AN ORE-GENETICAL STUDY OF PYRRHOTITE FROM MT. CSÁKÁNYKŐ

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INTRODUCTION

Several years ago, in the pyroxenic andesite quarry of Mt. Csákánykő, Mátra Mountains, North Hungary, inclusion-like nests of pyrrhotite, attaining even 4—5 cm in diametre, were found. The study of this peculiar, rather rare occurrence (with a view to the geological and petrographical conditions of the region) was a tentative for settling the problem of the genesis of these interesting minerals and of their eventual connection with the other ore mineralizations of the region.

GEOLOGICAL AND PETROGRAPHICAL CONDITIONS OF THE REGION

Belonging to the eastern part of the Mátra Mountains, Mt. Csákánykő lies at a distance of about 3 air kilometres south of Recsk. The inclusion-dotted rock was encountered during quarry operations.

In this region the most ancient rocks (red and grey limestone, clay and siliceous shale) can be referred to the Ladinian stage of the Triassic.

The diabases of the Miklós valley, which petrographically coincide with the spilitized vesicular diabases of Mt. Darnó at Sirok, are of Middle Triassic age (or possibly Cretaceous). The Oligocene is only represented by Rupelian clay-marls.

The Miocene formations are more significant in the eastern marginal zone of the Mátra Mountains. On the one hand, they are represented by sedimentary desposits (sandstone, sandy clay, schlier); on the other hand, by various volcanic rocks of considerable thickness (rhyolitic tuff, dacitic tuff, andesitic tuff, and pyroxenic andesite).

The phytofossiliferous sandstones, referred to the Aquitanian or Burdigalian stages, are overlain by variegated clays and conglomerates. Finally, the Burdigalian ends with the so-called Lower Rhyolite Tuffs.

The volcanic complex, making up the Mátra Mountains, was formed in Late Helvetian and Tortonian times. Initially, eruptions of andesitic, dacitic, and rhyolitic tuffs took place and after that the andesite mantle dikes were formed. As suggested by I. Kubovics [1963], the chronological order of the eruptions of the Helveto—Tortonian volcanic complex was the following:

TABLE 1

Chronological Order of Helveto-Tortonian Eruptions

Serial number	Formation	Stage
1.	Andesite mantle and dikes	
2.	Middle Andesite Tuff II Biotitic Dacitic Tuff Middle Andesite Tuff I	Tortonian
3.	Middle Rhyolite Tuff	
4.	Lower Andesite Tuff	Helvetian

The latest volcanic products and the andesite dikes of funnel or broadening laccolith shape show hardly any difference in mineralogical composition. The main
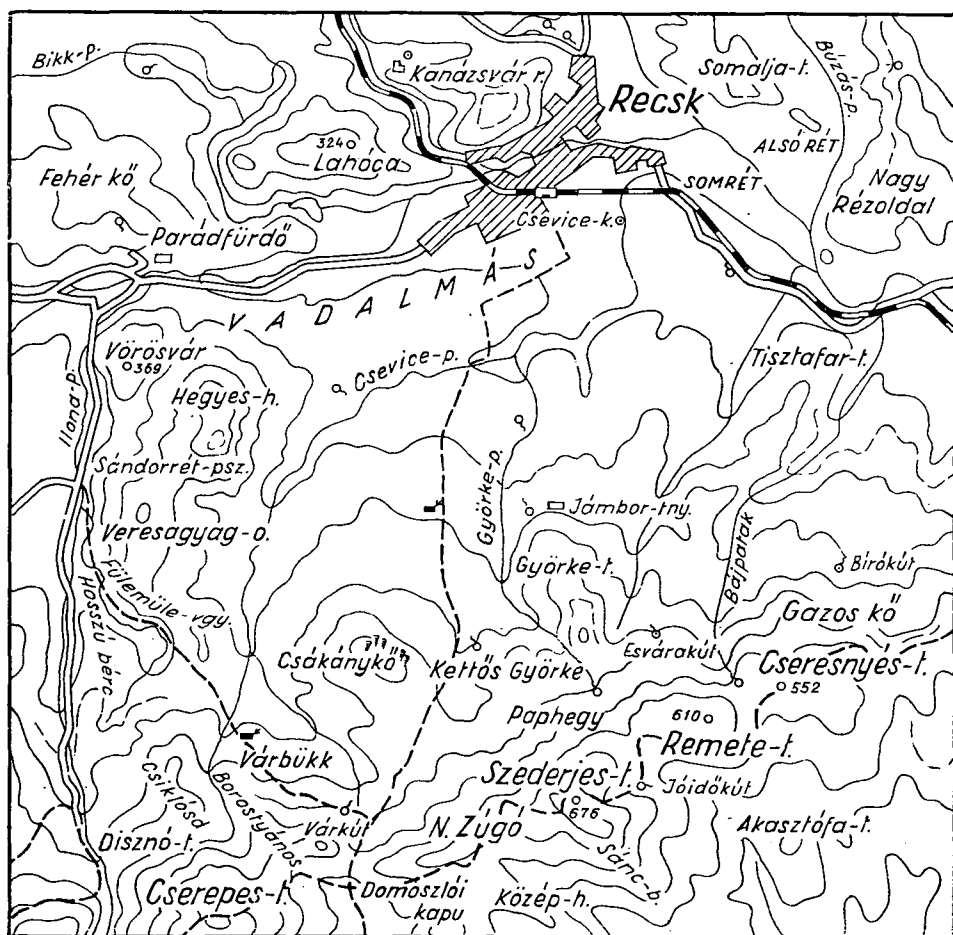

