

## Errata

Str.	Wiersz		Jest	Powinno być
	góra	dół		
4		18	$n_\gamma - n_\alpha = 0.080 - 0.079$	$n_\gamma - n_\alpha = 0.080 - 0.079$
9	13		(Ch) transformed	(Ch) partially transformed
15	9		16.4	16.4%
19	11		Fig. 1 12	Fig. 1, 12
19	12		MgCO <sub>3</sub>	MgCO <sub>3</sub>
22		7	burned	burned
46	2		by activation	activation by
47		13	CZENKO N. S.	CHENKO N. S.
plansze kredowe po str. 100			WOŁOSIŃSKI	WŁOSIŃSKI

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## STABLE CARBON ISOTOPE COMPOSITIONS OF MARBLE AND GRAPHITE FROM PRZEWORNO (LOWER SILESIA)

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**Abstract:** The samples of marble from Przeworno quarry have been analyzed using the mass spectrometer MICROMASS-602C for isotopic composition of carbon and oxygen.  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values for carbonate and graphite dispersed matter were determined.

$\delta^{13}\text{C}$  values in marble range from + 2.4 to - 1.7‰ whereas in graphitic dispersed substance extracted from the rock vary from - 9.0 to - 16.4 vs PDB.

The results confirm previously published data that carbonates in marble are isotopically heavier than coexisting graphite. The graphite from Przeworno shows an increased content of heavy  $^{13}\text{C}$  isotope, in comparison with other graphites from metamorphic rocks. This could be due to: 1) biogenic origin of graphitic matter disseminated in dark varieties of marble and 2) interaction between heavy carbonates and lighter micro-organisms during geochemical processes occurring in the complex metamorphic history of these rocks.

## INTRODUCTION

Among the diversified rock series making up the crystalline Strzelin hills (metamorphic mantle of the Variscan granitoid rocks of Strzelin) are marbles. Originally, they were assigned to the Devonian but, according to Oberc (1966) they represent the Proterozoic. The marbles in question outcrop at Przeworno (Lower Silesia) where they are still being quarried.

There are a great many publications dealing from different standpoints with the rocks occurring in the Przeworno quarry. Geological-stratigraphic (Oberc 1966, Głazek *et al.* 1971), mineralogical-petrographical (Pentlakowa and Wojno 1952, Olszyński 1973) and paleontological studies have been carried out, yet none of the investigations has attempted so far to determine the composition of the stable carbon and oxygen isotopes. The authors thought such studies might yield interesting results, all the more so as

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the marbles appear in several varieties differing in colour, structure, texture and mineralogical composition. If the colour is assumed to be the most important diagnostic feature, then white, grey and black varieties of marble are macroscopically discernible (Pentlakowa and Wojno 1952). The white variety is represented by coarsegrained calcitic marbles with a sugary texture, containing practically no foreign minerals. The grey variety is a fine-crystalline flaser marble which contains variable amounts of dispersed graphitic pigment. In the black, thick-laminated varieties the content of graphitic substance increases and abundant idioblasts of tremolite can be found.

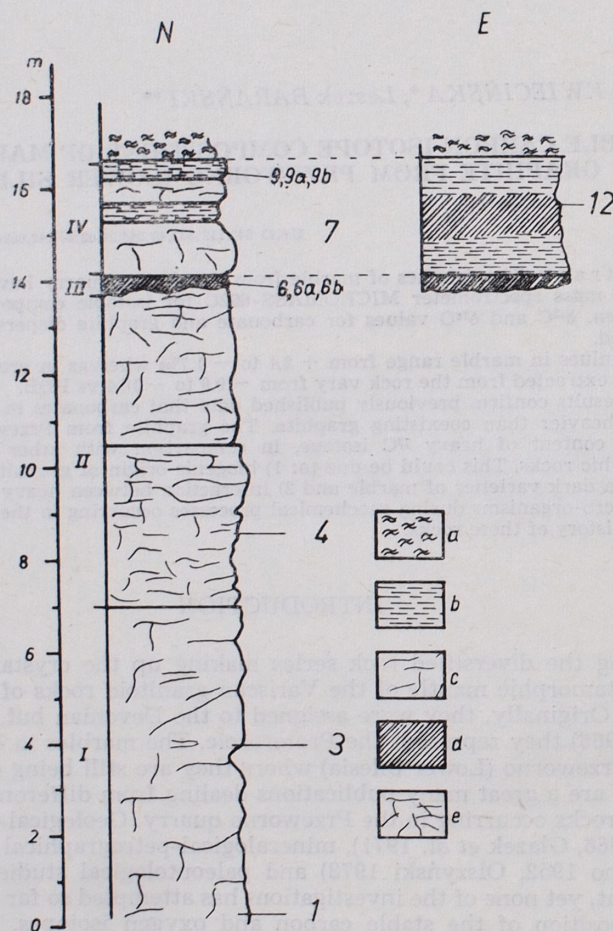


Fig. 1. Profiles of the northern (N) and eastern (E) walls of the quarry of marbles in Przeworno:

I — unit consist of white marble, II — unit consist of white-grey flaser marble, III — unit consist of dark marble, IV — unit consist of white marble with laminated, flaser intercalations, a — amphibole-sericite top schists, b — laminated marble, c — white marble, d — black marble, e — white-grey marble, 1—12 samples no

The presence of fossil diatoms (Kwiecińska, Siemińska 1973) and other fossil micro-organisms (nannofossils) (Kwiecińska, Siemińska 1974) embedded *in situ* in the dark varieties of the Przeworno marbles (Fig. 1 samples 6, 9, 12) was another argument for making a detailed mineralogical-petrographical study of those rocks. Analysis of the composition of the stable carbon and oxygen isotopes, treated as a subsidiary research method, was included in this study. In view of the enormous amount of available but widely divergent data concerning the isotopic composition of C and O in sedimentary and metamorphic rocks of different age, the authors did not expect to find an unequivocal answer to all the unsolved questions connected with the Przeworno marbles.

The only aim of isotopic investigations carried out by the present authors was to determine the interrelations between the compositions of the stable carbon and oxygen isotopes present in the white, grey and black varieties of marble. The variability of marbles is well marked in the profiles of the northern (Fig. 1, I) and eastern (Fig. 1, II) walls of the quarry, made for the lower mining level.

It must be pointed out that neither the top rocks (amphibole-sericite schists) nor the intermediate carbonate schists or calc-silicate rocks nor clays and silts making karst infillings found in the southern part, in intensely tectonically disturbed areas (Głazek *et al.* 1971) and in the western wall of the quarry (Oberc 1966) were embraced within the scope of the present investigations. Samples collected from the crystalline marbles alone were to provide information on the variability of carbon participating in the mineralogical (inorganic, carbonate) and biochemical cycles, the latter being associated with the presence of organic fossils and graphite.

## MINERALOGICAL CHARACTERISTICS OF MARBLES

Macroscopic observations made in the northern wall of the quarry have shown that the differentiation of marble is pronounced in the vertical section of the wall. Due to this, four units were distinguished in the complex studied (Fig. 1):

I — the lowermost position in the profile is occupied by white calcitic marble which is compact, medium-crystalline and sugargrained. Sometimes it contains intercalations of light-grey and cream-yellow marble, which attain a thickness of a dozen or so centimetres and show a similar textural features. The marble of this part of the complex is faintly bedded and fissured in many directions.

II — higher in the profile is white-grey flaser marble, fractured into slabs of different thickness. Streaks of different colour have different strikes and variable thickness (1—10 cm). The rock shows a fine-crystalline, sugary texture.

III — a layer of dark marble, about 18 cm in thickness. It has a fairly fixed position in the profile (Fig. 1, I and II) and may therefore be considered as an index layer. The marble is thicklaminated, black-grey, almost black when wet, with thin, streaky light-grey laminae. The thickness of the laminae is variable as well, in places horizontal or wavy, sometimes fine-folded. Flaser marble exhibits very diversified appearance, manifesting



Table 1

Bulk chemical analyses of dark varieties of marble from Przeworno (in weight %)

Content	Samples	
	6b	12
SiO <sub>2</sub>	8.5	16.2
Al <sub>2</sub> O <sub>3</sub>	2.6	5.3
CaO	33.5	38.0
MgO	11.4	3.1
Fe <sub>2</sub> O <sub>3</sub>	0.80	1.80
Na <sub>2</sub> O	0.90	1.60
K <sub>2</sub> O	0.30	1.20
loss on ignition	40.54	31.59
H <sub>2</sub> O(-)	0.28	0.28
H <sub>2</sub> O(+)	0.12	0.07
graphite	0.24	0.40
Total	99.18	99.54

Analyses: M. Sikora and J. Tarkowski.

itself on one hand in changes of the colour intensity and, on the other, in changes of structural and textural characteristics. Its dark colour is due to dispersed graphitic pigment. There is a direct relationship between the colour of the rock and its texture. Dark laminae have a very fine-crystalline texture. The marble layer is intensely fissured in places. The fissures striking in all directions are cicatrized with white coarse-crystalline calcite. Fairly abundant idioblasts of tremolite have been found in places in marble. Their presence had been already noted by Traube (1888). The tremolite crystals vary in size, attaining a maximum length of 3—5 cm and a thickness of 0.5 cm. They are black with an intensely shining lustre and intergrow calcium carbonate in all directions, sometimes forming feathery aggregates. Some idioblasts are fractured and disrupted with the fissures infilled with calcite.

