

Stable Isotopes Carbon C¹³ and Oxygen O¹⁸ as Indicators of Triassic Limestone Sedimentation Environment and Diagenesis

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Research Article

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Abstract

The results of researches of the stable isotopes, carbon ^{13}C and oxygen ^{18}O , measured in Triassic limestones of Opole Silesia in Poland were presented in this article. The study was carried out to obtain data for interpretation of the environment of these rocks formation. Moreover, it was possible to form the theory about diagenetic processes which influenced on the mineral composition of limestone and some of their carbonate phases.

The results of study show a general differentiation of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ contents in carbonate minerals. All $\delta^{18}\text{O}$ values are less than 0 ‰. It indicates that the origin oxygen isotope composition could be probably reset by diagenesis. The crystallization temperatures of low-Mg calcite and high-Mg, calculated on the basis of $\delta^{18}\text{O}$ values are greater than 25 °C. They are higher than typical for sea basin and are also not be related to the presence of hydrothermal solutions. The increased temperatures of calcites crystallization are related to diagenetic processes that took place after the deposition and burial of carbonate material. The preservation of high-Mg calcite, an unstable carbonate phase, which is usually transformed into low-Mg calcite during diagenesis, is probably connected with the increased salinity of the sea basin in which studied limestones were formed.

1. Introduction

Stable isotopes, carbon ^{13}C and oxygen ^{18}O , are usually measured for interpretation of the environment of rock formation (Migaszewski, 1986, 1989; Migaszewski, 1990a,b; Morse and Mackenzie, 1990; Hałas et al., 1993; Migaszewski et al., 1996; Hałas, 1997; Dolenc et al., 2003; Lécuyer et al., 2012; Pearson, 2012; Levitt et al., 2018). The results of stable isotope measurements are given in the form of δ value (Migaszewski, 1989; Tripathi et al., 2010). It is defined as the deviation of the isotope ratio from the standard value. The standards used for determining ^{13}C and ^{18}O isotopes are PDB (Pee Dee Belemnite) standard (a chalk belemnite rostrum from Pee Dee Formation in South Carolina) or V-SMOW standard (Standard Mean Ocean Water – average oceanic water) (Migaszewski et al., 1995).

Stable isotope geochemistry has been also used as an indicator of palaeoclimate. The potential oxygen isotope compositions could be used for palaeotemperature reconstruction (McCrea, 1950; Epstein et al., 1951, 1953; Urey et al., 1951; Friedman and O'Neil, 1977; Tucker and Wright, 1990; Romanek et al., 1992; Leng and Marschal, 2004; White, 2013; Henkes et al., 2014). A problem in the quantitative interpretation of the climate geochemical factors is that the variables that can be measured in the sediments, especially $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ in carbonates, are influenced by a wide range of interlinked environmental processes and not a single factor (McCrea, 1950; Urey et al., 1951; Leng and Marschal, 2004). A change in temperature will be able to produce a shift in the equilibrium oxygen isotope composition of carbonates forming in lakes, will affect the isotope composition of the rainfall and may also affect rates of evaporation, both in the lake and in the catchment (Leng and Marschal, 2004; Ghosh et al., 2006).

Limestones are one of the most important of all the sedimentary rocks used in different branches of industry. They are composed mostly of calcite mineral (CaCO_3 – low magnesium calcite). Sometimes

includes other carbonate phases, like high-Mg calcite, protodolomite, ordered dolomite or huntite. These carbonate phases were identified in Triassic limestones of Polish part of Germanic Basin (South-West part of Poland – area of the Opole Silesia) (Szulc, 1990, 2000; Stanienda, 2005, 2006, 2011, 2013a,b; 2016a,b; Stanienda-Pilecki, 2018, 2019, 2021). There are numerous Triassic limestone deposits in this territory. These limestones are Lower Muschelkalk (Middle Triassic) sediments. The Muschelkalk profile contains Gogolin Beds (the bottom of profile – initial sea transgressive stage), Górażdże Beds (advanced sea transgression stage), Dziewkowice (Terebratula) Beds (sea transgression peak stage) and Karchowice Beds (the upper formation of profile – sea regression stage). The formation names are regional. They come from the names of nearby towns. The limestones of these units are built of carbonate phases different in Ca and Mg content.