Fig. 1. Map scheme of environs of Csákánykő

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difference between the two kinds of rock is in their texture: the degree of crystallization of the matrix. Geologically and petrographically, the andesite dikes can be included in two groups: the Györke dikes and the Farkashegy dikes. The first group is characterized by a development at subvolcanic depth. As for mineralogical composition, the Györke dikes are of carbonate character, whereas this cannot be observed either in the Farkashegy dikes or in the rock of the andesite mantle.

The Csákánykő andesite belongs to the Györke dikes, its carbonate content is considerable (3—5% on the average). The more so, large cavities or pockets (nests), containing crystallized carbonate minerals, are also frequent. As shown by the measurements of B. NAGY [1967], the carbonate content of the andesite is very high close to the pockets. This indicates that the carbonate-bearing pockets must have been formed by gradual saturation. According to B. NAGY [1967], the sequence of carbonate mineralization was the following: spherosiderite → siderite → ankerite → dolomite → calcite → aragonite. This succession indicates an incrase in Ca with decreasing temperature. The source for carbonatization is believed to have been provided by the melting of great amounts of carbonate rock. The Csákánykő andesite, itself, was formed in Helvetian schlier, and GY. VARGA (personal communication) found various types of foreign xenoliths in it.

The lack of carbonates in certain dikes and in the andesite mantle as well as their varying abundance in other dikes seems to be due to differences in pressure during the consolidation of the magma. A comparatively higher pressure — such as would be required for the formation of carbonates — can be supposed to have existed at the subvolcanic level only. Because of its high partial pressure, CO_2 will escape from the magma, if the pressure due to the overburden is low or zero.

Thus the carbonatization of the Csákánykő andesite suggests a consolidation under the conditions of considerable overburden pressure. Accordingly, the degree of crystallization of the matrix is high. The average size of the matrix feldspars varies between 100 and 20 μ. The mineralogical components of the andesite have shown the following percentage distribution:

Porphyric impregnation:

plagioclase	33,2%
hypersthene	10,1%
carbonate	4,3%
opaque (mainly ilmenite)	1,6%

Matrix:

plagioclase	40,5%
augite	10,3%
Total:	100,0%

Most abundant among the porphyric constituents, plagioclase is usually of labradoritic-bytownitic composition; the nucleus of the largest porphyric plagioclases is mainly bytownitic, and even a plagioclase of An = 90% composition was measured. The most common twin laws are the albite, albite-Carlsbad, and albite-Ala laws. The frequency order is only approximate.

Over the majority of plagioclases a multiple zoning can be observed.

The second, significant porphyric component is hypersthene. For the most part, it shows parallel extinction, though some zonation in inner of the crystals can also be observed. This suggests the incorporation of some Ca. The augitization of the

margin of hypersthene indicates changes which must have occurred during crystallization.

