

CONTRIBUTION TO THE KNOWLEDGE OF THE MAGNETITE-HEMATITE SYSTEM OF OXYVOLCANITES

by

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INTRODUCTION

In an area of Tertiary volcanism volatile-rich hypomagmatites with crystallization temperatures ranging from 1200°C to 50°C often exhibit various degrees of alteration. These rocks are primarily characterized by volatile-rich minerals of low temperature of formation. One type of these altered rocks is represented by oxyandesites, whose characteristics were described — after SZÁDECZKY-KARDOSS [1958] — by G. PANTÓ [1961]. They are red to red-brown and always connected with an oxidative environment of formation.

In oxyvolcanic masses they are confined to rather narrow zones or bands, though they can be found in the surroundings of volcanic vents too. The unconsolidated porous rock often contains minute hematite platelets of red stain, sometimes visible to the naked eye. The single common feature of these two different types of rock is their colour, as, on the one hand, the hematite occurring in volcanic masses was formed at a high temperature; on the other hand, in the surroundings of volcanic vents hematite may be formed under the influence of volatiles.

It is well-known that whereas in igneous rocks $Fe^{2+} > Fe^{3+}$, in oxyvolcanites an inverse ratio is the case, these rocks being characterized by a higher degree of oxidation. As pointed out earlier [1961, 1964], it would be, however, inadequate to specify a rock merely by its oxidation value. In a study of the possible formation mechanism of oxyvolcanites, SZÁDECZKY-KARDOSS [1953, 1958] concluded that in the case of orthovolcanites at increasing values of the oxidation-reduction potential, first opacitization would take place and thereafter, at higher values, oxyvolcanites would be formed. In the case of metavolcanites the pH value of the solutions also influences rock alteration. As to the oxyvolcanites, there it is after all the magnetite content of the rock that changes into hematite representing a higher degree of oxidation, being responsible, itself, for the highly characteristic red to red-brown stain of the rock.

THE MAGNETITE-MAGHEMITE-HEMATITE SYSTEM

Magnetite and hematite are common accessory minerals of igneous rocks. For this very reason, several workers subjected them to special analysis. Primary hematite only occurs in acid, supersaturated, igneous rocks, being represented chiefly as inclusions in quartz and feldspar as well as in the porous rock of the neighbourhood of volcanic vents. Magnetite, in turn, is common in all types of igneous rocks.

RAMDOHR [1926] found that between Fe_2O_3 and Fe_3O_4 there is an interval of immiscibility, and also that mixing would take place at a high temperature only. At low temperatures the natural magnetite forms, in a great many of cases, a mechanical mixture with hematite, a phenomenon observable under the microscope, but evident from analyses as well.

In the Fe_3O_4 - FeTiO_3 system the formation temperature of magnetite provides a wide scope for mixing. If in the case of crystalline mixtures of titanomagnetite the melt — the magma — cools quickly, no dissociation will take place. On slow cooling, however, titanomagnetite will dissociate into magnetite and ilmenite and the two minerals will be completely interlaced. Relying on the products of natural dissociation, we may conclude that the beginning of the process is somewhere about the values of 600° and 700°C [1962, 1967].

In the Fe_2O_3 - FeTiO_3 system of igneous rocks mixing at high temperatures is unlimited. At rapid cooling the mix-crystals are preserved here too, whereas low cooling is associated with dissociation, just as was the case with the former system, but the process is markedly slower compared to titanomagnetite.

GRUNER [1926, 1962] studied magnetites from various localities. He could find no essential difference between the particular types. As believed by him, subaerial magnetite at 150° to 200°C slowly oxidized into hematite and oxidation begins on the (111) faces like in the case of natural martites, above 530°C it changes, however, into another modification. He found the X-ray patterns of martite and hematite identical, but they could always be distinguished from those of magnetite. According to GRUNER, on octahedral faces oxygen can enter the magnetite lattice.