IV — white calcitic (monomineral) marbles showing textural features similar to those of the bottom 7 m bed. They contain laminated flaser intercalations which in the eastern wall of the quarry (Fig. 1, II) grade into a complex of dark, in places black, compact limestones. The content of graphitic substance and accessory minerals is here the highest compared with the other layers.

Microscopic examinations have revealed that white marble is a purely calcitic rock. Calcite grains vary 0.1—1.0 mm in size, those of the size 0.5—0.8 mm being most common. The grains are usually polygonal or, occasionally, tooth-shaped. They are homogeneous, transparent, with pronounced twin striation showing no deformations. The white variety has the lowest content of accessory minerals which are also the least diversified. They are represented by quartz grains and single, very fine muscovite flakes appearing both in the form of inclusions and on the contacts of calcite grains.

Grey marble with a light (Fig. 1 samples 4, 7) or dark tinge (Fig. 1 samples 9a, 9b) shows flaser lamination. Grey laminae contain finely dis-

seminated graphite, mica flakes and quartz grains. Calcite grains making up the grey laminae are somewhat smaller in diameter (0.2—0.3 mm).

As was mentioned earlier in this paper, the content of accessory components increases in the black varieties of marble. Calcite grains have isometric shapes and range from 0.01—0.05 mm in diameter. Chemical analysis of samples 6b and 12 derived from black marbles is given in Table 2 and compared with the results obtained for black marble (Table 2 sample 26) by Pentlakowa and Wojno (1952).

To compare the contents of calcite and dolomite in marble, two samples were selected, representing the extreme varieties: white, pure (Fig. 1, 1) and black (Fig. 1 12). The contents of CaO and MgO obtained from parts soluble in HCl were expressed in terms of CaCO<sub>3</sub>, MgCO<sub>3</sub>, calcite and dolomite contents. The results were compared again with the data given by Pentlakowa and Wojno for respective samples, i.e. white (Table 2 sample 25) and black (Table 2 sample 26). A good agreement was obtained between the data for samples of white marbles (Table 2).

Table 2

Contents of CaO, MgO, CaCO<sub>3</sub>, MgCO<sub>3</sub>, calcite and dolomite in white and black varieties of marble from Przeworno (in weight %)

Content	Samples			
	white (1)	black (12)	after Pentlakowa, Wojno 1952	
			white (25)	black (26)
CaO	54.0	25.0	54.69	43.00
MgO	0.36	1.37	0.51	1.09
CaCO <sub>3</sub>	96.23	44.68	97.60	76.74
MgCO <sub>3</sub>	0.75	2.87	1.05	2.27
calcite	95.34	41.27	96.66	73.97
dolomite	2.11	6.28	2.29	4.95

The black varieties, which are substantially mineralized were subjected to detailed mineralogical analyses. The residue left after dissolution of calcite in HCl has been found to contain; amiant (actinolite asbestos), antigorite, Mg-Fe chlorites, phlogopite, graphite, quartz, pyrrhotite, pyrite, siderite and tremolite. Those minerals were identified using X-ray diffractometry, IR absorption spectroscopy, DTA, as well as optical and electron microscopy. It has been found that the dominant accessory mineral is tremolite. Its detailed mineralogical description was given by Kwiecińska (1973). It is interesting to note that microscopic observations are consistent with IR analyses. The angle of extinction for tremolite crystals is 15—18°, which suggests the presence of the ferrotremolite member Ca<sub>2</sub>Fe<sub>3</sub><sup>2+</sup>[(OH)Si<sub>8</sub>O<sub>11</sub>]<sub>2</sub>. In the IR spectrum (Fig. 2) two additional bands appear in the range of 3652 and 3630 cm<sup>-1</sup>, evidencing the presence of a certain amount of Fe<sup>2+</sup> substituting for Mg<sup>2+</sup> in the crystal lattice (Burns, Strens 1966). In thin section tiny black plates showing concentric arrangement are visible on the surface of tremolite crystals. They are presumably microcrystalline graphite inclusions.



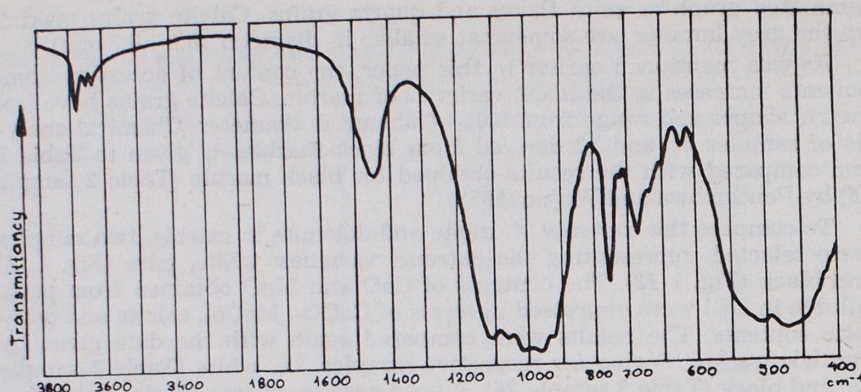
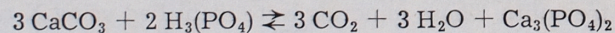


