GEOLOGY AND ORIGIN OF THE PYROPHYLITE - DEPOSITS IN THE PÜTÜRGE MASSIF (MALATYA - EASTERN TURKEY)

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ABSTRACT.- The pyrophyllite deposits of Pütürge massif (Malatya - Eastern Turkey) have been increasingly used in last years for white cement production because of their low iron and chromium content. Around 25 pyrophyllite occurrences are explored along a nearly 15 km's long belt south of Pütürge, where 10 quarries are opened. The co-existence of high-Al pyrophyllite and kyanite indicate that the pyrophyllites were formed during a retrograde greenschist metamorphic phase, which the massif had experienced. Five different types of pyrophyllite are identified: pyrophyllite with high Al content, pyrophyllite with sericite, pyrophyllite with high silica module, pyrophyllite with low silica module and pyrophyllite with low alkaline content respectively. In this study, mineralogical and geochemical properties of these pyrophyllites are described.

Key Words: Pyrophyllite, Pütürge massif, mineralogy, genesis, geochemistry.

INTRODUCTION

The first Identification of pyrophyllite (Al₂O₃·4SiO2·H₂O) in Turkey rests up to beginning of 1970’s. As it resembles talc, pyrophyllites were mined for a while as talc in limited amounts. In 1976, pyrophyllite was mentioned in the Turkish Mining Law. Up to 1990’s the annual Production was around 2-3000 typ (tones per year) and used in refractory industry. Starting with this date it has become an important row material since ÇİMSA Cement industry Comp., has started to use pyrophyllite instead of kaolin in white cement production. Recently, it has been consumed in the rate of 100-120.000 tpy.

According to the US Geological Survey statistics (Harben, 1999), undifferentiated world talc and pyrophyllite production is about 2.2 Mt’s per year, China’s Production excluded. Turkey is one of the 10 pyrophyllite producing countries and is at the fifth rank after Japan, South Korea, Brazil and India. In Far East, rocks with mixed composition of pyrophyllite, sericite, kaolinite and quartz are termed as "roseki". However, in Brazil, the blend of pyrophyllite, sericite, diasporite, kyanite and quartz is termed as "agalmatolite". In South Africa, the mixture of pyrophyllite, chloritoid, rutile and epidote is termed as "wonderstone" (Harben, 1999).

In this study, the authors present their own data and observations on the genesis, properties and geological setting of pyrophyllite occurrences, gained during their study within last 10 years in Malatya - Pütürge region.

Evaluations are based on a Series of geochemical and mineralogical investigations in the laboratories, besides the photogeology, geological mapping and drilling with coring or by reverse circulation.
GEOLOGY AND DISTRIBUTION OF PÜTÜRGE PYROPHYLITES

Within the first investigations in the region, Danış (1978) mentioned that the pyrophyllite-bearing schists were located between quartz-sericite-schists and tourmaline-schists. Cornish (1983) reported the presence of 3 types of pyrophyllites, which were formed as a result of hydrothermal alteration of dacitic tuffs. Presence of pyrophyllite in Pütürge massif was reported by in Yazgan (1984) and in the explanations of the Malatya İ-27 sheet of 1/100.000 scaled geological map Series of Turkey (MTA, 1986) as “the pyrophyllite, kyanite, diaspore assemblage is formed within the shear-zones in tourmaline-rich orthogneisses. According to Erdem and Bingöl (1977), pyrophyllite developed along a main shear-zone between the Lower and Upper units of Pütürge massif.

The Pütürge massif, composed of augen gneisses, amphibolite - prasinite, mica schists with pelitic origin, orthogneisses and marbles, radiometric ages of 70 - 85 Ma (MTA, 1986) were obtained from the metamorphic rocks. Widespread amphibolites and augen gneisses forming the core of the massif outcrop in the area between Babik stream and Tepehan at the southern of the massif (Fig. 1). At the southern part of Pütürge where pyrophyllites are frequently observed, orthogneisses and mica schists dominate, however meta-carbonates take place mostly at the northern part of Pütürge (MTA, 1986).