MASON [1943] points out that although numerous varieties of Fe_2O_3 have been described, only two forms of this compound — γ - Fe_2O_3 or maghemite and α - Fe_2O_3 or hematite — are stable in nature, the latter being so at any temperature. Since the alteration of γ - Fe_2O_3 into modification α under natural conditions is a slow process, it occurs even in the nature. The natural formation of maghemite takes place in the zone of oxidation. Although its presence in effusive rocks has also been shown, the influence of thermal water or other agents has always been felt in such cases. Maghemite reacts keenly on metamorphic processes, so its occurrence in older deposits is improbable.

In connection with the relation of martite and maghemite, it should be noted that the original martite is a post-magnetite pseudomorph occurring exclusively in the oxidation zone, being confined to definite crystallographic orientations. On the other hand, maghemitic alteration is controlled by thermal action and independent of crystallographic orientations. Accordingly, martitization and maghemitization are the results of two different genetic processes.

In the typical spinel structure the O^{2-} ions form a face-centered lattice. The cations occupy octahedral and tetrahedral positions between the O^{2-} ions. In the lattice of magnetite one and the same chemical element, iron, occurs in two different positions, thus representing one of the types of the inverse spinel structure. In the

FeO lattice of rock salt-type not all the cationic positions are filled, i. e. the amount of Fe is smaller than would be required by the stoichiometric ratio. The edge of the unit cell of magnetite is of 8,30 Å and includes 32 O²⁻ ions. The number of the Fe²⁺ positions ought to have the same value. Since, however, there is always a shortage of Fe²⁺ and a part of Fe²⁺ changes into Fe³⁺, the iron ions in the cell occupy but a total of 24 positions, of which 8 are Fe²⁺ ions and 16 are Fe³⁺ ions. If the number of iron ions goes on decreasing to 21 1/3 positions, the structure of γ -Fe₂O₃ will result. Thus the increasing subtraction — induced lattice failure — will give rise to an increase of the oxidation value.

Earlier DT analyses — known both from literature and our own experience — have unanimously shown [1952, 1957] the existence of well-definable inversion points. Two definite peaks appear — one between 360° and 375°C and one at 580°C. The synthetic magnetites have behaved similarly; the first peak would represent an initial oxidation, the second exothermic one the point of inversion of modification γ - to modification α .

In studying the DTA graph of a natural magnetite from Mineville, LEPP [1957, 1962] also observed two exothermic peaks, but these appeared at 430° and 500°C. The composition of the original substance was close to the ideal one: the Fe₂O₃:Fe₃O₄ ratio was 34 to 66% in a sample heat-treated at 430°C and 45 to 55% at 500°. While analysing X-ray patterns LEPP could observe only the strongest hematite lines beside the lines of magnetite.

Examination of the DTA patterns of magnetites of different genesis permitted to observe that in the case of titanomagnetites (Szarvaskő) the peaks were very indistinct, while for contact-pneumatolitic magnetites (Magyaregry, Vaskő) very distinct exothermic peaks were obtained at 400°C and 600°C (Fig. 1).

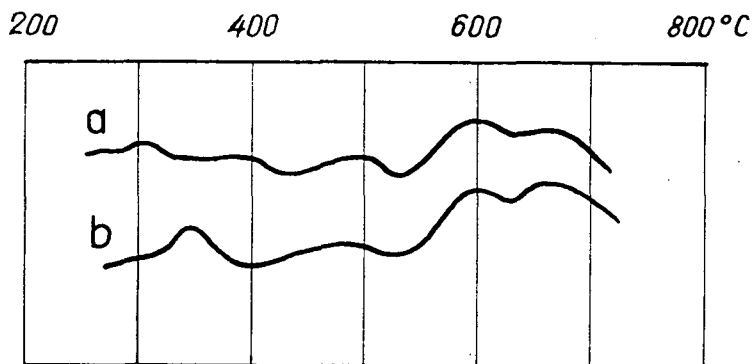


Fig. 1. DTA curves of magnetite samples from a) Magyaregry, b) Vaskő (Ocna de Fer)

For the hematites — both the contact-pneumatolitic type (Elba) and the exhalative one (Kakukhegy) — again, distinct peaks were obtained, at 400° and 580°C respectively (for the exhalative type at 400°, 500°, and 600°). Since these minerals always contain some magnetite in form of solid solution, as shown by analyses and observations under the microscope, the aforementioned peaks are likely to represent points of inversion of γ to α (Fig 2). The inversion temperatures

are influenced by the genetic characteristics of the mineral, its impurity, and grain-size.

