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## IDOCRASE FROM POLYANTHOS AREA (THRACE)

#### by

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Abstract: A compact mass of vesuvianite with a light green colour found within metamorphic rocks in Polyanthos village between Xanthi and Komotini cities is described. Physical and optical properties are referred. Chemical analysis by the X-ray Fluorescence spectrography has been performed. The Barth's (1963) formula fits the analytical result better than any other formula so far proposed. The cell constants obtained by least squares from  $\theta$  value measurements on the X-ray powder diffractometer are: a = 15.59636 Å, c = 11.77531 Å and V = 2864.3023 (Å)<sup>3</sup>

#### INTRODUCTION

The name Vesuvianite first applied by Werner (1795) after its occurrence on the Mt. Vesuvius, Italy, where it is found in ejected dolomite blocks. Haüy (1797) suggested the name «Idocrase» from Greek words «eidos» and «krasis», mixed-appearing. Since then a great number of names has been given a) relating to the composition (e.g. Beryllianidocrase; titan vesuvianite, cerian-idocrase etc). b) referring to the colour (e.g. cyprine; xanthite; from the Greek words «kypros» and «Xanthos», means blue and yellow respectively) and c) based on the location of occurrence (Wiluite; Frugardite, and Gokumite, from Wilui River, Siberia; Frugard, Filand and Gokum, Sweden respectively). But idocrase is the most popular name and remains in very widespread use.

Idocrase (vesuvianite) occurs principally in contact metamorphic zones associated with limestones. It is commonly associated with garnet, diopside, wollastonite and other calcium silicate minerals. Vesuvianite

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is also found in wide range of metamorphic grade rocks and in rodingite, in veins and pockets associated with mafic and ultramafic rocks and rearly in alkalic rocks. The diversity of conditions demostrated by the occurrences of vesuvianite suggests that it is stable over a considerable wide range of temperature and pressure.

Although idocrase is one of the most exhaustively studied minerals, there are still, a lot of uncertainties and inconsistencies of the true symmetry, optical behavior, structural character, chemical composition and factors influencing the formation of this mineral in various geological settings. Thus the study of a greek idocrase for first time, should not be without interest.

## OCCURRENCE AND PHYSICAL PROPERTIES

The studied idocrase has been found in southwestern slopes of the «329» hill about one km northeastern of the Polyanthos village that is between the cities of Xanthi and Komotini.

The mineral observed within metamorphic rocks where gneisses and chlorite schists are among the persistent petrographic - types.

The host material of the mineral has not been found but is beleived that it may be a marble or a limestone bed. It has been found commonly in compact mases up to 15 cm in length composed of small crystal aggregates without any clear habit. The mineral is associated with small amount of moscovite.

Specific gravity determined by heavy liquids is 3.42. Hardness is between 6 and 6.5. It was insoluble in hydrochloric acid although hoted preliminary. Cleavage has been observed. Its colour is light green showing a greasy lustre. The colour of idocrase appears to be controlled mainly by the amount and oxidation state of the iron present as well as from the TiO<sub>2</sub> and MnO content (Deer et al., 1962). The 4.29 percent content of total iron as  $Fe_2O_3$  and the low concentration of TiO<sub>2</sub> and MnO in the studied mineral, Table 1, justified the observed light green colour.

## OPTICAL DATA

In thin sections under plane polarised light the mineral is not pleochroic and the crystals show very low birefringence so that they are almost uniform in appearance. This low birefringence may he related to the amount of (OH) in the structure, because as the hydroxyl content is reduced the birefringence is increased (Deer et al., 1962). In the studied idocrase the birefringence decreases so that it becomes almost isotropic.

Under crossed polarized light fine scale intergrowths with other not identified minerals are observed. In some cases zonal structure (Fig. 1 A + B) occurs and abnormal, blue to violet birefringent colours are also found. The mineral is uniaxial, negative, but biaxial figure in one case has also been observed.

Because the mineral, as cited above, exhibits an extremely low birefringence, and might, for practical purposes, be considered isotropic, only one index was determined by the immersion method and the Becke line and is reported as a «mean index». It was found to be 1.716  $\pm 0.002$ .

No unified theory has yet been proposed to account for the huge diversity of optical effects seen in idocrase for a long time. Some workers concluded that optical anomalies had to be the result of twinning. Others decided that idocrase was composed of two substances combined in a way that would produce the observed optical anomalies and still give a reasonable chemical range of composition.

#### CHEMISTRY

Owing to the complexity of idocrase chemical composition its formula is discussed by a great number of workers.