The mafic constituent of the matrix is chiefly augite-pyroxene. The carbonate inclusions appear in the form of radial nests. The nests are of completely irregular shape. In the neighbourhood of carbonates, some chalcedony also occurs. Close to the porphyric constituents, carbonate is abundant. The shape and environment of the carbonate nests allow to conclude that the carbonates have resulted from the displacement of the matrix before the rock was completely consolidated. The Ca of the displaced matrix feldspars was bound as $CaCO_3$. Thus the alkali content of the feldspar laths relatively increased, i. e. their composition was shifted toward albite. With increasing alteration, the feldspar was completely decomposed, and chalcedony precipitated. A comparatively higher volatile content may considerably decrease the final temperature of consolidation of the rock. For this reason, the carbonatization of the matrix took place as late as the hydrothermal phase. As already mentioned, the Csákánykő hypersthene andesite contains plenty of xenoliths. Of these, we have to deal with the crystalline quartz inclusions, too. The rare pyrrhotite inclusions are mostly associated with these quartz inclusions. However, both the volume and the abundance of the quartz inclusions are much greater than those of pyrrhotite. At the same time, some pyrrhotite can be observed in the andesite even independently of the quartz inclusions.

The quartz inclusions are of hypidiomorphic character, their grain size averages 0,6 to 0,3 mm. They have an elongated form, and the combination of $(10\bar{1}0)$ and $(10\bar{1}1)$ can sometimes be observed. The fine cracks of the quartz inclusions and the interstices have been filled later by carbonates. Occasionally, it can be observed that both the quartz inclusions and the adjacent andesite are traversed by a carbonate streak. This seems to suggest that while entering the magma the silica was not accompanied by carbonate, but when later the andesite was carbonatized, the solution impregnated the quartz inclusions, too. As observed by the author, on the margin of the quartz crystals (characterized, otherwise, by totally faultless optics), at their contact with the andesite, an undulated, imperfect extinction is obtained and the resolution and recrystallization of the quartz are associated phenomena. This anomalous extinction is due to crystallization-induced volume increase and to the resultant tension stresses.

The contact between the quartz inclusions and the andesite is locally sharp, in other places a wreath-shaped diopside-augite rim of 0,50 to 0,35 mm width can be observed.

The quartz and the various xenoliths derive from the basement, their source rocks being not known sufficiently as yet. All that which seems to be probable is that, on the basis of its textural and morphological characteristics, the quartz must have been formed as a low-temperature α-quartz in a late-crystallization phase of the magma. This suggestion is supported by B. Nagy's X-ray analyses, too (personal communication).