Consequently, upon changes in temperature the magnetite reacts with changes in structure. As shown by the investigations of HUGGETT and CHAUDRON [1928],

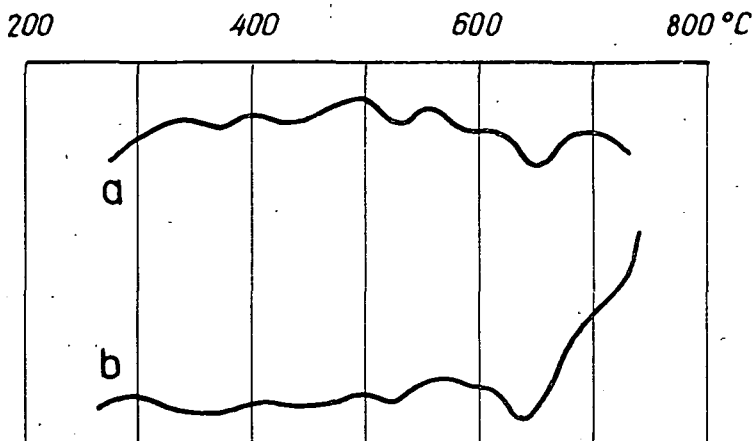


Fig. 2. DTA curves of hematite samples from a) Island of Elba, b) Kakukhegy (Mt. Cucu)

the susceptibility of magnetite also changes as a function of temperature. In fact a significant change is observed at 570°C — the temperature at which $\gamma\text{-Fe}_2\text{O}_3$ changes into $\alpha\text{-Fe}_2\text{O}_3$.

As stated by TWENHOFEL [1927], the „oxidized magnetite” is of magnetic nature of Fe_2O_3 composition, and it appears, upon oxidation and heating, as an intermediary product between magnetite and hematite. TWENHOFEL believes that the X-ray patterns of both „oxidized magnetite” and magnetite are identical, despite four oxygen atoms have entered the unit cell.

The lattice of hematite is a typical corundum lattice which can be conceived as a rhombohedrally deformed rock salt structure. Accordingly, between magnetite and hematite lattices there is such a marked similarity that the threefold axis of magnetite will become the main axis for hematite.

For the oxidation of magnetite, PAULING and HENDRICKS admitted a volume increase of 5,2%, while the value inferred from density by HISE was as low as 2,5%.

In volcanic tuffs magnetite is often associated with limonite and/or goethite. Since, these too, may undergo oxy-changes, their behaviour upon changes in temperature should also be taken into consideration. Lepidocrocite can only be formed at pH ranging from 2 to 6, thus being uncommon. Limonite and/or goethite undergo gradual changes upon an increase in temperature. After dehydration maghemite and, finally, hematite will result, the process of alteration thus corresponds, after all, to a dehydration or oxidation series, respectively. The effusion of lava on tuffs in volcanic areas is common. The temperature of the lava is higher than the temperature of $\gamma \rightarrow \alpha$ -hematite inversion. So the development and occurrence of oxyvolcanite is granted here too.

EXPERIMENTAL RESULTS

For studying the alteration suit of magnetite-maghemite-hematite — or that of magnetite-hematite in the oxyvolcanites — first of all the X-ray diffraction analysis of magnetites and hematites of different genesis was performed. The samples from Magyaregregy (1) and Vaskő (2) represented contact-pneumatolitic magnetite, those of Kiruna the ore-forming magma (3); while the magnetites of Szarvaskő were titanium-bearing (4).

The X-ray diffraction patterns were obtained at Fe $K\alpha$ radiation with an Mn filter, at 30 kV and 10 mA.

What was analysed was the fraction <0.06 mm of the pure material selected, from the individual samples.

The values obtained for the pure substances are given in Table I.