Fig. 2. Infrared spectrum of the tremolite from Przeworno

Electron microscopy was the only method capable of affording more precise mineralogical data on graphite. It has been noticed on the carbon-platinum replicas obtained from fresh fractures of black marbles that graphite appears in the form of very fine, irregular or rugged particles of the size up to some  $\mu\text{m}$ . Their electron diffraction patterns show the presence of weak (002) lines and distinct (100) (110) and (112) lines. They are evidence of the ordering of the structure of graphite. Identical electron diffractograms were obtained by one of the authors (B.K.) for graphite dispersed in the metamorphic rocks of Poland, originating from the amphibolite facies.

### MASS — SPECTROMETRIC MEASUREMENTS

A double collector mass spectrometer MICROMASS-602C for stable isotope of carbon and oxygen determination has been used. In spectrometer we can analyze the isotopic composition of C and O only in gas- $\text{CO}_2$  form. Carbon dioxide was obtained by treatment with phosphoric acid 100% from calcium carbonate:



The liberation of  $\text{CO}_2$  should be without changing of its  $^{13}\text{C}/^{12}\text{C}$  and  $^{18}\text{O}/^{16}\text{O}$  ratios. Detailed experimental procedure for the measurements is described by e.g. Barański (1976).

In the literature concerning fractionation effects of carbon stable isotopes in the investigated samples all results in  $\delta$  values (in permil ‰) are expressed.

$$\delta = \frac{C_{\text{sample}} - C_{\text{standard}}}{C_{\text{standard}}} \cdot 1000 \text{ (‰)}$$

where:

C = is the abundance ratio of carbon  $^{13}\text{C}/^{12}\text{C}$  or oxygen  $^{18}\text{O}/^{16}\text{O}$ .

Practically all  $\delta$  values are referred to the international standard PDB, whose isotopic ratios have been determined by Craig (1953, 1957). The standard PDB is the carbon dioxide obtained by treatment with  $\text{H}_3\text{PO}_4$  100% at  $25.2^\circ\text{C}$ , from the  $\text{CaCO}_3$  of the rostrum of a Cretaceous belemnite from the Pedee formation of South Carolina. Up to day this standard is not available any more, but other international standards are available for intercalibration e.g.

— NBS-20-Solenhofen limestone from National Bureau of Standards (Washington, USA), — Toilet Seat marble from International Atomic Energy Agency (Vienna, Austria), — Carrara Marble from University of Pisa (Italy).

In the Mass Spectrometry Laboratory of the Institute of Physics and Nuclear Techniques internal standard Marianna Biała marble has been calibrated versus PDB. Its values are reported in Table 3.

Analysis of the measurements of the IAEA and NBS standards shows a good correlation with the results obtained by other well established laboratories. The demonstrated reproducibility agrees with values generally quoted. The standard deviation of single determination of  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  is  $\pm 0.1\text{‰}$ .

In the varieties of marble in which dispersed graphitic substance was determined (grey and black varieties) the composition of stable carbon

Table 3  
International standards for C and O isotopes in ‰ vs PDB

Standards	$\delta^{13}\text{C}$	$\delta^{18}\text{O}$
Marianna Biała	+1.68	-5.70
Toilet Seat	+1.88	-1.88
Carrara Marble *	+2.40	-1.41
NBS-20	-1.06	-3.75

\* Results obtained from the Laboratorio di Geologia Nucleare dell'Università, Pisa, Italy in 1969.

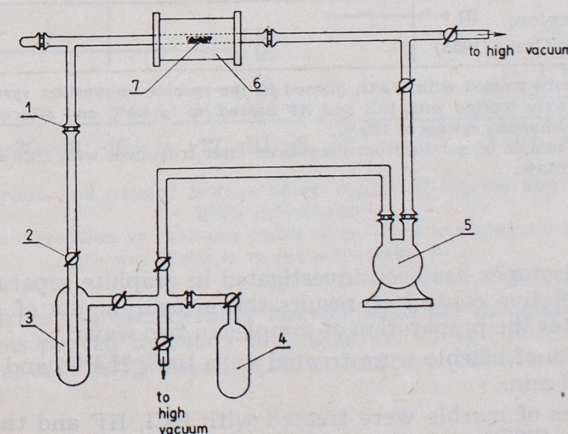


Fig. 3. Schematic diagram showing the graphite combustion arrangement  
1 — O-ring seal, 2 — vacuum valve, 3 — cold trap ( $\text{CO}_2$ ) 4 — measuring bottle for  $\text{CO}_2$ , 5 — circulating membrane pump, 6 — tubular furnace for combustion of samples, 7 — graphite sample mixed with oxidant ( $\text{CuO}$ )



