР (ПЬЕНИНЫ)

Резюме

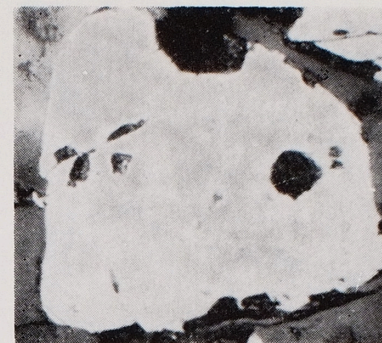
В младшей разновидности андезита горы Вжар наблюдались две генерации окислов Fe-Ti. Первую из них составляют корродированные крупные фенокристаллы титаномagnetита. Некоторые фенокристаллы однородны, другие же включают проявления другой шпинелевой фазы. Химические анализы показали, что включения сложены титаномagгемитом. Данные, полученные путем химического анализа на рентгеновском микроанализаторе, свидетельствуют о сложности процесса маггемитизации. Он выражается не в простом окислении Fe^{2+} до Fe^{3+} , но связан с разнонаправленной диффузией катионов. Нетипичное проявление окисления лишь некоторых кристаллов титаномagnetита с превращением их в титаномagгемит представляет, вероятно, следствие ассимиляции известняков магмой. Вторую генерацию окисных минералов Fe-Ti составляют идиоморфные, однородные, мельчайшие (мельче 0,05 мм) обособления титаномagnetита в продообразующей массе.

ОБЪЯСНЕНИЯ К ФИГУРАМ

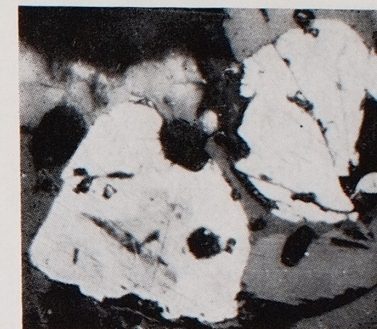
- Фиг. 1. Фазы в системе $\text{FeO}-\text{Fe}_2\text{O}_3-\text{TiO}_2$. Молярные проценты. Кружком указано положение анализируемого магнитного концентрата
 Фиг. 2. Распределение Fe, Ti, Ca, Si вдоль линии M—M, отмеченной на фото 3
 Фиг. 3. Распределение Fe, Ti, Al, Zn, Mn, Mg, Ca, Si вдоль линии отмеченной на фото 8

PLATE I (PLANSZA I, ТАБЛИЦА I)

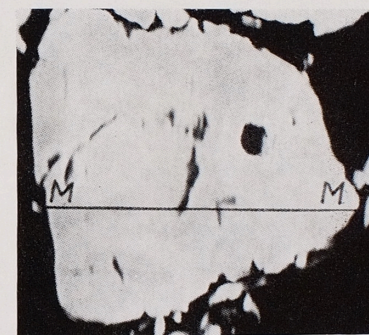
- Phot. 1. Photomicrograph. Intergrowths of two spinel phases. Darker phase — titanomagnetite, light phase — titanomaghemite, enlarged 480 ×
 Mikrofotografia. Przerosty dwóch faz spinelowych. Faza ciemniejsza — tytanomagnetyt, faza jasna — titanomaghemit. Pow. 480 ×
 Микрофотография. Прорастания двух фаз шпинелей. Темная фаза — титаномagnetит, светлая фаза — титаномеггемит. Увел. 480 ×
- Phot. 2. Grains from Phot. 1 after treatment with HCl, enlarged 290 ×
 Ziarna z fotografii 1 po trawieniu HCl. Pow. 290 ×
 Зерна с фотоснимка 1 после травления HCl. Увел. 290 ×
- Phot. 3. Absorption electron image of the grain from Phot. 1, enlarged 480 ×
 Obraz elektronowy absorpcyjny ziarna z fot. 1. Pow. 480 ×
 Электронный абсорбционный образ зерна с фотоснимка 1. Увел. 480 ×
- Phot. 4. FeK α distribution in the grain shown on Phot. 1, enlarged 480 ×
 Rozmieszczenie FeK α w ziarnie pokazanym na fot. 1. Pow. 480 ×
 Распределение FeK α в зерне, показанном на фото 1. Увел. 480 ×
- Phot. 5. TiK α distribution in the grain shown on Phot. 1, enlarged 480 ×
 Rozmieszczenie TiK α w ziarnie pokazanym na fot. 1. Pow. 480 ×
 Распределение TiK α в зерне, показанном на фото 1. Увел. 480 ×
- Phot. 6. Photomicrograph. Darker phase — titanomagnetite, lighter phase — titanomaghemite, enlarged 400 ×
 Mikrofotografia. Faza ciemniejsza — tytanomagnetyt, faza jaśniejsza — titanomaghemit. Pow. 400 ×
 Микрофотография. Темная фаза — титаномagnetит, светлая фаза — титаномеггемит. Увел. 400 ×