Accordingly, in the above samples the characteristic values of d_{hkl} , 311, 511, 220 and 440, did exist. The lattice planes (111) parallel to the octahedral face

Table I

1			2			3			4		
<i>d</i>	<i>hkl</i>	<i>I</i>	<i>d</i>	<i>hkl</i>	<i>I</i>	<i>d</i>	<i>hkl</i>	<i>I</i>	<i>d</i>	<i>hkl</i>	<i>I</i>
									5.142	olivine 021	1.5
4.803	111	1	4.834	111	1	4.845 4.286	111 200	2.5 5	4.848	111	1
									3.912 3.740	olivine ilm. 102	1.5 3
3.246		1				3.269 3.124		2 2	3.273 3.133	amf.? amf.?	1.5 10
2.973 2.784	220 300; 221	3 2	2.965	220	6	2.973 2.796	220 300; 221	8 6.5	2.796	300; 221	7
									2.745	ilm. 104	2
2.521	311	10	2.526	311	10	2.532	311	10	2.532 2.476	311 ol.	10 4
2.413 2.303	222 320?	1 1	2.408	222	1	2.422 2.319	222 320	1 3	2.292	320?	7
			2.197 2.094	321 400	2 4	2.094 1.886	400 420	6 1	1.900 1.821	420 ilm. 204	1 1
1.777	322?	1				1.780	322?	2			
1.711	422	2	1.711	422	2	1.711	422	3.5	1.758 1.722	amf.? 422 ilm. 116	1 3
1.631	431; 510	2				1.634	431; 510	2	1.650		2
1.609	333; 511	5	1.611	333; 511	5	1.614	333; 511	8			
									1.498	ilm. 214	10
1.484	440	7	1.483	440	4	1.484	440	8,5	1.493	440?	5

were, as a rule, poorly represented. In the titanomagnetite of Szarvaskő, along with the strongest line, 2.53, representing magnetite, the ilmenite was also represented by a distinct line ($d=1.498$).

The X-ray diffraction values obtained for these same samples, after temperation at 400°C for 20 hours, were as follows (Table II).

Table II

1			2			3			4		
<i>d</i>	<i>hkl</i>	<i>I</i>	<i>d</i>	<i>hkl</i>	<i>I</i>	<i>d</i>	<i>hkl</i>	<i>I</i>	<i>d</i>	<i>hkl</i>	<i>I</i>
			4.834	111	2	2.834	111	1 ¹ / ₂	4.724	111	2
			3.905		1	3.827		1/2	4.599		1
3.680?		1	3.676		1				3.946		4
									3.765	ilm.	2
			3.255		1	3.555		1/2	3.533		1
3.031		2				3.201		1/2	3.261		1
2.958	220	4	2.973	220	5	2.970	220	3	3.003		2
			2.784	300	1	2.787	300	1/2	2.958	220	1
									2.885		10
									2.800	ilm.	10
									2.751	204 amf.?	8
2.695		3	2.701		3	2.695		2			
2.519	311	10	2.529	311	10	2.524	311	10	2.534	311	2
			2.430		1	2.422		1	2.480		2
			2.315		1	2.307		1/2	2.282		8
			2.099	400	2	2.096	400	3	2.168		1
2.091	400	2							2.015		1
1.924		1							1.924		1
1.916		1							1.901	420	6
			1.840	420	2				1.866		3
									1.840	204	2
									1.788	amf.	4
									1.723	ilm.	2
									116		
1.693		1	1.694	422	1	1.692	422	1/2			
1.612	333; 115	2				1.615	511; 333	4	1.632	431; 510	1
1.484	440	4	1.595		5	1.483	440	3			
			1.485	440	5						
1.455		1	1.455		1	1.452		1/2	1.467	440	1
1.445		1	1.423		1	1.448		1/2	1.442		1

Upon heating, the samples showed no change in colour. No substantial changes in the characteristic d_{hkl} values could be observed. The only sample in which (111) $d=4.83$ failed to occur was that of Magyaregregy, while in the rest of the samples even the intensity has remained unchanged. The characteristic $d=2.52$ (311) has been preserved with invariable intensity. In the samples from Vaskő, Magyaregregy, and Kiruna a mean intensity of $d=1.48$ was also characteristic. These characteristics were somewhat less marked (400). Though of lower intensity, (220) ($d=2.97$) has also been preserved. As for $d=1.61$ (511 ; 333), it lacks completely in the Vaskő sample, being represented with a lower intensity in the rest of the samples as well.