Warren & Modell (1931) from X-ray structural analysis proposed an ideal chemical formula which can be written as  $Ca_{20}(Mg, Fe)_4AI_8Si_{18}O_{68}$ (OH, F)<sub>8</sub>. Machatschki (1932) suggested an alternative formula  $X_{19}$  Y<sub>13</sub>  $Z_{18}$  (O, OH, F)<sub>76</sub> where X = Ca (Na, K, Mn), Y = Al, Fe<sub>2</sub>, Fe<sub>2</sub>, Mg, Ti, Mn, Zn) and Z = Si. But this is essentially the same as that of Warren and Modell. Beus (1957) gave a formula of idocrase as  $Ca_3$  (Al, Fe, Mg)<sub>6</sub> (Si, Be)<sub>9</sub> (O, OH, F)<sub>36</sub>. Rapp & Smith (1958)  $Ca_{20}$  Al<sub>16</sub> Si<sub>68</sub> (OH)<sub>8</sub> and Christophe - Michel - Lévy (1960)  $Ca_{20}$  Al<sub>12</sub> Si<sub>18</sub> O<sub>68</sub> (OH)<sub>8</sub>. Barth (1963) proposed the formula  $X_{10-u}$  Y<sub>6+u</sub> Z<sub>9</sub> (O, OH, F)<sub>38</sub> where X = Ca, Na, K, Mn, Y = Fe, Mg, Ti, Al, Cu, Z = Si with small amounts of Al and u = 1. This formula agrees with the results of Norwegian vesuvianite analyses. He also found that the Machatschki formula fits the analytical results generally, better than any other formula so far proposed.

Walter (1966) suggested another formula  $Ca_{19} Al_{10} (Al, Mg)_4 Si_{17} O_{68} (OH)_4 (O, OH)_4$  which is again essentially the same with that proposed by Warren & Modell (1931).



Fig. 1 (A). Single crystal of idocrase from Polyanthos area in crossed polars showing distinct zonal features.



Fig. 1 (B). A part of idocrase crystal showing fine zonal structure.

None of the above formulas agrees with all published analyses of vesuvianite. This mineral remains one of a small number of silicates whose formula is not fully established.

The chemical analysis of the studied mineral was carried out by X-ray fluorescence spectrography at the Department of Geology, Manchester University, England. The result with formula calculated on the basis of 76 oxygen equivalents are listed in Table 1.

#### TABLE 1.

Chemieal analysis of idocrase from Polyanthos area.

${ m SiO}_2$	35.59	Si	18.391	
${ m TiO}_2$	.08	Ti	.030	
$\mathrm{Al}_2\mathrm{O}_3$	15.57	Al	9.227	
$* \mathrm{Fe}_{2}\mathrm{O}_{3}$	4.29	Fe³ ⊦	1.623	
MnO	.04	Mn	.017	
MgO	3.93	Mg	2.944	
CaO	35.62	Ca	19.725	
$K_2O$	.24	К	.154	
$Na_2O$	.12	Na	.117	
$\mathrm{P}_{2}\mathrm{O}_{5}$	.05	Р	.021	
$\rm H_2O^+$	2.14	OH+	3.802	
Total	99.67			

\* Total iron calculated as Fe<sub>2</sub>O<sub>3</sub>.

The material for the above analysis was taken from the compact mass of the mineral the purity of which was checked microscopically before powdering.

The results of the analysed mineral listed on the Table 1. show that there is a closer approach of the Y group (Al, Fe, Mg, Ti, Mn) to 13 than 12 and the X group (Ca, K, Na, Mn) to 20 than 19. This means that the idocrase formula of the Polyanthos area fits better with the formula given by Barth (1963).