The results of researches of the stable isotopes Carbon C^{13} and Oxygen O^{18} , measured in the carbonate minerals – low-Mg calcite, high-Mg calcite and dolomite, of the Triassic limestones of the Opole Silesia in Poland were presented in this article. Moreover, the temperature of low-Mg calcite and high-Mg calcite crystallization was calculate based of the results of stable isotope Oxygen O^{18} content. On the basis of the research results, the theory connected with the conditions of carbonate minerals formation and possible diagenetic processes was presented there.

2. Materials And Methods

The samples for laboratory tests of the stable isotopes Carbon C^{13} and Oxygen O^{18} content were collected in different places of the Opole Silesia: in Gogolin Quarry (samples G1, G6), Ligota Dolna Quarry (samples LD9, LD11), the area of Saint Anne Mountain (samples SA2, SA5, SA12), Strzelce Opolskie Quarry (samples SO1, SO14, SO17, SO20), Szymiszów Quarry (sample S8), Wysoka Quarry (samples W1, W5) and Tarnów Opolski Quarry (samples T7, T15, T62) (Fig. 1). In all 17 samples were analysed: 4 samples from Gogolin Unit (G1, G6, LD9, LD11), 3 – from Górażdże Unit (SA5, W1, W5), 3 – from Terebratula (Dziewkowice) Unit (SA12, SO1, S8) and 7 – from Karchowice Unit (SA2, SO14, SO17, SO20, T7, T15, T62).

The measurements were carried out in the Mass Spectrometry Laboratory in Lublin (Institute of Physics of the Maria Curie-Skłodowska University) using a mass spectrometer on CO_2 gas samples prepared from original geological samples.

The quantities of $^{13}C/^{12}C$ and $^{18}O/^{16}O$ were determined in the samples. Then values of $\delta^{13}C$ and $\delta^{18}O$ of calcite, magnesium calcite and dolomite in PDB scale were calculated. CO_2 from calcites and magnesium calcites was separated at the temperature $25^\circ C$, using a reaction time of 1 h and 24 h. Delta values were normalized according to the NBS-19 standard to the VPDB scale. CO_2 of dolomites were separated at the temperature $50^\circ C$, after CO_2 separation from the calcite fraction (at the temperature $25^\circ C$).

3. Results Of Study

Seventeen samples taken from all four limestone formations were selected for studies of stable isotopes $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$. The values of $^{13}\text{C}/^{12}\text{C}$ and $^{18}\text{O}/^{16}\text{O}$ were determined in these samples and calculated on the PDB $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ scale of low magnesium calcite (Fig. 2a), high magnesium calcite (Fig. 2b) and dolomite (Fig. 2c) (Stanienda, 2011, 2013a). The results are presented in Table 1 and in the Figures from 3 to 6.

Table 1
Carbon and oxygen stable isotope values in the PDB scale (Stanienda 2011, 2013a).