The pyrophyllite occurrences in Pütürge massif are aligned along a 10 km long belt, trending about N 60° W starting from around Karataş hill at 6 Km’s SE of Pütürge at the eastern tip through south of Yıldırım hill, Keşan hill, north of Babik, Ümik hill, Şahantaşı hill, Sinik hill, Aytez hill, and Vaktık hill. To the west of Vaktık hill the belt is branched, with a southern arm following the Keşen hill, Kösemustafa hill, Hopan ridge, Çuneslu hill. The northern one follows the line of Kütüleş hill, Güreş hill, west of Tümbelek hill and east of Şiro stream. The position of the pyrophyllite occurrences and main fault systems around Pütürge are presented in figure 1. The quarries opened on these occurrences within last 10 years are as follows:

1-) Karataş hill - İmrün quarry
2-) Keşen hill
3-) Ümik hill
4-) Aytez hill
5-) 1407 m. hill
6-) West Vaktık hill
7-) East Vaktık hill
8-) Kösemustafa hill
9-) Güreş hill
10-) Mukul hill

Pyrophyllite occurrences are of lensoidal form with different sizes. At the bottom of the lenses, 2-mica orthogneisses or schists are usually observed. Schists with muscovites or sericites are observed as wall rocks. Quartzites observed together with pyrophyllites are mostly quartz-dykes. No stratigraphic relationship between these quartzites and rare tourmaline-schists with pyrophyllite could be encountered.

Although the pyrophyllite occurrences in Vaktık hill and Keşen hill are related to shear zones, there are also pyrophyllite occurrences without any relationship with tectonic zones (e.g. Ümik hill and Sinik hill). This situation relates pyrophyllite-formation with retrograde metamorphism rather than to a structural control, as it will be explained in the next chapter.
Fig. 1- Location map of the main pyrophyllite mines and occurrences in Püürüge area (Eastern Turkey).
Length of the pyrophyllite lenses reach up to 600m in Vaktık hill, and 400m's in Keşen hill and widths of the lenses range between 20 - 50 m's. Depths are around 20 - 30 m's maximum. The maximum thickness of pyrophyllites cut in bore-holes is 39 m's in Ümik hill section.

MINERALOGY AND GEOCHEMISTRY OF PYROPHYLLITE OCCURRENCES

In the pyrophyllite occurrences in Pütürge, pyrophyllite and quartz are main observed minerals. Kyanite, muscovite, sericite, illite, kaolinite, dickite and alunite are the accompanying minerals at some places. Pyrophyllite is mainly gray or greenish gray or greenish white in color and oily and dull in appearance. Its association with fine-grained quartz gives a resistant appearance to the rock.

Theoretically the $\text{Al}_2\text{O}_3$ content in pure pyrophyllite, is about 28.3%. $\text{Al}_2\text{O}_3$ contents around 30.52% from trenches of western Vaktık hill, are found out to be due to the presence of kyanite determined by microscope and XRD studies. The electron microprobe analyses have shown that the kyanites contain 60 - 62 % $\text{Al}_2\text{O}_3$ (Uygun, 1995). Our suggestion that pyrophyllites were formed by retrograde metamorphism is evidenced by the replacement of the kyanite porphyroblasts by pyrophyllite observed on the microphotograph (Fig. 2).

Pyrophyllite occurrences are usually divided into two groups (Carnish, 1983).

a- By loss of alkalies and iron of acidic volcanic rocks by the effect of hydrothermal fluids along the fault zones. The main examples to this first group are the pyrophyllites derived from porphyries and liparites in Japan, from quartz porphyry and trachyandesite in South Korea, from rhyolitic volcanics in North Carolina in USA, and from rhyolitic pyroclastics in Australia.

b- Podiform pyrophyllites of metamorphic origin where metamorphosed volcanic tuff and ashes are associated with schists, as those in Brazil.