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d	I	d	Ι	d	I	d	Ι	d	I	d	1
10.98	10	11.05	30	11.1	30	1.850	10	1.666	50	1.666	50
5.91	20	9.42	10	9.42	10	1.799	10	1.625	80	1.625	80
4.90	20	5.91	40	5.91	40	1.762	10	1.576	10	1.576	10
4.73	20	5.53	10	5.53	10	1.739	10	1.562	40	1.562	40
4.02	30	5.19	10	5,19	10	1.720	10	1.545	10	1.545	10
3.917	20	4.697	20	4.70	20	1.682	10	1.530	10	1.530	10
3.801	30	4.038	30	4.04	30	1.660	10	1.517	10	1.517	10
3.473	40	3.899	20	3,90	20	1.632	20	1.500	30	1.500	30
3.242	20	3.485	40	3.49	40	1.621	20	1.478	10	1.478	10
3.070	20	3.246	30	3.25	30	1.571	10	1.425	10	1.425	10
3.052	30	3.064	40	3.06	40	1.561	10	1.413	10	1.413	10
2.998	20	3.013	40	3.01	40	1.559	10	1.391	30	1.391	30
2.950	70	2.948	60	2.948	60	1.539	10	1.376	10	1.376	10
2.901	20	2.905	10	2.905	10	1.525	10	1.348	30	1.348	30
2.850	20	2.823	10	2.823	10	1.513	10	1.329	10	1.329	10
2.752	100	2.759	100	2.759	100	1.498	10	1.301	40	1.301	40
2.671	10	2.672	10	2.672	10	1,476	10	1.283	20	1.283	20
2.592	80	2.599	80	2.599	80	1.465	10	1.267	30	1.267	30
2.530	10	2.530	10	2.530	10	1.450	10	1.226	10	1.226	10
2.492	10	2.465	60	2.465	60	1.441	10	1.200	10	1.200	10
2.461	60	2.383	10	2.383	10	1.436	10	1.175	10	1.175	10
2.440	10	2.354	10	2.354	10	1.389	10	1.142	10	1.142	10
2.390	10	2.329	10	2.329	10	1.347	10	1.105	30	1.105	30
2.350	10	2.291	10	2.291	10	1.298	10	1.094	10	1.094	10
2.321	20	2.208	20	2.208	20	1.269	10	1.078	20	1.078	20
2.272	10	2.167	10	2.167	10			1.072	20	1.072	20
2.240	10	2.128	50	2.128	50			1.063	10	1.063	10
2.201	20	2.093	10	2.093	10			1.043	10	1.043	10
2.160	10	2.070	10	2.070	10			1.035	20	1.035	20
2.130	20	2.049	10	2.049	10			1.026	10	1.026	10
2.102	10	1,998	20	1.998	20			1.008	10	1.008	10
2.083	10	1.971	10	1.971	10			0.968	10	0.968	10
2.070	10	1.934	10	1.934	10			0.953	10	0.953	10
2.042	10	1.892	30	1.892	30			0.947	10	0.947	10
1.999	10	1.868	10	1.868	10			0.940	10	0.940	10
1.960	10	1.829	10	1.829	10			0.928	10	0.928	10
1.950	10	1.799	10	1.799	10			0.921	20	0.921	20
1.931	10	1.767	50	1.767	50			0.885	20	0.885	20
1.921	10	1.726	20	1.726	20			0.875	20	0.875	20
1.890	10	1.682	30	1.682	30			0.070	20	0.070	мU
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# TABLE 2.

Comparison between X-ray data of idocrase.

## X-RAY DATA

The structure of vesuvianite was originally determined by Warren & Modell (1931) on a crystal from the Wilui River U.S.S.R. They showed that its structure is closely related to that of grossular garnet and that certain parts of the structure are in fact common in both minerals.

Since this initial work, although numerous attempts have been made to refine the structure (Arem & Burnham, 1969; Arem, 1970; Coda et al., 1970) the basic features of the original model remain unchanged.

X-ray powder data from the studied mineral obtained from both a PHILIPS powder diffractometer and a 114.6 mm camera (Cu Ka radiation, Ni filter, were used with Si as an internal standard). In Table 2 are listed the intensities and spacings of the various reflections as well as data from and J.C.P.D.S. for comparison.

## TABLE 3.

## Cell constants of Idocrase.

	a (Å)	c (Å)	v (Å) <sup>3</sup>
1. Neumann Svinndal (1965)	15.500	11.773	2840.200*
2. Ito & Arem (1970). Asbestos, Quebec	15.523	11.817	2847.400
3. Ito & Arem (1970). Sanfor, Maire	15.533	11.777	2841.810
4. Coda et al., (1971)	15.565	11.816	2862.660*
5. Ito & Arem (1971)	15.600	11.829	2878.710*
6. This paper	15.59636	11.77531	2864.3023

\* Values calculated for comparison.

The unit cell dimensions on the basis of  $2\theta$  values of 65 reflection have been determined using the lattice parameter least square program CSD 104 (Venetopoulos, 1977) of the Department of Applied Physics and the results are given in Table 3. In the same Table the cell dimensions of idocrase from other localities are also listed. The good agreement between observed and calculated d-values and the indices for all reflections are given in Table 4.

The crystal studied confirms the vesuvianite unit cell with a = 15.59636 Å, c = 11.77531 Å and V = 2864.3032 (Å)<sup>3</sup>.