In the case of the titanomagnetite of Szarvaskő the heated samples locally showed a rather marked presence of ilmenite; at the same time, the lattice plane

characterized by $d = 1.478$ and by an index of 214 disappeared in the heated sample, although it had been represented with an intensity amounting to 10 in the original sample.

Thus, we may conclude that upon a long-lasting heat-treatment at 400°C no substantial structural change takes place.

Of the maghemite values quoted in literature, the lattice planes parallel to hexahedral, rhombododekahedral, and deltoidikositetrahedral faces are characteristic. These did exist here: $d_{hkl} = 440, 400, 311, 511$. As for $\gamma\text{-Fe}_2\text{O}_3$, it has a lattice similar to that of magnetite, except for its deficiency of iron.

During the 10-hour heat-treatment of these samples at 600°C the following striking changes in colour were observed; dark-red, brownish-red. The changes in the value of oxidation thus could be observed. The scratch of samples like these was also found to be red, a phenomenon typical of hematite. The X-ray diffraction values of the samples are given in Table III.

Table III

1			2			3			4		
d	hkl	I	d	hkl	I	d	hkl	I	d	hkl	I
									10.008		2
									9.417		2
			4.803		1.5	5.361		2.5			
						4.823		1	4.855		1
3.687	$01\bar{1}2$	1				4.215		1			
									4.066		1.5
						3.555		1	3.692	$\bar{1}2\bar{1}3$	6
3.270		1							3.339		1.5
						3.228		5			
						3.079		4	3.113	1	
2.973	211	4	2.960	211	3.5				2.977	211	5
2.790		4	2.773		1	2.773	ilm.	1	2.787		1.5
2.705	$10\bar{1}4$	5	2.677	$10\bar{1}4$	2	2.677	$10\bar{1}4$	1	2.707	$10\bar{1}4$	10
									2.540	ilm.	7
2.528	$11\bar{2}0$	10	2.513	$11\bar{2}0$	10	2.519	$11\bar{2}0$	4	2.521	$11\bar{2}0$	7
									2.485		1
2.312		1									
						2.214	$11\bar{2}3$	1	2.208	$11\bar{2}3$	3
						2.137		4			
2.092		4	2.086		6				2.101		1
									2.032		1.5
1.842		1				1.931		1	1.840		4
						1.814		1			
						1.794		1	1.793		1
						1.753		5	1.764		1.5
									1.714		1
1.696	$11\bar{2}6$	1.5	1.708	$11\bar{2}6$	1.5	1.681	$11\bar{2}6$	2	1.695	$11\bar{2}6$	5
1.634	$21\bar{3}1$	1				1.648	$21\bar{3}1$	10	1.637	$21\bar{3}1$	1.5
1.609	$01\bar{1}8$	2	1.609	$01\bar{1}8$	4	1.620		1	1.613	$01\bar{1}8$	1
										$12\bar{3}2$	
1.481	$21\bar{3}4$	4	1.483	$21\bar{3}4$	4				1.489	$21\bar{3}4$	4
1.448	$30\bar{3}0$	2		$30\bar{3}0$					1.453	$30\bar{3}0$	2

Considering the values quoted in literature with reference to hematite, these readily correspond to the values obtained here. The characteristic lattice planes indexed $10\bar{1}4$, $11\bar{2}0$, $21\bar{3}4$, and $30\bar{3}0$ are encountered here too. For the Szarvaskő sample, the characteristics of ilmenite can be found associated with those of hematite. In this sample we have to reckon with residues of magnetite — as shown even by the ore microscope — which may be accounted for by the fact that MgO hinders $\gamma \rightarrow \alpha$ alteration. By the way, the presence of magnetite in these rocks should be allowed for even on the basis of the olivine content of the country rock. This is warranted by analyses. Although ilmenite and hematite are similar structures and though Fe and Ti ions of regular distribution occur in ilmenite, the patterns of the two minerals can be readily distinguished from one another.