No	Sample number	$\delta^{13}\text{C}_{\text{VPDB}} [\text{‰}]$			$\delta^{18}\text{O}_{\text{VPDB}} [\text{‰}]$		
		low-Mg calcite	high-Mg calcite	dolomite	low-Mg calcite	high-Mg calcite	dolomite
1	G1	0.37	-1.56	-0.45	-3.55	-4.36	-5.81
2	G6	-0.72	-2.30	-0.84	-7.47	-8.23	-7.86
3	LD9	1.44	0.79	2.08	-6.76	-5.19	-1.07
4	LD11	1.83	2.05	2.08	-5.17	-4.08	-6.36
5	SA5	-1.49	-1.08	-0.18	-9.84	-8.10	-8.29
6	W1	0.05	0.61	0.62	-8.35	-7.84	-7.67
7	W5	1.32	1.95	1.25	-9.12	-2.02	-7.20
8	SA12	-0.30	-0.31	0.97	-7.34	-6.36	-7.05
9	S01	-0.36	-0.65	1.03	-9.08	-8.12	-8.06
10	S8	-0.80	-0.14	0.01	-9.21	-6.28	-7.77
11	SA2	-8.12	-8.28	-7.15	-8.26	-6.41	-8.42
12	S014	0.13	1.12	2.68	-8.99	-7.04	-8.09
13	S017	-0.71	2.62	2.12	-8.85	-6.43	-9.17
14	S020	-2.61	-2.33	-1.90	-10.39	-8.76	-9.33
15	T7	-0.32	-	2.99	-7.97	-	-8.37
16	T15	-3.50	-	1.31	-8.19	-	-8.39
17	T62	-2.66	-	2.35	-7.84	-	-5.01

In samples taken from the **Gogolin Unit** these values are: $\delta^{13}\text{C}$, from -0.72 to 1.83‰ and $\delta^{18}\text{O}$, from -7.47 to -3.55‰ for low magnesium calcite, $\delta^{13}\text{C}$, from -2.30 to 2.05‰ and $\delta^{18}\text{O}$, from -8.23 to -4.08‰ for high magnesium calcite, and $\delta^{13}\text{C}$, from -0.84 to 2.08‰ and $\delta^{18}\text{O}$, from -7.86 to -1.07‰ for dolomite (Stanienda, 2013a).

In samples taken from the **Góraźdże Unit** these values are: $\delta^{13}\text{C}$, from -1.49 to 1.32‰ and $\delta^{18}\text{O}$, from -9.84 to -8.35‰ for low magnesium calcite, $\delta^{13}\text{C}$, from -1.08 to 1.95‰ and $\delta^{18}\text{O}$, from -8.10 to -2.02‰ for high magnesium calcite, and $\delta^{13}\text{C}$, from -0.18 to 1.25‰ and $\delta^{18}\text{O}$, from -8.29 to -7.20‰ for dolomite (Stanienda, 2013a).

In samples taken from the **Terebratula (Dziewkowice) Unit** these values are: $\delta^{13}\text{C}$, from -0.80 to -0.30‰ and $\delta^{18}\text{O}$, from -9.21 to -7.34‰ for low magnesium calcite, $\delta^{13}\text{C}$, from -0.65 to -0.14‰ and $\delta^{18}\text{O}$, from -8.12 to -6.28‰ for high magnesium calcite, and $\delta^{13}\text{C}$, from 0.01 to 1.03‰ and $\delta^{18}\text{O}$, from -8.06 to -7.05‰ for dolomite (Stanienda, 2013a).

In samples taken from the **Karchowice Unit** these values are: $\delta^{13}\text{C}$, from -8.12 to 0.13‰ and $\delta^{18}\text{O}$, from -10.39 to -7.84‰ for low magnesium calcite, $\delta^{13}\text{C}$, from -8.28 to 2.62‰ and $\delta^{18}\text{O}$, from -8.76 to -6.41‰ for high magnesium calcite, and $\delta^{13}\text{C}$, from -7.15 to 2.99‰ and $\delta^{18}\text{O}$, from -9.33 to -5.01‰ for dolomite (Stanienda, 2011, 2013a).

The results of researches indicate a visible variation in content $\delta^{13}\text{C}$ in low-Mg calcite, high-Mg calcite and dolomite of analyzed samples (Figures 3 to 5). The lowest values of $\delta^{13}\text{C}$ present sample SA2 (Table 1). The values of $\delta^{13}\text{C}$ in low-Mg calcite for this sample is -8.12‰, in high-Mg calcite – -8.28‰ and in dolomite – -7.15‰. Less differentiation in the content is observed in the case of $\delta^{18}\text{O}$ (Figures 6 to 8).

