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MINERALOGICAL CHARACTERISTICS RELATED TO THE QUALITY AND RECOVERY OF THE PANORAMA WOLLASTONITE, DRAMA AREA, NORTHERN GREECE

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ABSTRACT

Wollastonite of Panorama area is characterized by specific mineralogical properties related to its quality, as well as to its behaviour during beneficiation and to the relevant recovery. In order to determine these features, one representative bulk sample and beneficiation products have been studied. The methodology used was the combination of microscopical study, X-Ray diffractometry, I-R spectrometry, microprobe analysis, chemical analysis and image analysis. The wollastonite grade increases by means of ten percentage units by dry magnetic separation and by ten more units in the concentrate derived by "inverse" flotation. Wollastonite liberation degree is controlled rather by pyroxenes and less by garnets. L.O.I. is further related to the textural relationship between wollastonite and calcite, while the FeO and MnO content in wollastonite crystals varies from 0.15-0.56% and 0.59-1.58% respectively. Finally, the aspect ratio of wollastonite -0.212 mm grains, is estimated, by image analysis technique, at 4.87:1, depending on the grinding method being followed. The above characteristics will finally affect the quality of any, potential wollastonite end-products.

KEYWORDS: wollastonite, quality, recovery, image analysis, aspect ratio, Panorama, Drama, N. Greece.

1. INTRODUCTION

The Panorama area belongs to the Falakro series of Western Rhodope massif. The Western Rhodope massif is composed of polymetamorphic crystalline rocks. These rocks are divided in the lower basement unit (alternation of muscovite and augen gneisses of high-pressure metamorphism overprinted by upper-amphibolite facies), the transitional zone (two-mica gneisses, garnetiferrous gneisses, two-mica schists, actinolite schists, amphibolites, calc-schists and cipoline marble of upper amphibolite metamorphic facies), and the carbonate unit (massive marbles with domolitic intercalations - Falakron series - underlayed by thin banded marbles with intercalations of mica-shcists, calcareous schists and minor chert layers), (Zachos and Dimadis 1986, Chatzipanagis 1991). All these rocks have been affected by retrograde greenschist facies metamorphism. The Western Rhodope is also characterized by the presence of granitic bodies of Middle Cretaceous to Oligocene age, which intrude the lower members of the Falakron carbonate unit.

The wollastonite occurrences are developed in the skarns between marble and granite. Wollastonite was formed in the early skarnification stages in both the exo-skarn and endo-skarn. The larger wollastonite occurrence appears in the southern part of the area of interest, developed mainly in the exo-skarn, while the one in the endo-skarn is without any economic significance(Bitzios et al 1988, Bitzios 1995).

As an industrial mineral, wollastonite is used in ceramics, metallurgy, as well as in plastics and dye industry. Its chemical composition, specific mineralogical characteristics and certain technical properties evaluated together determine the suitability of wollastonite for specific uses.

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This study defines the mineralogical features being significant and contributing to (a) the evaluation of wollastonite quality and (b) the recovery by beneficiation processes.

Concerning the Panorama wollastonite, the following parameters are determined: (1) the mineralogical composition of the "wollastonitic rock", (2) the textural characteristics and particularly the specific relationship of wollastonite with associated minerals, (3) the wollastonite liberation degree, (4) the chemical composition of wollastonite crystals, as well as that of intergrown minerals (pyroxene and garnet), for defining the chemical content of Fe and Mn and (5) the aspect ratio (L/D) of wollastonite grains.

2. METHODOLOGY

The methodology followed in the present study was a combination of the following techniques: Microscopic study on a Leitz Ortholux II Pol-Bk microscope for the qualitative mineralogical composition, mineral size, textural associations and a first quantitative mineralogical composition appraisal (Ramdohr and Strunz, 1978). X-Ray Diffractometry was applied for qualitative and quantitative analysis. It was performed by an automatic X-Ray Diffractometer, Siemens D500, radiation Cuka, Ni-filter, graphite monochromator, goniometer angular, speed 1-2 degrees/minute, angular interval 3-65 degrees 2θ. The qualitative determination of the minerals was performed with the software Diffrac AT 3 from Siemens and Socabim, using the database JCPDS. The quantitative determination was performed by the complex standardless analysis method on the basis of X-Ray and chemical data (Le Maitre, 1982 and Zangalis, 1991).Infrared Spectrometry by a Perkin Elmer 283B Spectrophotometer for qualitative estimations (Farmer,1974). Microprobe analysis was applied for the chemical composition of minerals. A Jeol 730 Electron Microprobe with a Tracor Energy Dispersive Spectrometer was used. The high voltage was 20 kV and the electron beam current 3nA. Chemical analysis using AAS technique for the determination of the chemical assays of the samples. A Perkin Elmer spectrophotometer 2100 was used. Image analysis for the determination of aspect ratio of wollastonite grains. Data acquisition was achieved by the use of a Sony video color camera, combined with an Ortholux microscope and the measurements were performed by the Image Pro Plus software.