The X-ray analyses of the magnetite — $\gamma\text{-Fe}_2\text{O}_3$ — $\alpha\text{-Fe}_2\text{O}_3$ series led BASTA [1959] to the conclusion that the calculated lattice constant gradually decreased with increasing temperature, to turn again into an increases above the inversion point of modification α . This fact proved true for the investigations under consideration.

As shown by the results of investigations, modification $\alpha\text{-Fe}_2\text{O}_3$ is usually stable above 600°C . For this reason, X-ray patterns as bases of comparison were also obtained for a few samples of pure hematite. So the contact-pneumatolitic type has been confronted with a sample of Elba (1), the exhalative type with one from Kakukhegy (2), and the sedimentary type with the red ochre of Podagrec (3). These data are given in Table IV.

Table IV

1				2				3			
<i>d</i>	<i>hkl</i>	<i>hkil</i>	<i>I</i>	<i>d</i>	<i>hkl</i>	<i>hkil</i>	<i>I</i>	<i>d</i>	<i>hkl</i>	<i>hkil</i>	<i>I</i>
				4.302			1				
4.028	110	01 $\bar{1}$ 2	1	4.007	110	01 $\bar{1}$ 2	2.5				
3.652	101	1 $\bar{1}$ 02	6	3.640	101	1 $\bar{1}$ 02	8	3.699	101	1 $\bar{1}$ 02	2
2.955	112	01 $\bar{1}$ 4	3	2.948	112	01 $\bar{1}$ 4	2				
2.757	101	11 $\bar{2}$ 0	1.5	2.751	101	11 $\bar{2}$ 0	1				
2.682	211	10 $\bar{1}$ 4	10	2.674	211	10 $\bar{1}$ 4	10	2.699	211	10 $\bar{1}$ 4	9
2.503	101	11 $\bar{2}$ 0	8.5	2.503	101	11 $\bar{2}$ 0	7.5	2.508	101	11 $\bar{2}$ 0	10
2.422	102	1 $\bar{2}$ 1 $\bar{3}$	1	2.417	102	1 $\bar{2}$ 1 $\bar{3}$	1				
2.192	210	11 $\bar{2}$ 3	2	2.191	210	11 $\bar{2}$ 3	2.5	2.204	210	11 $\bar{2}$ 3	2
				2.065	200	20 $\bar{2}$ 2	1				
2.015	202	2 $\bar{2}$ 04	1.5	2.015	202	2 $\bar{2}$ 04	1				
1.859	123	11 $\bar{2}$ 0	1	1.857	123	11 $\bar{2}$ 6	1	1.845	123	11 $\bar{2}$ 6	2
1.832	220	02 $\bar{2}$ 4	8.5	1.832	220	02 $\bar{2}$ 4	4				
1.726			5								
1.687	321	11 $\bar{2}$ 6	1	1.687	321	11 $\bar{2}$ 6	4	1.692	321	11 $\bar{2}$ 6	4
1.631	201	21 $\bar{3}$ 1	1.5	1.634	201	21 $\bar{3}$ 1	1	1.644	210	21 $\bar{3}$ 1	5
				1.628			1				
1.593	233	10 $\bar{1}$ 8	2	1.594	233	10 $\bar{1}$ 8	3	1.598	233	10 $\bar{1}$ 8	1
		01 $\bar{1}$ 4				01 $\bar{1}$ 4				01 $\bar{1}$ 4	
1.566			1								
1.539			5					1.525			1
								1.500			1
1.479	310	21 $\bar{3}$ 4	6	1.483	310	21 $\bar{3}$ 4	3	1.483	310	21 $\bar{3}$ 4	1
								1.475			1
1.451	331	02 $\bar{2}$ 7	1	1.451	331	02 $\bar{2}$ 7	8	1.452			1
	211	30 $\bar{3}$ 0			211	30 $\bar{3}$ 0					

The data correspond well to those magnetite held at 600°, consequently, the change of magnetite into hematite takes place after a comparatively short heat treatment. This means that even the heat of a volcanic lava may provoke the formation of oxyvolcanites. In the hematites of volcanic origin the prevalence of completely flat rhombohedral lattice planes is quite distinct, as opposed to the case of the Elba and Podagrec types where these are manifested by poor intensities.