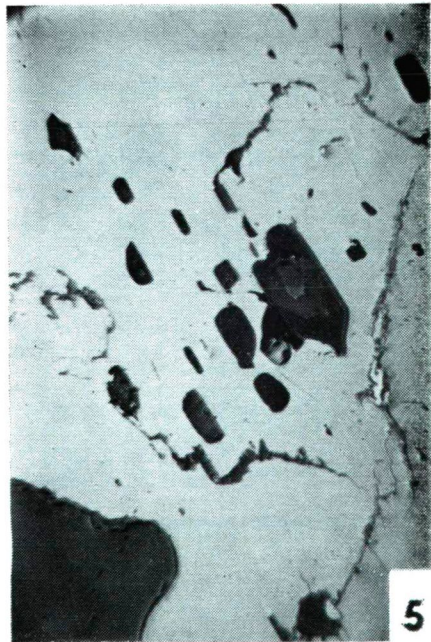*Fig. 2.* Pyrrhotite coating the porphyric feldspars.
  ‖N, ×33
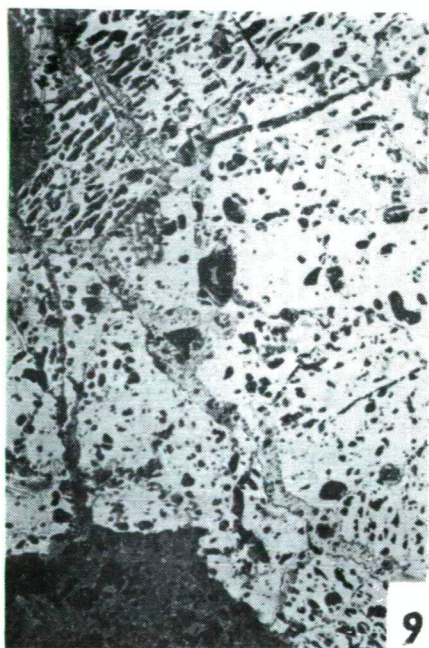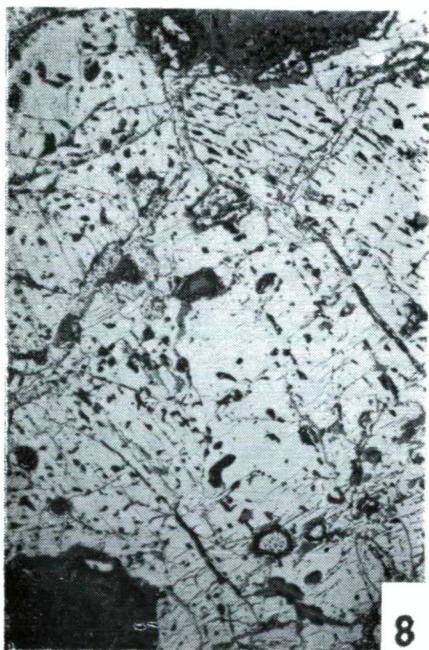*Fig. 3.* Pyrrhotite coating the porphyric feldspars.
  ‖N, ×33
Fig. 4. Quartz inclusions in pyrrhotite, ‖N, ×160
Fig. 5. Oriented quartz inclusions. ‖N, ×160

PLATE I.

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PLATE II.

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Pyrrhotite occurs in the form of minor nests, accumulations or of thin crusts, often close to — or even within — the quartz inclusions. In such cases, it appears along grain contacts or fills tiny cracks. However, it may sometimes appear in the andesite independently of the quartz inclusions. In such cases, the porphyric plagioclases of the andesite are coated by thin pyrrhotite films which have quasi protected the morphological and geometric characteristics of the crystal (Plate I, *Fig. 2, 3*).

Pyrrhotite is poorly crystallized, massive inclusion material. As already mentioned, the association of quartz inclusions and pyrrhotite is not compulsory. Hence, it is probable that there is no genetic relationship between them.

Under ore microscope, pyrrhotite is allotriomorphic, granular, sections according to the (0001) being rare. The predominant grain size is 2,5 to 0,5 mm. Its mean reflectivity corresponds to that of the Kisbánya (Gutin Mountains, Rumania) and Nagybörzsöny pyrrhotites which were examined for the sake of comparison. (Measured with a Zeiss photoelectric instrument in a green light, all three gave a value of 40%.)

Pyrrhotite may locally contain idiomorphic, elongated, prismatic quartz inclusions, some of which show a controlled orientation (Plate I, *Fig. 4, 5*). Along fissures and joints, pyrrhotite is slightly pyritized. The pyrite grains are of irregular shape; sometimes incompletely developed hexahedral faces are observable (Plate II, *Fig. 6, 7*). Pyrite is one of the ore minerals which possess the highest energy of attachment. That is why it is represented by an idiomorphic crystallization, even though belonging to the later separation.

The amount of chalcopyrite found in pyrrhotite was considerably higher than that of pyrite. On the basis of the X-ray spectroscopic results, the Cu content of the ore is estimated at about 1%. Chalcopyrite chiefly occurs at the margins of the pyrrhotite grains or in the fine cracks traversing them (Plate II, *Fig. 8, 9*). It is relatively abundant in the vicinity of idiomorphic quartz inclusions, and even in their skeleton-crystal-like cavities. It may occasionally look like a "pseudomorph" after hexagonal quartz. The chalcopyrite formed later has partly replaced the pyrrhotite and even the pyrite. At higher magnification, the isolated remnants of the displaced pyrrhotite in the chalcopyrite can be well observed (Plate III, *Fig. 10*).