Table 4

Carbon and oxygen isotope compositions of marble and graphite from Przeworno  
(in ‰ vs PDB)

Description of sample			$\delta^{13}\text{C}$				$\delta^{18}\text{O}$			
No	colour	grain size in mm	mar- ble	graphite			mar- ble	graphite		
				1*	2**	$\Delta$		1*	2**	$\Delta$
12	black	0.01—0.05	-1.7	-9.8	-11.6	1.8	-6.9	-22.7	-17.0	5.7
9b	dark		+1.0	-11.9	-10.0	1.9	-4.3	-17.4	-15.3	2.1
9a	light- grey	0.2—0.3	+1.2				-4.2			
9	grey		+0.8	-10.7	-12.1	1.4	-4.1	-18.2	-16.1	2.1
7	white- grey	0.5—0.8	+1.8				-2.9			
6b	black		+0.4	-11.0	-11.3	0.3	-4.6	-14.5	-17.9	3.4
6a	grey	0.01—0.05	+0.4	-11.1	-11.3	0.2	-1.7	-14.5	-10.5	4.0
6	dark		+0.8	-15.0	-16.4	1.4	-4.3	-10.8	-13.0	2.2
4	white- grey	0.5—0.8	+1.6				-2.4			
3	white	0.5—0.8	+2.4				-2.5			
1	white	0.5—0.8	+2.3				-2.6			
57***	grey	0.01—0.05			-9.0				-16.8	
18	Passava graphite			-19.3				-21.0		
61	Sri Lanka graphite			-8.7				-22.4		
Sri Lanka (Ceylon) graphite after Craig (1953)				-8.1						

\* Samples were treated with  $\text{H}_3\text{PO}_4$  burned in the special combustion system at  $1000^\circ\text{C}$ .

\*\* Samples were treated with HCl and HF heated up to  $400^\circ\text{C}$  and afterwards were burned in the special combustion system at  $1000^\circ\text{C}$ .

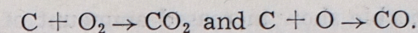
\*\*\* Average sample of marble from Przeworno after treatment with HCl and HF  $\sigma$  of single measurement =  $\pm 0.1\%$ .

and oxygen isotopes has been investigated in graphite separately. In order to get the relative control of results the measurements of graphite have been done after the preparation of samples in two ways:

1. Samples of marble were treated with  $100\%$   $\text{H}_3\text{PO}_4$  and burned at in  $1000^\circ\text{C}$  for 20 min.

2. Samples of marble were treated with HCl, HF and the yields were heated up to  $400^\circ\text{C}$  and afterwards were burned in the tubular furnace identically as in the first way. Schematic diagram for the graphite combustion arrangement is presented in Figure 3.

Oxidation process goes due to the following reaction



Particular attention was paid to complete combustion of graphite which was obtained, by multiple circulation of gas. This control is very important since entire oxidation of graphite to  $\text{CO}_2$  eliminates the possibility of formation of strong fractionation effect for both carbon and oxygen isotopes. A comparison of  $\delta^{13}\text{C}$  value obtained for samples received from both methods of graphite preparing shows the minor differences existing between the results of measurements (Table 4). The maximum difference in this case equal  $1.9\%$ .

The  $\delta^{13}\text{C}$  values obtained from graphite samples extracted from marble by second way (HCl, HF) there are in general more depleted in  $\text{C}^{13}$ . In one case (Fig. 1 sample 9b) the  $\delta^{13}\text{C}$  value is reversed.

## RESULTS

The results of stable carbon and oxygen isotope determinations obtained from marble and isolated graphitic substance which occur in Przeworno are shown in Table 4 and in Figure 4. A comparison of the isotopic composition of graphite and carbonate carbon illustrates that all samples of car-

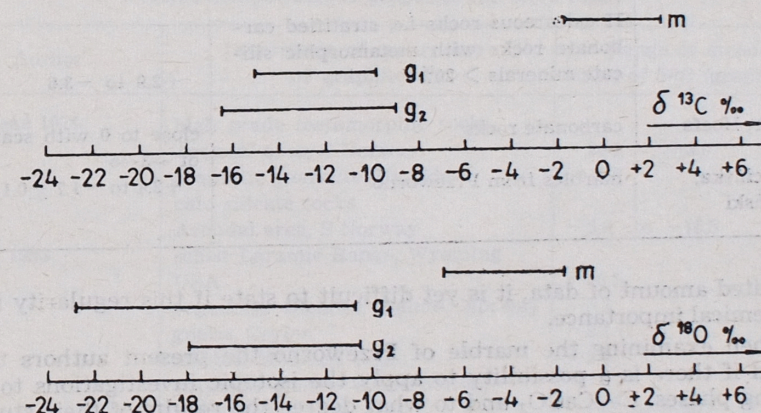


Fig. 4. Carbon and oxygen isotope compositions of marble and graphite from Przeworno