![Fig. 2- Micrograph showing the replacement of kyanite (Di) by pyrophyllite in the sample from Vaktık hill.](image)
Especially, the presence of kyanite together with pyrophyllites is critical for the metamorphic origin of Pütürge pyrophyllites. The presence of two successive metamorphic phases in Pütürge massif, one in prograding amphibolite facies and the other one in retrograding green schist facies were reported by Yazgan (1984) and MTA (1986). So, it is interpreted that kyanite was developed from tuffs with high Al content or kaolinites in granites or their volcanic equivalents in the progressive stage and replaced by pyrophyllites in the retrograde stage.

Bucher and Frey (1994) reported that kaolinite in the temperatures above 300°C and kyanite+quartz at temperatures of 400°C and $< 4 \text{ Kbar } P_{\text{water}}$ reacts to form pyrophyllites. Association of quartz either with pyrophyllites or with kyanite, and even presence of silicarich rocks together with pyrophyllites implies that transformations in this stage were below 400°C.

On the other hand, the distribution of pyrophyllite occurrences in the massif indicates that their formation can not be simply explained by their association with shear zones, but supports our suggestion for retrograde metamorphism. Besides, pyrophyllites do not show any oriented fabrics nor foliation, which could have been the case if formed in a shear zone. Moreover, their distribution in the massif also seem not, to be restricted to the contact between the lower and upper units as proposed by Erdem and Bingöl (1997).

Muscovite and sericite as other accessory minerals observed form more prominent zones in different outcrops. For example, marginal zones with muscovite (Keşen hill quarry), and with sericite have developed (Ümik hill and 1407m. hill). In these areas, they also include illite as determined by XRD studies.

Kaolinite and dickite are comparably rare and they are most probably mineralisations developed along hyrothermally activity zones or in secondary shear zones. This kind of kaolinite alterations with small dimensions are observed within very young shear systems associated with the east Anatolian Fault passing through Şiro stream at 10 Km’s west of Puturge.

Main characteristics of the Pütürge pyrophyllites is the whiteness of their firing colour due to their iron content below % 0.2 in average. Moreover, for the importance of white cement production, chromium with values less than 100 ppm, and Mn with less 10 ppm are far below the critical limits. Measured $SO_3$ values, which are secondary in origin, reach to maximum % 4.8 in alunitisations observed in east Vaktık hill and Sınik hill quarries. $TiO_2$ present in average of % 0.5 ratio in pyrophyllites is related with minerals like rutile of sphene.

5 types of ores have been identified (Table 1) in Pütürge massif according to XRD, microscopy and XRF analysis in based on samples obtained from field work, drilling and production:
A) High Al-Pyrophyllites.- $\text{Al}_2\text{O}_3$ content in this type are above 28%. They are rich in kyanite. $\text{Al}_2\text{O}_3$ content in these ores in west Vaktık hill and in Ümik hill reaches up to 38% at some samples. Here 40% of the rock is made up of kyanite. $\text{Al}_2\text{O}_3$ contents even reaching up to 40.1% are found in core samples of Aytez hill.

B) Low silica Pyrophyllites.- $\text{Al}_2\text{O}_3$ content of this type changes between 20 - 35%. The silica module reaches to about 2.5 - 3. In these pyrophyllites, cut in limited amounts in the borings of Ümik hill, Şahantaşı hill, and 1407 m. hill, kyanite is nearly not recorded.

C) High silica Pyrophyllites.- These types are pyrophyllites are originally with quartz and have $\text{Al}_2\text{O}_3$ with values ranging between 15 - 18%. In these types of ores observed in some places such as Karataş hill-imrün quarry, Keşen hill and 1407 m. hill, silica module (SM) is observed to be around 4-5. They are ores that can be directly used in white cement production.

D) Pyrophyllites with sericites.- Pyrophyllites with sericite including some alcalies (in average 2 - 4% $\text{K}_2\text{O}$) are observed in Keşen hill quarry, Ümik hill and in 1407 m. hill. They have schistose appearance and include primary feldspars.