The results obtained during the analyses of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ for calcite, high-magnesium calcite and dolomite are in many cases similar to the test results of samples taken from Strzelce Opolskie Deposit, investigated by J. Szulc (1990, 2000). Sometimes, the values of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of magnesium calcite, are between the values of "pure" calcite and dolomite, but such regularity is not always observed.

The determined $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values were converted on the SMOW scale, using the Friedman and O'Neil formula (1997) (1) (Graf and Goldsmith, 1982).

$$\delta_{\text{SMOW}} = 1,03086 * \delta_{\text{PDB}} + 30,86 \quad (1)$$

were:

δ_{SMOW} – delta value on the SMOW scale

δ_{PDB} - delta value on the PDB scale

The results were presented in the Table 2.

Table 2
Carbon and oxygen stable isotope values in the SMOW scale (Stanienda 2011, 2013a).

No	Sample number	$\delta^{13}\text{C}_{\text{SMOW}}$ [‰]			$\delta^{18}\text{O}_{\text{SMOW}}$ [‰]		
		low-Mg calcite	high-Mg calcite	dolomite	low-Mg calcite	high-Mg calcite	dolomite
1	G1	31.24	29.25	30.40	27.20	26.36	24.87
2				29.99			22.76
	G6	30.12	28.49		23.16	22.38	
3	LD9	32.34	31.67	33.00	23.89	25.51	29.76
4	LD11	32.75	32.97	33.00	25.53	26.65	24.30
5	SA5	29.32	29.75	30.67	20.72	22.51	22.31
6	W1	30.91	31.49	31.50	22.25	22.78	22.95
7	W5	32.22	32.87	32.15	21.46	28.78	23.44
8	SA12	30.55	30.54	31.86	23.29	24.30	23.59
9	S01	30.49	30.19	31.92	21.50	22.49	22.55
10	S8	30.04	30.72	30.87	21.37	24.39	22.85
11	SA2	22.49	22.32	23.49	22.35	24.25	22.18
12	S014	30.99	32.01	33.62	21.59	23.60	22.52
13	S017	30.13	33.56	33.05	21.74	24.23	21.41
14	S020	28.17	28.46	28.90	20.15	21.83	21.24
15	T7	30.53	-	33.94	22.64	-	22.23
16	T15	27.25	-	32.21	22.42	-	22.21
17	T62	28.12	-	33.28	22.78	-	25.69

Analyzing the results presented in Table 2, the tendency of an increase (in the case of 9 samples) in the content of $\delta^{13}\text{C}_{\text{SMOW}}$ from "pure" calcite to dolomite was observed.

The exceptions are:

- samples G1, G6 (limestones of Gogolin Unit, from Gogolin Quarry), LD9 (limestone of Gogolin Unit, from Ligota Dolna Quarry), SA2 (limestone of Karchowice Unit, from the area of Saint Anne Mountain), SA12 (limestone of Terebratula Unit, from the area of Saint Anne Mountain), S01 (limestone of

Terebratula Unit, from Strzelce Opolskie Quarry)- the $\delta^{13}\text{C}_{\text{SMOW}}$ value of high-Mg calcite is lower than the values of low-Mg calcite and dolomite;

- sample S017 (limestone of Karchowice Unit, from Strzelce Opolskie Quarry)- the $\delta^{13}\text{C}_{\text{SMOW}}$ value of dolomite is lower than the value of high-Mg calcite but higher than the value of low-Mg calcite;
- sample W5 (limestone of Góraźdże Unit, from Wysoka Quarry)- the $\delta^{13}\text{C}_{\text{SMOW}}$ value of dolomite is lower than the values of high-Mg calcite and low-Mg calcite.

The SA2 sample should be treated as specific because it was collected in the area of Saint Anne Mountain, from the Palaeogene-Neogene buffer zone, between limestone and basalt intrusion.

However, it is difficult to explain the reduced value of $\delta^{13}\text{C}_{\text{SMOW}}$ in Mg-calcite, compared to low-magnesium calcite, in samples LD9 and S01, which come from different formations. LD9 sample represent the limestone of Gogolin Unit and S01- is limestone of Terebratula Unit.