Upon heating, changes in the degree of oxidation take place in other iron compounds liable to breakdown too. From this point of view the study of siderite was carried out.

The thermal dissociation of siderite takes place between 500° and 600°, in dependence on the size of the crystal grains, on the one hand, and on the presence of Mn²⁺ and Mg²⁺ ions, on the other. After the siderite has broken down into FeO and CO₂, an exothermal process will lead to the oxidation of FeO to Fe₂O₃. In Table V the X-ray diffraction values obtained for a fresh siderite sample from Rudnany (1) and for the same siderite after a 10-hour treatment at 700° (2) are given.

Table V

1			2		
<i>d</i>	<i>hkl</i>	<i>I</i>	<i>d</i>	<i>hkl</i>	<i>I</i>
4.155		1			
3.905		1			
3.589	10 $\bar{1}$ 2	3	3.676	01 $\bar{1}$ 2	3
3.078		3			
2.787	10 $\bar{1}$ 4	10	2.965		2
			2.692	10 $\bar{1}$ 4	10
			2.519	11 $\bar{2}$ 0	6
2.339	11 $\bar{2}$ 0	2	2.202	11 $\bar{2}$ 3	2
			2.189		1.5
2.154	11 $\bar{2}$ 3	1/2			
2.123		1	2.096	20 $\bar{2}$ 2	1
1.950	20 $\bar{2}$ 2	6			
1.903		1/2			
1.891		1/2	1.838	02 $\bar{2}$ 4	3
1.758		2			
1.718	11 $\bar{2}$ 6	3	1.694	11 $\bar{2}$ 6	3
			1.616	21 $\bar{3}$ 1	1
			1.597	12 $\bar{3}$ 2; 01 $\bar{1}$ 8	1
			1.485	21 $\bar{3}$ 4	3
			1.453	02 $\bar{2}$ 7; 30 $\bar{3}$ 0	2

As evident from the tabulation, after heating siderite lost all its original characteristics; on the other hand, the characteristic *d* values of hematite, 2.69, 3.67, 2.51, 1.48, 1.45, did appear, while none of the lines of siderite was preserved, despite the presence of identical crystal classes.

Since in volcanic rocks too it is the magnetite of lava rocks, and the magnetite or limonite and goethite of volcanic tuffs that is altered under oxidative conditions

on the surface or close to it, magnetite separated from ground pyroxenic andesite samples of 0.06 mm grain size by using a magnet tool was also studied. The X-ray patterns obtained for these samples and for those heated to 600°C permitted to evaluate the process of magnetite-hematite alteration. In oxy-tuffs similarly the presence of hematite could be shown.

CONCLUSIONS

It can be stated that the red stain of volcanic rocks is always due to the presence of hematite. In the surroundings of volcanic vents or along cracks, where the escape of iron chloride and vapour can be allowed for, hematite may form even primarily. Such a rock is usually porous, and of red stain. Another mechanism of the red stain of volcanic rocks consists in that a lava of high temperature flows over an earlier volcanic rock and a red, so-called oxyvolcanite band varying in thickness in dependence on the volume of the lava is formed at the contact of the two rocks. If the lava flows over volcanic tuffs, the escaping vapour will produce a vesicular, scoriaceous rock — similarly red because of secondary hematite — on the boundary of the two rocks. Since the pressure is comparatively higher here because of the vapour formed in the rock, this condition is favourable for the development of modification α which is already stable in contrast with γ -Fe₂O₃. The transformation of $\gamma \rightarrow \alpha$ represents, at the same time, a monotropic polymorphy, as α -Fe₂O₃ does not regenerate to modification γ . This type of alteration also takes place under natural conditions on the surface, but this is extremely slow process, so that modifications γ and α may occur together.

Since primary hematite as an accessory mineral can only occur in igneous rocks abundant in silica, the total hematite content of oxyvolcanites and volcanic tuffs should be regarded as secondary.

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