$g_1$  — graphite prepared by first way (Table 4),  $g_2$  — graphite prepared by second way (Table 4), m — marble (Table 4)

bonates in marble are considerably heavier than the associated coexisting graphite. It was proved by many investigators: Craig (1953, 1954), Hahn-Weinheimer *et al.* (1967), Gavelin (1957), Andreae (1974) and others.

## Marble

The  $\delta^{13}\text{C}$  value determined in marble fall in the range from  $+2.4$  to  $-1.7\%$  for whole profile of the northern and eastern walls of the quarry.



White varieties of marble show increased amount of heavy  $^{13}\text{C}$  isotope, whereas black variety (Fig. 1, sample 12) is the most decreased in  $^{13}\text{C}$ .

Besides, the analysis of  $^{13}\text{C}/^{12}\text{C}$  ratios obtained for individual marble samples revealed another regularity: the increase of grain size of calcite is accompanied by rising of concentration of  $^{13}\text{C}$  isotope. However, because

Table 5

Carbon isotope compositions of marbles and limestones in ‰ vs PDB

Author	Description of samples	Range or mean of $\delta^{13}\text{C}$ (carbonate)
Craig 1953	Ordovician, West Rutland marble	+0.9
	Cambrian Murphy marble	+1.0 $\sigma$
	Pre-cambrian Grenville marble	+3.1
Keith, Weber 1964	Precambrian limestones	-0.26 $\pm$ 3.09
	Cambrian to Quaternary limestone	-0.13 $\pm$ 2.61
	Cambrian to Quaternary selected limestones	+0.56 $\pm$ 1.55
Vinogradov, Kuleshov 1976	I stratified marbles with no or little silicate minerals	+2.7 to -1.3
	II calcareous rocks i.e. stratified carbonate rocks with metamorphic silicate minerals > 20%	+2.9 to -3.6
Veizer, Hoefs 1976	carbonate rocks	close to 0 with scatter of $\sim$ 3-5
Kwiecińska, Barański	marbles from Przeworno	+2.4 to -1.7 $\pm$ 0.1

of limited amount of data, it is yet difficult to state if this regularity is of geochemical importance.

When examining the marble of Przeworno the present authors tried to find if there is a possibility to apply the isotopic investigations to co-existing phases:  $\text{C}-\text{CaCO}_3$  and to what degree the results of their studies are comparable with the literature data.

Comparative study of  $\delta^{13}\text{C}$  value range for marble from Przeworno with  $\delta^{13}\text{C}$  values concerning other limestones and marbles reported by Craig (1953), Keith *et al.* (1964), Keith and Weber (1964), Veizer and Hoefs (1976), Vinogradov and Kuleshov (1976) showed a good agreement of the results (Table 5). The previously quoted authors generally agree with the statement, that in the most cases it is impossible to estimate the sources and processes which changed the isotopic composition of carbonates during their diagenesis and metamorphism. The investigators argue that all the anomalies e.g. variation of chemical activity of water, circulation of  $\text{CO}_2$  and decay of hydrocarbons display but very small influence on the average carbon isotopic composition of limestones. Besides, they state, that marbles fall within the limestone range and metamorphism of these rocks does not seem to have produced any striking isotopic change.

Craig (1953, 1954) and his followers (Galimov 1968, Veizer and Hoefs (1976), Keith and Weber (1964) suggested that there are no sign, no evidence of a pronounced age effect. Moreover, Sheppard and Schwarz (1970) stated that  $^{13}\text{C}/^{12}\text{C}$  ratio in essentially pure marble is largely inherited from the sedimentary precursor.

The oxygen isotopic composition does not reveal any regularities connected with light and dark varieties of marble.  $\delta^{18}\text{O}$  values vary from -1.7 to -6.9‰ vs PDB for whole profile in the quarry.