However, no specific dependencies were observed in the case of differences in the content of $\delta^{18}\text{O}_{\text{SMOW}}$ in the analyzed carbonate phases, apart from the increased content of $\delta^{18}\text{O}_{\text{SMOW}}$ of magnesium calcite, in relation to "pure" calcite and dolomite, in nine of the analyzed samples – LD11, SA5, W5, SA12, S8, SA2, S014, S017 and S020. Five of them are limestone of the Karchowice Unit, two samples belong to Góraźdże Unit, one sample comes from Gogolin Unit and one – from Terebratula Unit.

Based on the obtained results, the crystallization temperatures of low-Mg calcite and high-Mg calcite were calculated according to the Epstein formula (1953) (2) for low temperatures (Fairbridge, 1950) (Table 3).

$$T [^{\circ}\text{C}] = 16,5 - 4,3 * (\delta_{\text{c}} - \delta_{\text{w}}) + 0,14 * (\delta_{\text{c}} - \delta_{\text{w}})^2 \quad (2)$$

where:

δ_{c} - delta ^{18}O of calcite on the PDB scale

δ_{w} - delta ^{18}O of water in the SMOW scale, $\delta^{18}\text{O}_{\text{SMOW}} = 0\text{‰}$

Table 3 Calcite crystallization temperatures calculated according to Epstein's formula (1953).

No	Sample number	T [°C]	
		low-Mg calcite	high-Mg calcite
1	G1	43.53	37.91
2	G6	56.43	61.37
3	LD9	51.96	42.59
4	LD11	42.47	36.37
5	SA5	72.37	60.51
6	W1	62.17	58.82
7	W5	67.36	25.76
8	SA12	55.60	49.51
9	S01	67.05	60.65
10	S8	67.98	49.02
11	SA2	61.57	49.81
12	S014	66.47	53.71
13	S017	65.52	49.94
14	S020	76.29	64.91
15	T7	59.66	-
16	T15	61.10	-
17	T62	58.82	-

The results of calculations show that the temperature values are higher than 25 °C. Therefore these values are too high for the seawater temperature, even if there would be strong evaporation in a very warm climate. Moreover, the results show that in most of samples the crystallization temperature of low-Mg calcite is higher than the temperature of high-Mg calcite crystallization. The exception presents one sample- G6 for which the reverse relationship is observed. It is the limestone of Gogolin Unit.

4. Discussion

The $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of calcite and dolomite are related to the conditions of the environment in which these minerals were formed (Hałas, 1997; Tripathi et al., 2010).

The average values of $\delta^{13}\text{C}$ of carbonates formed in the past and today are respectively in the range from -32 to 4‰, and the average values of $\delta^{18}\text{O}$, in the range from -22.12 to 0.5‰ in limestones (Migaszewski, 1989; Colombié et al., 2011; Huntington et al., 2011; Lécuyer et al., 2012; Kluge and John, 2015; Kelson et

al., 2017; Davies and John, 2019; MacDonald et al., 2019) and from 0.5 to 4.5‰ in dolomites (Migaszewski, 1989). Values of $\delta^{13}\text{C}$, in the range from -1.21 to 3.17‰ and $\delta^{18}\text{O}$, from -6.7 to 0.23‰, are characteristic for Triassic dolomites from the area of Chrzanów (Migaszewski, 1986).

The results of researches show that the values of $\delta^{13}\text{C}$ of low-Mg calcite are in the range from -8.12 to 1.83‰, that of high-Mg calcite vary from -8.28 to 2.62‰ and the values of dolomite are in the range from -7.15 to 2.99‰ (Table 1, Figures 3 to 5). Therefore, a general differentiation of the $\delta^{13}\text{C}$ content in carbonate minerals of studied samples was observed. However, there is no relations between the value of $\delta^{13}\text{C}$ and belonging the samples to any of the four units occurring in the analyzed profile. Samples from each formation vary in content of $\delta^{13}\text{C}$. Therefore, there is no relations between $\delta^{13}\text{C}$ content and the type of the stage of sea transgression or regression.