3. MINERALOGY

The mineralogical study has been carried out on the following samples: (a) on the representative bulk sample (WPR) of the Panorama wollastonite deposits (~1000 kgr) crushed at - 5 mm, (b) on the dry magnetic separation (pre-concentration) products: the magnetic product (WPR-M) and the pre-concentrate non-magnetic product (WPR-NM) and (c) on the flotation products, deriving from the treatment of the non-magnetic product.

Representative sample

It consists of 70.5% wollastonite, 9.5% pyroxene, 10.5% garnet, 5% calcite and 1% quartz (Table 1 and 2). The minerals: feldspar, iron oxides, pyrite, epidote and chlorite are minor constituents, participating with much lower percentages (total 2%).

Wollastonite appears in the form of unmixed and mixed grains as well (Fig. 1 and 2). In the case of mixed grains the prevailing mineral assemblages are:

a. Wollastonite + pyroxene ± garnet, calcite, quartz

b. Wollastonite + calcite ± pyroxene, garnet, quartz

In the first assemblage wollastonite contains inclusions of pyroxene crystals with size varying usually from a few to 80 μm. In the second, wollastonite is mainly mixed with calcite due to the calcification process and occasionally it is mixed with garnets (size up to 1200 μm).

A sufficient number of wollastonite grains present surficial oxidation of brownish color due to the Fe-release from the mafic mineral inclusions (Fig. 2). Microprobe analyses gave a FeO content ranging from

0.15-0.56% with a mode of about 0.3% and a MnO content ranging from 0.59-1.58% with a mode of about 0.9% (Table 3).Pyroxenes have diopside - salite composition (Table 3) and the most usual form is the pyroxene inclusions or intergrowths with wollastonite, sized from a few up to 800 μm (Fig. 1).

Garnets are composed mainly of andradite and less of grossularite (Table 3) and in the case of mixed grains, they have a size of up to 1000-1200 μm. Calcite occurs as unmixed grains or as mixed mainly with wollastonite. Quartz is rarely mixed with calcite or wollastonite and sized from 60 to 100 μm.

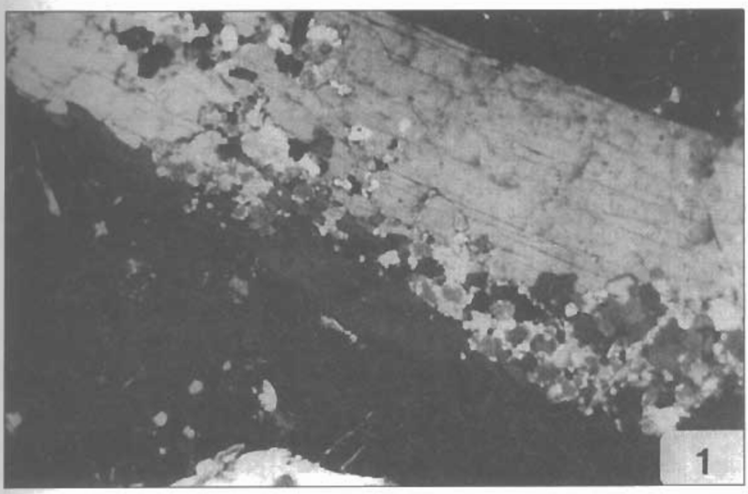

Fig.1: A typical texture of wollastonite grain mixed with fine-grained pyroxene inclusions. Representative sample. Crossed Nic., Magnification 40X.

Fig.2: Calcification of wollastonite grain, parallel to (100) cleavage. Representative sample. Crossed Nic., Magnification 40X.