## TABLE 4.

Observed intensities and comparison between observed and calculated d-values of idoerase from Polyanthos area.

dobs	d <sub>calc</sub> .	hk!	I	dobs	d <sub>calc</sub> .	hkl	I
10.98	11.02	110	10	2.042	2.047	730	10
5.91	5.89	002	20	1.999	1.999	415	10
4.90	4.93	310	20	1.960	1.962	006	10
4.73	4.75	301,202	20	1.950	1.951	425	10
4.02	4.02	222	30	1.931	1.932	116	10
3.917	3.899	400	20	1.921	1.922	713	10
3.801	3.806	103	30	1.890	1.890	624	10
3.473	3.485	322	40	1.850	1.850	802	10
3.242	3.250	402	20	1.799	1.800	822	10
3.070	3.071	313	20	1.762	1.765	554,714	10
3.052	3.058	510	30	1.739	1.742	416	10
2.998	3.000	422	20	1.720	1.722	910	10
2.950	2.943	004	70	1.682	1.681	734	10
2.901	2.906	323	20	1.660	1.661	436	10
2.850	2.844	114	20	1.632	1.635	217	20
2.752	2.754	204	100	1.621	1.624	526	20
2.671	2.674	503	10	1.571	1.569	941	10
2.592	2.596	224	80	1.561	1.566	606	10
2.530	2,527	314	10	1.559	1.559	664	10
2.492	2.496	442	10	1.539	1.538	10.1.1	10
2.461	2.466	620	60	1.525	1.523	853	10
2.440	2.442	530,433	10	1.513	1.514	950	10
2.390	2.385	541	10	1.498	1.499	636	10
2.350	2.350	612	10	1.476	1.474	825	10
2.321	2.323	414	20	1.465	1.465	556.716	10
2.272	2.274	622	10	1.450	1.449	863	10
2.240	2.231	215	10	1.441	1.441	854	10
2.201	2.205	550.710	20	1.436	1.436	755	10
2.160	2.162	632	10	1.389	1.389	627,774	10
2.130	2.127	641	20	1.347	1.347	954	10
2.102	2.107	721	10	1.298	1.298	448	10
2.083	2.088	623	10	1.269	1.269	817.747	10
2.070	2.069	543	10				

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#### ΠΕΡΙΛΗΨΉ

# ΙΔΟΚΡΑΣΗΣ (ΒΕΖΟΥΒΙΑΝΟΣ) ΕΚ ΤΗΣ ΠΕΡΙΟΧΗΣ ΠΟΛΥΑΝΘΟΥ ΚΟΜΟΤΙΝΗΣ (ΘΡΑΚΗ)

#### ٬Υπό

## Η. ΣΑΠΟΥΝΤΖΗ - Σ. ΘΕΟΔΩΡΙΚΑ - Κ. ΣΟΛΔΑΤΟΥ

'Εξετάζεται συμπαγής μᾶζα τοῦ ὀρυκτοῦ Βεζουβιανοῦ ἀνοικτοῦ πρασίνου χρώματος εύρεθεῖσα ἐντὸς μεταμορφωμένων πετρωμάτων εἰς τὸ χωρίον Πολύανθος μεταξὺ τῶν πόλεων Ξάνθης καὶ Κομοτηνῆς. 'Αναφέρονται αἱ φυσικαὶ καὶ ὀπτικαὶ ἰδιότητες αὐτοῦ. Ἐκτελεῖται χημικὴ ἀνάλυσις διὰ τῆς μεθόδου φασματογραφήσεως τοῦ φθορισμοῦ διὰ τῶν ἀκτίνων Χ καὶ διαπιστοῦται ὅτι ἐν σχέσει πρὸς ὅλους τοὺς τύπους ποὺ ἔχουν μέχρι σήμερον προταθεῖ διὰ τὸ ὀρυκτόν, τὰ χημικὰ δεδομένα εὑρίσκονται πολὺ πλησιέστερον πρὸς ἐκεῖνα ποὺ ἀναφέρονται ὑπὸ τοῦ Barth (1963). Αἱ σταθεραὶ τῆς κυψελίδος ληφθεῖσαι διὰ τῆς μεθόδου τῶν ἐλαχίστων τετραγώνων ἀπὸ τὰς μετρηθείσας τιμὰς θ ἐπὶ τοῦ περιθλασιμέτρου κόνεως εὑρέθη ὅτι εἶναι: a = 15.59636 Å, c = 11.77531 Å καὶ v = 2864.3023 (Å)<sup>3</sup>.