The results of researches show that the average values of $\delta^{18}\text{O}$ vary in the range from -10.39 to -3.55‰ in low-Mg calcite, from -8.76 to -2.02‰ in high-Mg calcite and from -9.33 to -1.07‰ in dolomite (Table 1, Figure 6 to 8). Therefore, also in the case of $\delta^{18}\text{O}$, a general differentiation of $\delta^{18}\text{O}$ content in carbonate minerals of studied samples was observed. However all values are less than 0‰. Low $\delta^{18}\text{O}$ values are usually measured in diagenetic products such as cement or vein calcite (Ha et al., 2019). Low values of $\delta^{18}\text{O}$ indicate that the primary oxygen isotope composition of the studied carbonates could be reset by diagenesis. There is also no relations between $\delta^{18}\text{O}$ content and the type of the stage of sea transgression or regression.

The calculated crystallization temperatures of low-Mg calcite and high-Mg calcite are greater than 25°C. Results of researches show that there is no relationship between the value of $\delta^{13}\text{C}$ of low-Mg calcite and high-Mg calcite and the crystallization temperature of these carbonate phases (Figures 9 and 10). However, a relationship between the value of $\delta^{18}\text{O}$ of low-Mg calcite and high-Mg calcite and the crystallization temperature of these carbonates was observed (Figures 11 and 12). The crystallization temperature of low-magnesium calcite and high-magnesium calcite increases as the of $\delta^{18}\text{O}$ value decreases. This relationship is almost linear (Figures 11 and 12).

The results of the earlier conducted research show that the isotope exchange of oxygen takes place between minerals and seawater at elevated temperatures (Epstein et al., 1953; Tucker and Wright, 1990; Hałas et al., 1993). Therefore, the value of $\delta^{18}\text{O}$ of primary carbonates depends on the $\delta^{18}\text{O}$ of seawater, and also on the temperature at which their crystallization takes place and the isotope exchange is completed (Migaszewski, 1989; Huntington et al., 2011). Usually, slowly crystallizing calcite can be formed in the temperature range from about -1 °C to about 79 °C (McCrea, 1950). Calcite crystallizing from seawater is usually formed at temperatures between 14 and 29°C (Epstein et al., 1953; Ghosh et al., 2006; Lécuyer et al., 2012; Pearson, 2012; Levitt et al., 2018). Crystallization temperatures of dolomites are inversely correlated with $\delta^{18}\text{O}$ values. Calculated $\delta^{18}\text{O}_{\text{VSMOW}}$ values for water in equilibrium with dolomites are correlated with crystallization temperatures (Ryb and Eiler, 2018). According to the influence of diagenesis processes on changes occurring in mineral phases, it should be considered what extent

carbonate minerals retain their initial isotopic composition (Hałas et al., 1993; White, 2013). Carbonates easily undergo recrystallization processes in conditions of low temperature, also in the initial stages of diagenesis. It leads to significant changes in their isotopic composition. Therefore, it is much easier to determine the processes of mineral transformations than the original conditions of their formation, especially in the case of older rocks. The high variability of the $\delta^{18}\text{O}$ value (from approx. -20 to -7‰) indicates the hydrothermal origin of the minerals, because during these processes the hydrothermal solutions are cooled, mainly in contact with air (Illing, 1959; Hałas et al., 1993; Migaszewski et al., 1996; Ryb and Eiler, 2018).

The calculated crystallization temperatures of low-Mg calcite vary in the range from 43.53 °C to 76.29 °C, the temperature values of high-Mg calcite changes in the range from 25.76 °C to 64.91 °C. These temperatures are higher than the temperatures of calcium carbonates crystallization from the seawater. Increased calcites crystallization temperatures are also not be related to the presence of hydrothermal solutions, but rather to diagenetic processes that took place after the deposition of carbonate material in the sea basin. At elevated temperatures, during diagenetic processes recrystallization of carbonate minerals are going. It usually happened after the burial (Ryb and Eiler, 2018; Leutert et al., 2019; Veillard et al., 2019).