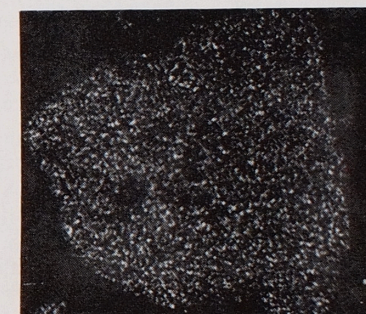
Phot. 1



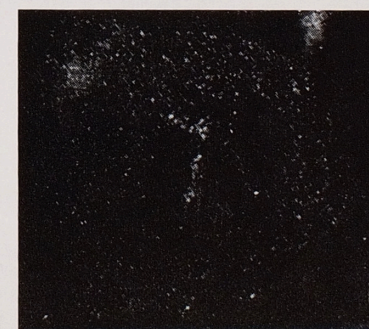
Phot. 2



Phot. 3



Phot. 4



Phot. 5

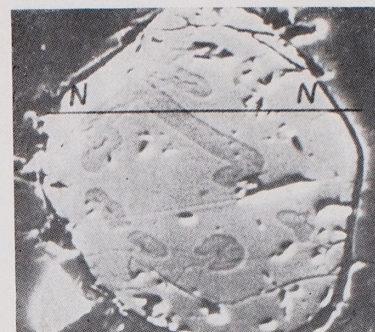


Phot. 6

Maria HUBICKA-PTASIŃSKA — Fe—Ti oxide minerals in andesite from the Wzar Mountain (Pieniny Mts.)

PLATE II (PLANSZA II, ТАБЛИЦА II)

- Phot. 7. Absorption electron image of the grain from Phot. 6, enlarged 400 ×
 Obraz elektronowy absorpcyjny ziarna z fot. 6. Pow. 400 ×
 Электронный абсорбционный образ зерна с фото 6. Увел. 400 ×
- Phot. 8. Reflected electron image of the grain from Phot. 6, enlarged 400 ×
 Obraz elektronowy odbiciowy ziarna z fot. 6. Pow. 400 ×
 Электронный отраженный образ зерна с фото 6. Увел. 400 ×
- Phot. 9. FeK_α distribution in the grain shown on Phot. 6, enlarged 400 ×
 Rozmieszczenie FeK_α w ziarnie pokazanym na fot. 6. Pow. 400 ×
 Распределение FeK_α в зерне, показанном на фото 6. Увел. 400 ×
- Phot. 10. TiK_α distribution in the grain shown on Phot. 6, enlarged 400 ×
 Rozmieszczenie TiK_α w ziarnie pokazanym na fot. 6. Pow. 400 ×
 Распределение TiK_α в зерне, показанном на фото 6. Увел. 400 ×
- Phot. 11. Absorption electron image of the grain fragment from Phot. 6, enlarged 1200 ×
 Obraz elektronowy absorpcyjny fragmentu ziarna z fot. 6. Pow. 1200 ×
 Электронный абсорбционный образ фрагмента зерна, показанного на фото 6. Увел. 1200 ×
- Phot. 12. TiK_α distribution in the grain fragment shown on Phot. 6 and 11, enlarged 1200 ×
 Rozmieszczenie TiK_α dla fragmentu ziarna przedstawionego na fot. 6 i 11. Pow. 1200 ×
 Распределение TiK_α во фрагменте зерна, показанного на фото 11. Увел. 1200 ×



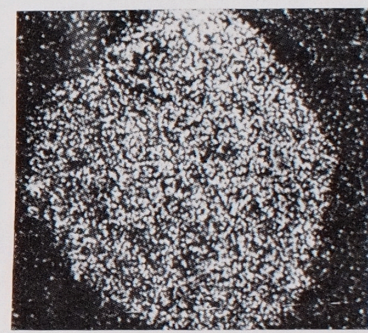
Phot. 7



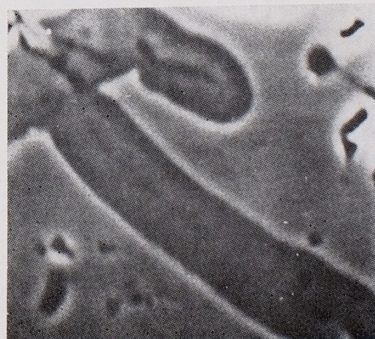
Phot. 8



Phot. 9



Phot. 10



Phot. 11



Phot. 12

Maria HUBICKA-PTASIŃSKA — Fe—Ti oxide minerals in andesite from the Wzar Mountain (Pieniny Mts.)