Table 1. Quantitative mineralogical composition of samples

Sample	Wollastonite	Pyroxene	Garnet	Calcite	Quartz
WPR	70.5	9.5	10.5	5.0	1.0
WPR-M	16.4	12.2	66.3	3.1	<1
WPR-NM	81.0	6.5	5.5	4.0	1
CL-CONC	22.7	14.7	27.3	35.6	<1
TM-TAIL	54.5	29.0	20.5	1.0	<1
SLIM	75.9	17.5	3.7	4.4	<1
W-CONC	91.0	2.5	3.0	1.0	1.0

Table 2. Chemical assays of samples

Sample	SiO_2	CaO	Fe_2O_3	Al_2O_3	MgO	MnO	L.O.I.
WPR	46.72	42.25	3.75	1.21	0.90	0.81	2.95
WPR-M	40.07	34.62	14.12	4.95	1.11	0.85	2.46
WPR-NM	49.03	43.25	1.70	0.58	0.84	0.81	2.90
CL-CONC	30.8	42.10	5.90	2.05	1.20	0.65	17.4
TM-TAIL	52.0	36.80	5.65	0.75	3.50	1.20	0.35
SLIM	50.80	41.90	1.10	0.30	0.85	0.85	4.20
W-CONC	52.20	44.45	0.85	0.10	0.40	0.85	0.80

Abr. for Table 1 and 2:
WPR = Representative sample, WPR-M = Magnetic product, WPR-NM = Non Magnetic product (pre-concentrate), CL-CONC = Cleaner concentrate, TM-TAIL = Total magnetic tailings, SLIM = Slimes, W-CONC = Wollastonite concentrate.

Table 3. Representative electron microprobe analyses of wollastonite (1-8), pyroxene (9-12) and garnet (13-16).

No	SiO_2	Al_2O_3	FeO	Mgo	CaO	K_2O	MnO	Total
1	51.22	0.11	-	-	45.86	0.18	1.97	99.34
2	51.11	0.10	-	-	45.99	0.16	1.99	99.35
3	51.02	0.09	-	-	46.02	0.15	1.98	99.26
4	51.21	0.09	-	-	46.13	0.13	2.01	99.57
5	51.45	0.09	0.44	0.34	45.90	0.22	1.58	100.02
6	51.28	0.09	0.40	0.39	46.02	0.20	1.48	99.86
7	51.55	-	0.35	0.29	45.95	0.19	1.46	99.79
8	51.36	-	0.63	0.34	45.85	0.12	1.38	99.68
9	53.49	0.15	5.02	14.37	25.32	0.23	0.83	99.42
10	53.28	0.16	5.46	14.21	24.99	0.20	0.99	99.29
11	51.67	0.30	10.02	10.65	24.89	0.23	1.36	99.12
12	52.01	0.31	10.20	10.40	24.75	0.19	1.22	99.09
13	37.52	14.86	9.24	-	35.75	0.14	1.52	99.03
14	37.71	15.13	9.04	-	35.77	0.13	1.38	99.16
15	36.08	4.73	22.55	0.05	32.87	-	1.06	99.34
16	37.20	10.52	15.37	0.10	32.95	-	1.68	99.82

Products of dry magnetic separation (pre - concentration)

During the pre-concentration process of the representative sample, dry magnetic separation, the magnetic and the non-magnetic products (WPR-M and WPR-NM) have been produced. The magnetic product consists of 66.3 % garnets, 12.2% pyroxene, 16.4% wollastonite, 3.1% garnet and <1% quartz. The majority of garnet and pyroxene grains are mainly unmixed, whereas these of wollastonite are mainly mixed with pyroxene inclusions. Thus, the magnetic product led to a satisfactory removal of garnets and pyroxenes from the representative sample. The non-magnetic product contains: 81% wollastonite, 6.5% pyroxene, 5.5% garnet, 4% calcite and 1% quartz (Table 1 and 2). Wollastonite occurs mainly as unmixed grains, with only a few of them containing pyroxene inclusions. Moreover, some wollastonite grains present a surficial oxidation of brownish colour (Fig. 3). Thus, the result of the dry magnetic separation was the increase of the wollastonite grade by 16 percentage units (from 65.5% to 81%) compared with the representative sample, while pyroxene+garnet total content has been decreased by 8 percentage units (from 20% to 12%).

Beneficiation products

The wollastonite pre-concentrate has been further processed "by inverse" flotation followed by high intensity wet magnetic separation and desliming of the non-magnetic product (Patronis M., 1995) The four products (cleaner concentrate, total magnetic tailing, wollastonite concentrate and slimes) of the most successful test were studied microscopically and their quantitative mineralogical compositions are given in Table 1. The cleaner concentrate is dominated by calcite (35.6%) and garnet (27.3%) unmixed grains, the total magnetic tailings by mixed wollastonite grains (54.5%) and the slimes by extremely fine-grained wollastonite (75.9%) displaying oxidized and calcified surfaces.