## Graphite

The  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values of graphite extracted from marble of Przeworno are presented in Figure 4. The  $\delta^{18}\text{O}$  values range from -10.5 to -22.7‰ and  $\delta^{13}\text{C}$  values vary from -9.0 to -16.4‰ vs PDB. Taking into account all the available, very often divergent data (Andreae 1974, Barker and Friedman 1969, Craig 1953, 1954, Degens 1969, Degens and Epstein 1964, Fairbridge 1972, Gavelin 1957, Galimov 1968, Hahn-Weinheimer *et al.* 1968, Hoefs 1973, Hoefs and Frey 1976, Polański 1961, Rankama 1954,

Table 6

Isotopic composition of graphites (in ‰ vs PDB)

Author	Description of occurrence of graphites	Range or mean value of $\delta^{13}\text{C}$ (graphite)
Andreae 1974	high grade metamorphic rocks	
	Arendal area, S Norway	-20.2 $\pm$ 3.9
	graphitic quartzite, Uganda	-18.7
Craig 1953	calc-silicate rocks	
	Arendal area, S Norway	-5.9 to -15.5
	schist Laramie Range, Wyoming USA	-35.5
	pegmatite Bleiklia, Bamle, Norway	-9.7
	gneiss, Ceylon	-8.1
	marble, Montana USA	-2.7
	graphitic gneiss, Westerbotten, N Sweden	-19.6 to -30.8
	phyllite, Norbotten, N Sweden	-27.2
	marble or limestone, Bavaria, GFR	-10 to -24
	gneiss or amphibolite, Bavaria, GFR	-14 to -26
Gavelin 1957 Hahn-Weinheimer, Markl, Raschka 1967 Hoefs, Frey 1976	carbonates from metamorphic profile of the Swiss Alp (up to lower greenschist facies)	-25
	carbonates from amphibolite facies of the Swiss Alp	-11
	graphitic carbonates, Norberg, Sweden	-8.9 to -11.2
	carbonates metamorphosed, Austria	-6.1 $\pm$ 1.5
Landergren vide Galimov 1968	marble from Przeworno, Poland	-9.0 to -16.4
Schoell, Morteand, Hörmann 1973		
Kwiecińska, Barański		



Schoell *et al.* 1973, Veizer and Hoefs 1976, Wickman 1956) and, simultaneously, distinct lack of sufficient evidences on geologic conditions of formation of graphite, the pattern of its isotopic composition cannot be definitely interpreted.

The compilation of  $\delta^{13}\text{C}$  values published by many above mentioned authors with those for graphite from Przeworno (Table 6) shows that variation range of  $^{13}\text{C}/^{12}\text{C}$  ratio for graphite dispersed in marble from Przeworno overlaps in general with those found for graphites derived from carbonate rocks of various regions of the whole world. In comparison with graphites from various metamorphic rocks like quartzite, phyllite, schist, amphibolite the graphite in question displays increased content of heavy isotope.

When assuming Proterozoic age for marble from Przeworno (Oberc 1966) and biogenic origin for graphite contained in it, we may look for the source of carbonaceous matter in water microorganisms of planktonic type, the remnants of which, preserved *in situ*, were found by electron microscopy (Kwiecińska and Siemińska 1973, 1974). Water micro-organisms when compared with continental ones are isotopically heavier (Craig 1953, Polański 1961) what is presumably reflected in  $^{13}\text{C}$  enrichment of resulting graphite. Biological activity e.g. photosynthesis of organic matter, processes of its decomposition,  $\text{CO}_2$  and  $\text{CH}_4$  circulation and then pyrolysis involved both organic and inorganic carbonate material have lead finally to formation of graphite. In these processes an interaction of organic matter with carbon derived from heavy carbonates and reaction with  $\text{CO}_2$  in gaseous phase cannot be entirely excluded. These reactions can also be the cause of increased content of heavy isotope  $^{13}\text{C}$  (Andreae 1974).

The results of investigations of marble from Przeworno have confirmed the thesis that carbonates in marble are isotopically heavier than the coexisting graphite. In this particular case they are enriched in  $^{13}\text{C}$  by approximately 10‰. However, at the moment the authors are not able to determine the correct factors for isotopic equilibrium in such environment. From the theoretical point of view this problem was a general topic of investigations and considerations carried out by Craig (1957) and Bottinga (1969). The latter author explained explicitly the carbon fractionation factors in the system calcite-graphite and finally concluded that isotope equilibrium cannot have been reached.

It is still a matter of dispute if such interpretation can be applied in our concrete case of marble from Przeworno.

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## SKŁAD TRWAŁYCH IZOTOPÓW WĘGLA W MARMURZE I GRAFICIE Z PRZEWORNA (DOLNY ŚLĄSK)

### Streszczenie

Przeprowadzono pomiary składu trwałych izotopów węgla i tlenu w marmurze występującym w Przewornie (Dolny Śląsk), przy zastosowaniu spektrometru mas MICROMASS-602C. Sprofilowano północną i wschodnią ścianę kamieniołomu i podano szczegółowy opis makro- i mikroskopowy wyróżnionych odmian marmuru. W odmianach ciemnych stwierdzono m.in. obecność tremolitu i grafitu. W graficie wyekstrahowanym z marmuru oznaczono również skład izotopów C i O. Wartości  $\delta^{13}C$  kształtują się odpowiednio: dla marmuru od +2,4 do -1,7‰ a dla grafitu od -9,0 do -16,4‰ względem PDB. Wyniki pomiarów porównano z danymi literaturowymi. Grafity rozproszony w marmurze z Przeworna jest wzbogacony w izotop  $C^{13}$  w porównaniu z innymi grafitami występującymi w skałach metamorficznych. Powodem zwiększonego udziału ciężkiego izotopu C może być biogeniczne pochodzenie grafitu z mikroorganizmów wodnych oraz możliwość wzajemnego oddziaływania węglanów i świata organicznego w czasie procesów bio- i geochemicznych.