In a very small amount galena is also present in the ore inclusion. Its mostly poorly developed tiny crystals occur in the chalcopyrite veinlets traversing the pyrrhotite. The centre of the veinlets is filled by the last-precipitated carbonates. The more or less circular, carbonate-filled nests and pockets in the pyrrhotite exhibit the same arrangement. The pockets are ring-like covered by a thin chalcopyrite film, and on the inner side of the ring there are one or two hexahedral crystals of galena. Finally, the centre of the pocket is filled by carbonate (Plate III, *Fig. 11, 12, 13*). The galena, occurring on the margins of the pockets, is composed of greater but fewer grains than the galena in the veinlets. In the larger crystals of galena even cleavage could be observed.

Fig. 6. Pyrite grains of irregular shape. ‖N, ×80
Fig. 7. Half-developed pyrite hexahedra. ‖N, ×80
Fig. 8. Chalcopyrite streaks between pyrrhotite grains. ‖N, ×33
Fig. 9. Chalcopyrite streaks between pyrrhotite grains. ‖N, ×33

Pyrrhotite Csákánykő		Pyrrhotite Kisbánya		Pyrrhotite ASTM/2-1341		Chalcopyrite ASTM/5-0490	
I	d_{hkl}	I	d_{hkl}	d_{hkl}	I	d_{hkl}	I
· mst	3,03	w	3,04	—	—	3,03	100
st-mst	2,97	st-mst	2,97	2,98	60	—	—
st	2,635	st	2,643	2,64	80	—	—
vw	2,442	vw	2,450	2,45	10	—	—
w	2,265	w	2,263	2,26	10	—	—
vst	2,058	vst	2,055	2,06	100	—	—
w	1,887	w	1,884	1,88	10	—	—
vw	1,868	—	—	—	—	1,865	40
st	1,719	st	1,718	1,72	70	—	—
mst	1,603	mst	1,606	1,61	40	1,591	60
vvw	1,569	—	—	—	—	1,573	20
mst-d	1,424	mst	1,425	1,43	40	—	—
mst-st	1,320	mst-st	1,320	1,32	60	1,323	10

vst: very strong
st: strong
mst: middle strong   FeKα, 40 kV, 8 mA, Exp: 5^h
w: weak
vw: very weak
d: diffuse

The paragenetic sequence of the ore mineral association of Csákánykő was the following: quartz → pyrrhotite → pyrite → chalcopyrite → galena → carbonates.

The carbonate, which was formed last, seems to be identical with the carbonate which displaced the andesite matrix. The carbonatization of the andesite must have taken place under hydrothermal conditions, in the last stage of the magmatic process. This suggestion appears to be warranted by the paragenesis.

Practically, that is all which can be deduced from the observed characteristics of the ore minerals of "transient" character.

The examination of the minor element content of pyrrhotite suggests a hydrothermal origin.

The Co content of the Csákánykő pyrrhotite is about four times greater than the Ni content. In the liquid-magmatic pyrrhotite, connected with peridotite or norite, the Ni content exceeds that of Co. The highest value of Co is 1%, whereas that of Ni may even attain 8 to 10%. Consequently, in the liquid-magmatic minerals Co is always less abundant than Ni. Thus the liquid-magmatic pyrrhotite described by S. KOCH [1955] from Szarvaskő in the Bükk Mountains and characterized by a pentlanditic intergrowth, contained 28 700 ppm Ni and only strong traces of Co.

However, hydrothermal processes may enrich the residual Co of the magma in a greater measure. That is the reason why the hydrothermal iron minerals, e. g. pyrite, are dominated by Co, while their Ni is quite poor.

Fig. 10. Chalcopyrite displacing pyrrhotite. ||N, ×315
Fig. 11. Carbonate-filled cavity with a chalcopyrite ring at its margin and with crystals of galena on the inner side of the ring. ||N, ×33
Fig. 12. Hexahedral crystals of galena among chalcopyrite and carbonate grains. ||N, ×250
Fig. 13. Pyrrhotite, chalcopyrite, and galena at the margin of a carbonate-filled cavity. ||N, ×250.

PLATE III.