Wollastonite concentrate

It consists of 91% wollastonite, 2.5% pyroxene, 3% garnet, 1% calcite and 1% quartz. (Table 1 and 2). Wollastonite, practically the only mineral, occurs mainly as unmixed grains, indicating that the wollastonite liberation degree has been significantly increased (Fig.4). The mixed grains are very few, usually including pyroxenes of a size exceeding 10μm. Some of the wollastonite grains preserve their surficial brownish colour oxidation. The 5.5% pyroxene and garnet total content, into the concentrate, is mainly due to inclusions and intergrowths with wollastonite grains, sized from 10μm up to 350μm.

Quantitative image analysis was carried out on the wollastonite grains of the concentrate, for the determination of their aspect ratio (L/D). Nine images were quantitatively analyzed and the maximum length and width of 752 wollastonite grains were measured, resulting in an aspect ratio of 4.87:1.(Constadinidou et al., 1995). The distribution of the aspect ratio values has shown that 66.5% of the measured grains have an aspect ratio of <5:1, 30% a value of 5-10:1, while 3.5% of the grains show an aspect ratio >10:1(Fig. 5).

4. CONCLUSIONS

The conclusions derived from the mineralogical study, being of importance for the quality and recovery of the wollastonite concentrate are the following:

a). The wollastonite grade of the representative sample being 70%, has been increased to 81% in the pre-concentrate and to 91% in the concentrate (Fig. 6).

b). The complete wollastonite separation from the other silicate minerals seems to be difficult because of their close textural associations. The total percentage of pyroxene and garnet (5.5%) in the wollastonite concentrate (Fig 6) is mainly due to the above fact.

c). The wollastonite liberation degree is mainly defined by the sizes of pyroxene inclusions, and in a lesser extent from garnet, since the latter is coarser sized and consequently is more easily separated from wollastonite. With dry magnetic separation a satisfactory removal of pyroxenes and garnets was achieved.

d). The calcite participation in the representative sample is relatively low (5%), but calcite is closely associated with wollastonite, due to the calcification. In the cleaner concentrate a considerable amount of calcite (35.6%) has been reported, thus resulting in the decrease of the relevant wollastonite concentrate's L.O.I. (0.8%).

e). The surficial oxidation of wollastonite, due to alteration, gives a brownish color in a certain amount of its grains, affecting the whiteness. However, the above amount of brownish colored grains is low and the sub-white color grains prevail.

f). The chemical composition of the wollastonite crystals obtained by microprobe analysis shows a FeO content ranging from 0.15-0.56% (mode 0.3%) and a MnO content ranging from 0.59-1.58% (mode 0.9%). The above figures justify the somewhat increased Fe_2O_3 and MnO content of the wollastonite concentrate.

g). The aspect ratio (L/D) of the -0.212 mm wollastonite grains in the concentrate has been estimated at 4.87:1. However, the above value depends on the grinding method being followed.