Due to the research results it is necessary to consider the conditions of the basin environment in which the studied limestones were formed. It is also necessary to analyse the conditions in which the diagenetic processes took place. During these processes despite the influence of high temperatures and pressures (characteristic of advanced diagenetic processes) on the sediment, the unstable carbonate phase – high-magnesium calcite was preserved. Therefore, it can be concluded that the studied limestones underwent to diagenetic processes, during which the isotopic composition changed, and carbonate minerals at elevated temperatures underwent recrystallization, agradation and neomorphic processes. High-Mg calcite, an unstable carbonate phase, which, such as aragonite, is usually transformed during burial into low-Mg calcite. The preservation of this carbonate phase is probably connected with the increased salinity of sea basin in which studied limestones were formed. Analyzing the processes, which influence on the Muschelkalk limestones of the Opole Silesia (South-West part of Poland) formation it is necessary to remember that the Triassic sediments of the South-West part of Poland are the sediments of the East part of the Epicontinental Germanic Basin, shallow sea basin, probably characterized by increased salinity.

5. Conclusions

Stable isotopes, carbon ^{13}C and oxygen ^{18}O , were measured in Triassic (Muschelkalk) limestones from the area of Opole Silesia in Poland. Research was carried out to obtain data for interpretation of the environment of these rock formation and diagenetic processes which influenced on the present mineral composition of limestone and some properties of carbonate phases.

The results of $\delta^{13}\text{C}$ study show a general differentiation of the $\delta^{13}\text{C}$ content in carbonate minerals. Moreover, there is no relations between the $\delta^{13}\text{C}$ value and belonging the samples to any of the four units

occurring in the profile. A general differentiation of $\delta^{18}\text{O}$ content in carbonate minerals of studied samples was also observed. However all values are less than 0‰. It can indicate that the primary oxygen isotope composition of the studied carbonates could be reset by diagenesis. There is also no relations between $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ contents and the type of the stage of sea transgression or regression.

The crystallization temperatures of low-Mg calcite and high-Mg calcite calculated on the basis of the of $\delta^{18}\text{O}$ are greater than 25 °C. Therefore, they are temperatures higher than typical for sea basins. Increased crystallization temperatures are also not be related to the presence of hydrothermal solutions. They are rather related to diagenetic processes that took place after the deposition and burial of carbonate material.

However, the presence of high-magnesium calcite in the studied limestones should be explained. This carbonate phase is unstable and such as aragonite is usually transformed into low-magnesium calcite during diagenesis. The results of my study show a differentiation of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ contents in high-Mg calcite and crystallization temperature higher than 25 °C. Therefore, it should be explained how this carbonate phase was preserved. I suggest that it may be connected with the increased salinity of sea basin in which studied limestones were formed. We know that the carbonate rocks of the area of Opole Silesia were formed in the shallow sea which was the Eastern part of the Epicontinental Triassic Germanic Basin. The water of this basin was probably characterized by increased salinity. It might explain why high-Mg calcite – an unstable phase was preserved in studied limestones.

Declarations

Author contribution

I am the only author of this article. All published results are the results of my own research. The interpretation and analysis of the results of the research were done by myself.

Ethical statements

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Conflicts of interest/Competing interests- No conflict of interest.

Ethics approval- The results of this manuscript are presented clearly, honestly and without fabrication, falsification or inappropriate data manipulation. I have followed editorial ethics and academic ethics in this manuscript. I have not used any unethical languages in any part of the manuscript.

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Consent to participate- I have used scientific method of research.