E) Low alkali Pyrophyllites.- This type of ores observed in eastern Vaktık hill can be differentiated from high silica pyrophyllites with their very low alkaline content (max. 0.5%).

The melting point of pyrophyllite, which is actually a refractory mineral, is given as 1200°C. In mixtures such as "algaimatolite" and "wonderstone", it is given as 1530°C and even as 1630°C. However, easy participation of Puturge pyrophyllites in reactions, in kiln temperatures are reasoned by presence of

\begin{table}
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\begin{tabular}{|c|c|c|c|c|c|}
\hline
 & TYPE-A (high Al) & TYPE-B (low silica) & TYPE-C (high silica) & TYPE-D (with sericite) & TYPE-E (low alkaline) \\
\hline
$\text{SiO}_2$ & 54.5 & 64.4 & 74.9 & 77.7 & 75.8 \\
$\text{Al}_2\text{O}_3$ & 37.9 & 25.6 & 17.4 & 15.6 & 16.2 \\
$\text{Fe}_2\text{O}_3$ & 0.4 & 0.3 & 0.2 & 0.2 & 0.2 \\
$\text{K}_2\text{O}$ & 0.5 & 0.9 & 1.1 & 2.8 & 0.3 \\
$\text{Na}_2\text{O}$ & 0.1 & 0.3 & 0.6 & 0.1 & 0.1 \\
$\text{SO}_3$ & 0.1 & 0.1 & 0.1 & 0.1 & 0.6 \\
$\text{TiO}_2$ & 0.4 & 0.5 & 0.5 & 0.6 & 0.6 \\
$\text{Cr (ppm)}$ & 100 & 120 & 58 & 55 & 69 \\
$\text{Mn (ppm)}$ & 7 & 4 & 1 & 10 & 9 \\
$\text{AK}$ & 2.6 & 4.7 & 2.7 & 3.2 & 5.0 \\
$\text{SM}$ & 1.4 & 2.5 & 4.2 & 4.9 & 4.6 \\
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\end{tabular}
\caption{Typical chemical compositions of the 5 types of pyrophyllites of Puturge massif: Type-A: Ümik hill (Drilling Nr 9), Type-B: Şahantaşı hill (Drilling Nr 5), Type-C: Keşen hill quarry production, Type-D: production of the 1407 m. hill quarry, Type-E: Eastern Vaktık hill quarry production}
\end{table}
either low temperature quartz or fluxes such as F and B. The F content of pyrophyllites used for fiberglass production is found to be around 1500 ppm, which might be controlled by coexisting apatite.

Abundance of boron in pyrophyllites associated with granitic gneisses depends on presence of tourmaline and even dumortierite (Al₇[O₃/B₇O₃/(SiO₄)₃]). This paragenesis is observed in microscopic investigations (Cemal Göncüoğlu, personal communications) of some Pütürge samples. Especially, in the Hollan dere occurrences, pyrophyllites with tourmaline are observed.

CONCLUSIONS

Around 25 pyrophyllite occurrences have been detected in a 15 km long, E-W trending belt in the Pütürge massif. The massif was subjected to two successive phases of metamorphism; an earlier progressive one within the amphibolite facies and a retrogressive one in green schist facies, respectively. Mineralogical and geochemical data indicate that originally high-alumina tuffs, clays or kaolinites gave way in the first phase to the formation of kyanite and in retrograde conditions, kyanite - pyrophyllite transformations were realized.

The Pütürge pyrophyllites are increasingly used in white cement production because of their low iron and chromium content. Due to these properties it is used for the production of the best quality European white cement in ÇİMSA-Mersin, termed as "Super White" that has "whiteness" around 90.

The 5 different groups of Pütürge pyrophyllites with their outstanding mineralogical and geochemical properties, if elaborated in to economically more valuable products in ceramics, refractory, fiberglass, fillings, paper, and plastic industry will have high importance for economy of the country in the future.

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