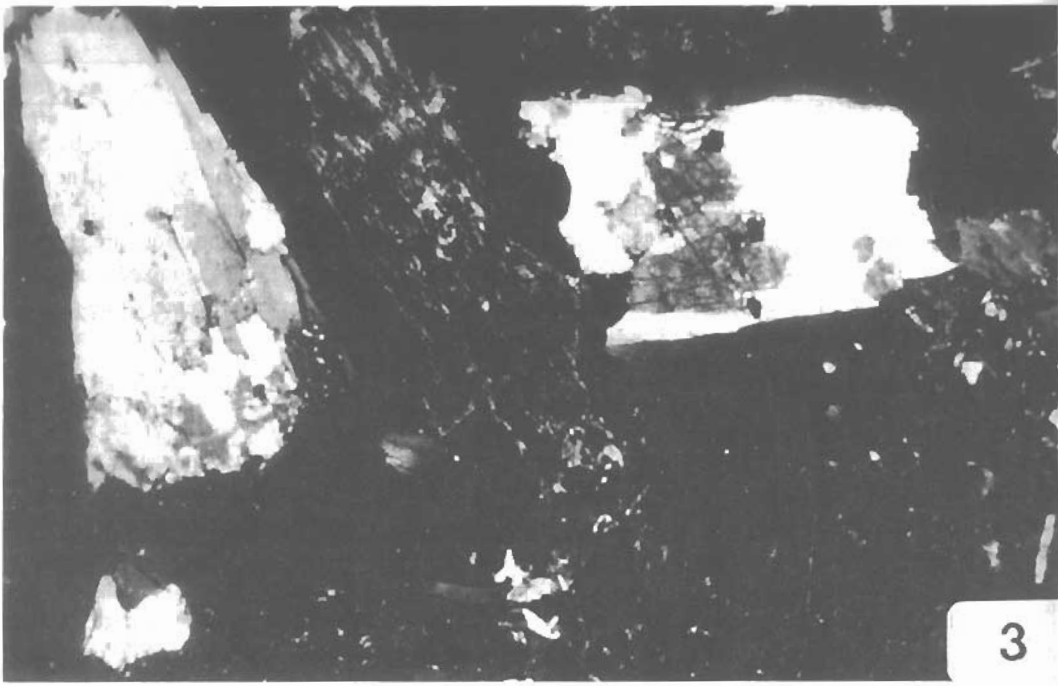

Fig.3: Wollastonite grains of which the central one presents surficial oxidation of brownish color. Representative sample. Crossed Nic., Magnification 40X.

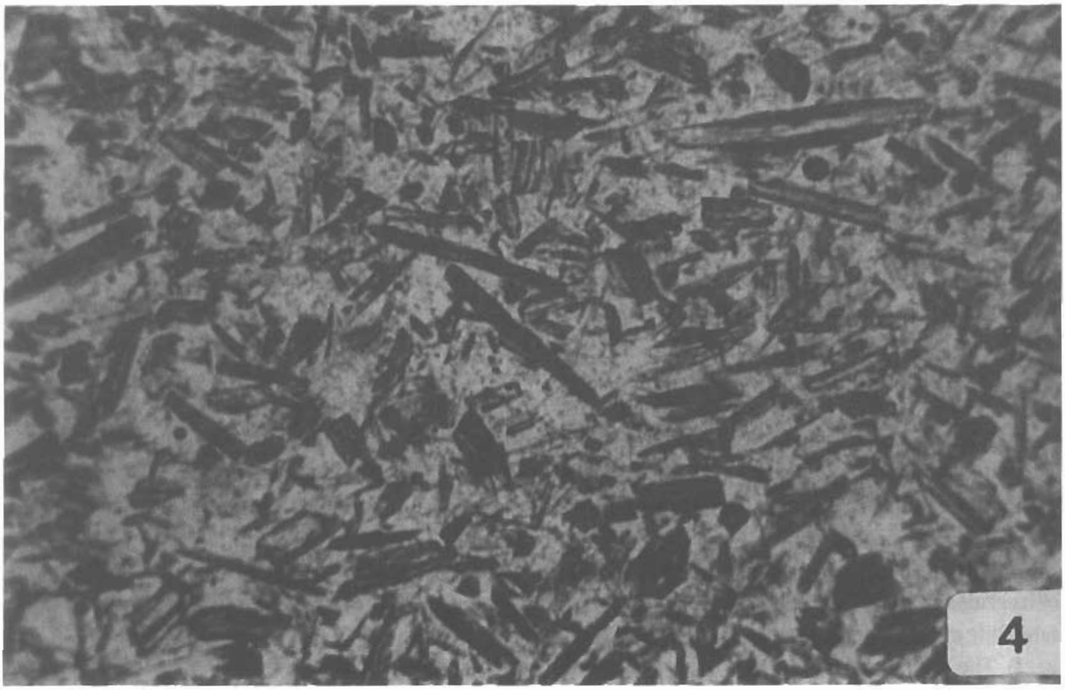

Fig.4: Fine unmixed wollastonite "fibres" in the wollastonite concentrate. Parallel Nic., Magnification 40X.

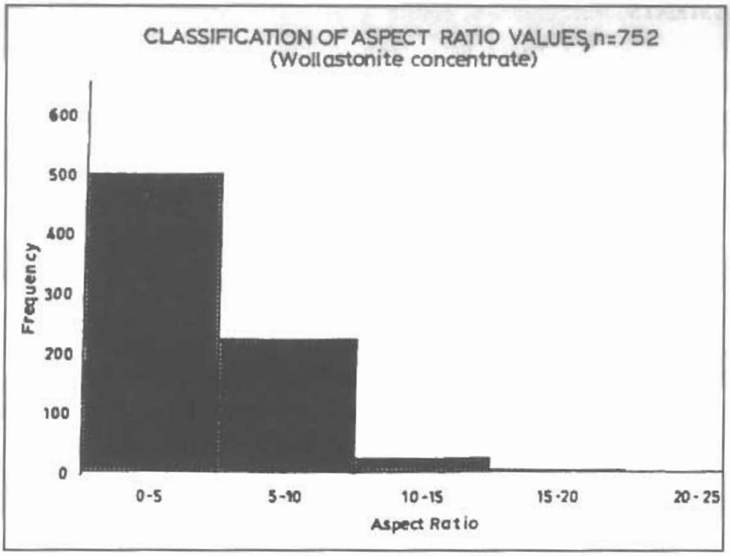

Fig. 5 Classification of aspect ratio values, n=752, of the wollastonite grains.