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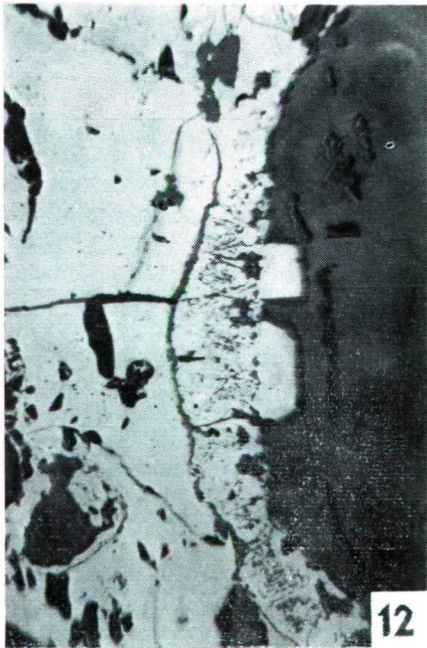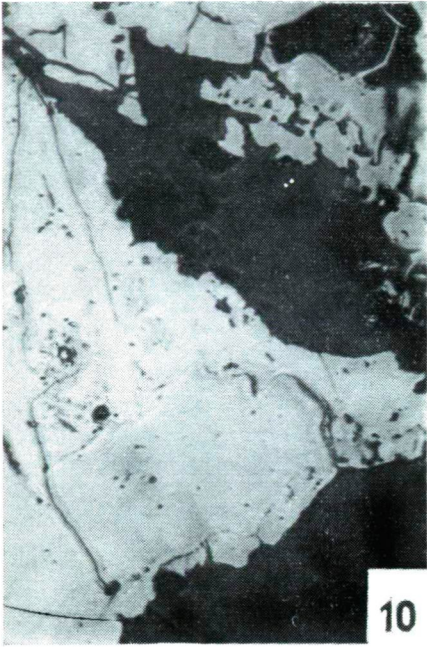
In this case too, Co seems to be camouflaged by Fe. The bivalent Ni has such a small ionic radius that it can no longer enter the pyrrhotite under hydrothermal conditions. The abundance of Ni is also insufficient, thus being indetectable by X-ray analysis in an eventual separated phase.

Platinum metals cannot be detected by conventional spectroanalytical methods. However, B. NAGY (paper presented at the ordinary session of the Mineralogical Section of the Hungarian Geological Society), who used a method of enrichment, could detect a very low Pt content.

TABLE 3

Semiquantitative results (in ppm) of the spectral analyses of pyrrhotite, quartz grains and andesite from Csákánykő

	Pyrrhotite	Quartz grains	Andesite
Ag	—	1,6	—
B	25	10	< 10
Ba	—	100	1000
Co	6000	20	60
Cr	—	6	60
Cu	1000	100	50
Ga	—	1	6
Li	< 4000	—	1600
Mn	1000	2500	1600
Ni	< 1600	16	40
Pb	—	160	25
Sr	250	1600	2500
Ti	6000	600	16000
V	—	< 2,5	250
Zn	160	160	160

The origin of the Csákánykő pyrrhotite ore inclusion is characterized by assimilation process during which the assemblage of elements has changed. In the process the high volatile content of the magma must have played a decisive role, and the volatiles may have been largely enriched by the wet sedimentary environment on which the volcanic products were deposited. Because of the abundance of volatiles, the final consolidation (crystallization) of the magma took place, as already referred to by the author, at a considerably lower temperature (hypomagmatic character). Consequently, the rock was not yet consolidated when the volatile vapours percolated it, so that the volatiles themselves could be crystallized in cavities and pockets of varying size scattered throughout the rock body. Mineralized pockets can only be formed under the effect of a corresponding counter-pressure (damping effect). Consequently, they can develop at the subvolcanic level only. The source of the Csákánykő ore mineralizations seems to have had something in common with the near-by mineralizations. The ironpoor (enargitic) mineralization of the Mt. Lahóca lies rather close to the Csákánykő exposure. It can be supposed that the inclusions of the andesite derive from the basic-igneous basement of Bükk type. It is known that near Recsk a deep-seated pyrite-chalcopyrite mineralization was disclosed by deep drilling. As believed by the author, this deep subsurface process of great importance may be connected with the ore sources from which the pyrrhotite inclusions of the Csákánykő derive.

ACKNOWLEDGEMENT

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