### OBJAŚNIENIA DO FIGUR

Fig. 1. Profile północnej (N) i wschodniej (E) ściany kamieniołomu marmuru w Przewornie

I — ogniwo zbudowane z marmuru białego, II — ogniwo zbudowane z marmuru biało-szarego, smużastego, III — ogniwo zbudowane z czarnego marmuru, IV — ogniwo zbudowane z marmuru białego i wkładek smużastych, laminowanych, a — łupki stropowe amfibolowo-serycytowe, b — marmur laminowany, smużasty, c — marmur biały, d — marmur czarny, e — marmur białoszary, 1-12 — numery próbek

Fig. 2. Widmo absorpcyjne w podczerwieni tremolitu z Przeworna

Fig. 3. Schemat stanowiska spalania próbek granitu

1 — złącze próżniowe typu O-ring, 2 — szlifowany zawór próżniowy, 3 — wymrażarka  $CO_2$ , 4 — zbiornik pomiarowy na  $CO_2$ , 5 — membranowa pompa cyrkulacyjna, 6 — piec do spalania próbek, 7 — próbka grafitu wymieszana z utleniaczem CuO

Fig. 4. Skład izotopowy węgla i tlenu w marmurze i w graficie z Przeworna

$g_1$  — grafity przygotowane do pomiarów pierwszym sposobem (tab. 4),  $g_2$  — grafity przygotowane do pomiarów drugim sposobem (tab. 4), m — marmur (tab. 4)

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## СОСТАВ СТАБИЛЬНЫХ ИЗОТОПОВ УГЛЕРОДА В МРАМОРЕ И ГРАФИТЕ ИЗ ПШЕВОРНА (НИЖНЯЯ СИЛЕЗИЯ)

### Резюме

Производились измерения состава стабильных изотопов углерода и кислорода в мраморе из Пшеворна (Нижняя Силезия), путём использования спектрометра массы MICROMASS-602C. Был сделан профиль северной и восточной стены каменоломни и были составлены подробные макроскопическое и микроскопическое описания выделенных разновидностей мрамора. В темных разновидностях обнаружено, между прочими, присутствие тремолита и графита. В графите добытом из мрамора измерено также состав изотопов C и O. Величины  $\delta^{13}C$  равны соответственно: для мрамора от +2,4 до -1,7‰, а для графита от 9,0 до -16,4‰ относительно PDB. Результаты измерений были сравнены с литературными данными. Графит содержащийся в мраморе из Пшеворна обогащён изотопом  $C^{13}$  по сравнению с другими графитами, которые были найдены в метаморфических породах. Причиной увеличенного количества тяжёлого изотопа C может быть биогеническое происхождение графита из водных микроорганизмов и возможность взаимодействия бикарбонатов и органического мира во время био- и геохимических процессов.

### ОБЪЯСНЕНИЯ К ФИГУРАМ

Фиг. 1. Профили северной (N) и восточной (E) стены каменаламни мрамора в Пшеворне

I — звено состоящее из белого мрамора, II — звено состоящее из бело-серого, полосатого мрамора, III — звено состоящее из чёрного мрамора, IV — звено состоящее из белого мрамора и полосатых, мелкослоистых вкладышей, a — верхние амфиболо-серицитовые сланцы, b — мелкослоистый, полосатый, мрамор, c — белый мрамор, d — чёрный мрамор, e — бело-серый мрамор, 1-12 — номера образцов

Фиг. 2. ИК-спектр поглощения тремолита из Пшеворна

Фиг. 3. Схема стенда для сжигания образцов графита

1 — вакуумное соединение типа O-ринг, 2 — шлифованный вакуумный клапан, 3 — выморозитель  $CO_2$ , 4 — измерительный бак для  $CO_2$ , 5 — циркуляционный насос с мембраной, 6 — печь для сжигания образцов, 7 — образец графита смешанный с окислителем CuO

Фиг. 4. Изотопный состав углерода и кислорода в мраморе и графите из Пшеворна

$g_1$  — графит приготовленный для измерений 1-ым способом (таб. 4),  $g_2$  — графит приготовленный для измерений 2-ым способом (таб. 4), m — мрамор (таб. 4)