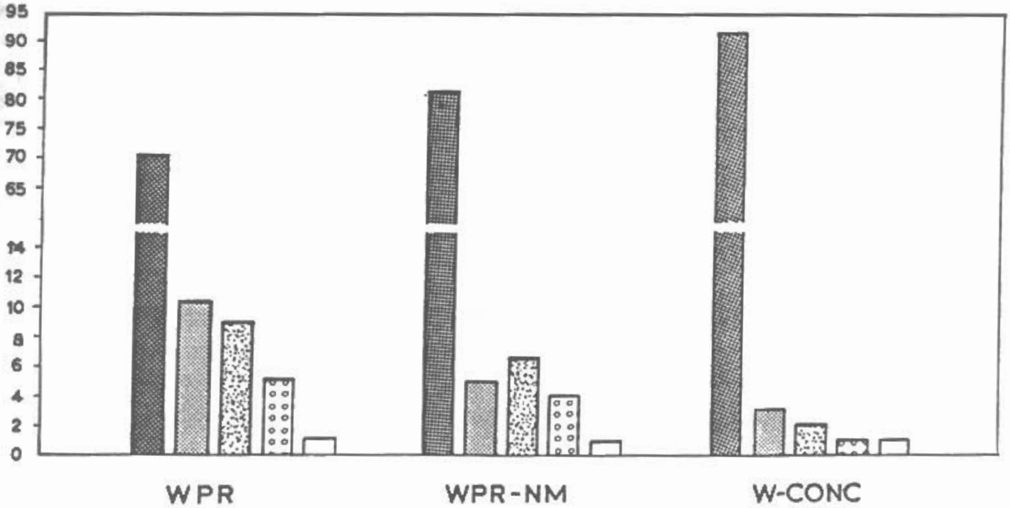

Fig. 6 Quantitative mineralogical composition of the representative sample (WPR), the non-magnetic product (WPR-NM) and wollastonite concentrate (W-CONC).

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REFERENCES

BITZIOS D. (1995) : Final Technical Report of I.G.M.E. for BRITE/EURAM II Project "Development of Exploration and Industrial Technology to Exploit New Wollastonite Sources in Europe", BRE-CT92-0134, Athens.

BITZIOS D., ECONOMOU G., CONSTANDINIDOU H., FONTEILLES M., ROGER G., BENKERROU C. (1988): L' indice de wollastonite de la region de Panorama (Drama). Comparaison avec les gisements et des indices de wollastonite mondials. Int. report, I.G.M.E.

CHATZIPANAGIS J. (1991): Geologic structure of the Falakron Mountain area, PhD, Athens, Nat. Techn. Univ., p. 179.

CONSTANTINIDOU H., ZANGALIS K., ECONOMOU G. (1995) : Mineralogical study on samples from the Panorama wollastonite deposit: Representative bulk sample and beneficiation tests products. In: Final Technical Report for the Project: BRE-CT92-0134, Athens

DEER W.A., HOWIE R.A. and ZUSSMAN J., (1967) : Rock Forming Minerals. Longmans, London

FARMER V.C., (1974) : The Infrared Spectra of Minerals. Mineralogical Society, London.

PATRONIS M. (1995) : Beneficiation study on a representative bulk sample from the wollastonite deposit of the Panorama area (Drama) Northern Greece. In : Final Techical Report for the Project : BRE-CT92-0134, Athens.

LE MAITRE R.W., (1982) : Numerical Petrology Statistical Interpretation of Geochemical Data. Elsevier Scientific Publishing Company-Amsterdam-Oxford-New York.

RAMDOHR P. and STRUNZ H., (1978) : Lehrbuch der Mineralogie. Ferdinand Enke Verlag Stuttgart.

ZACHOS S. and DIMADIS E. (1986): Generalized geological map of Eastern Macedonia-Thrace, 1:200.000, I.G.M.E.

ZANGALIS K. P., (1991) : A Standardless Method of Quantitative Mineral Analysis Using X-Ray and Chemical data. J.Appl.Cryst, 24, 197-202.