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Figures

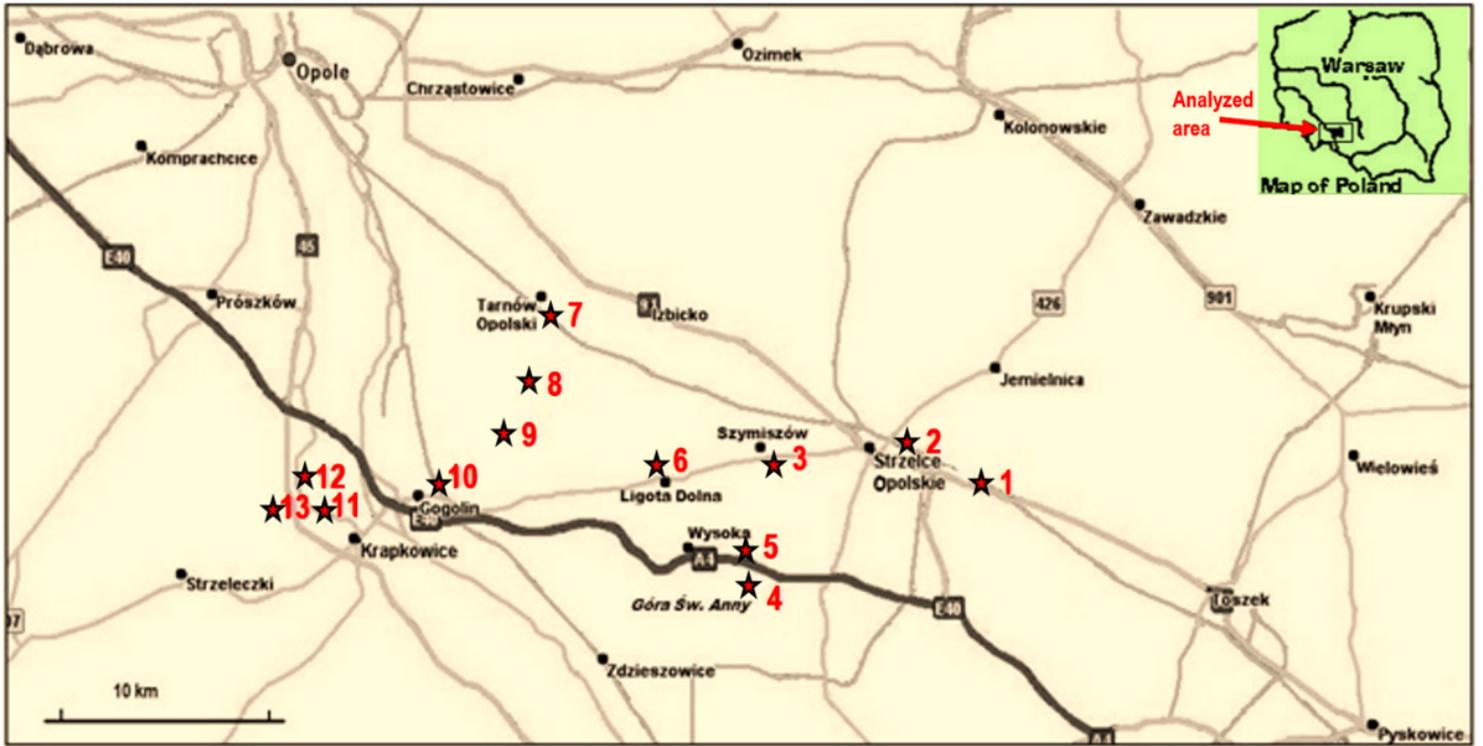


Fig. 1 Location of quarries and exposures of Triassic rocks in the study area

1- Błotnica Strzelecka; 2- Dziewkowice; 3- Szymiszów; 4- Saint Anne Mountain; 5- Wysoka; 6- Ligota Dolna and Kamienna; 7- Tarnów Opolski; 8- Kamień Śląski; 9- Górażdże and Kamionek; 10- Gogolin; 11- Malnia; 12- Chorula; 13- Rogów Opolski

★ areas of sampling

Figure 1

See image above for figure legend.

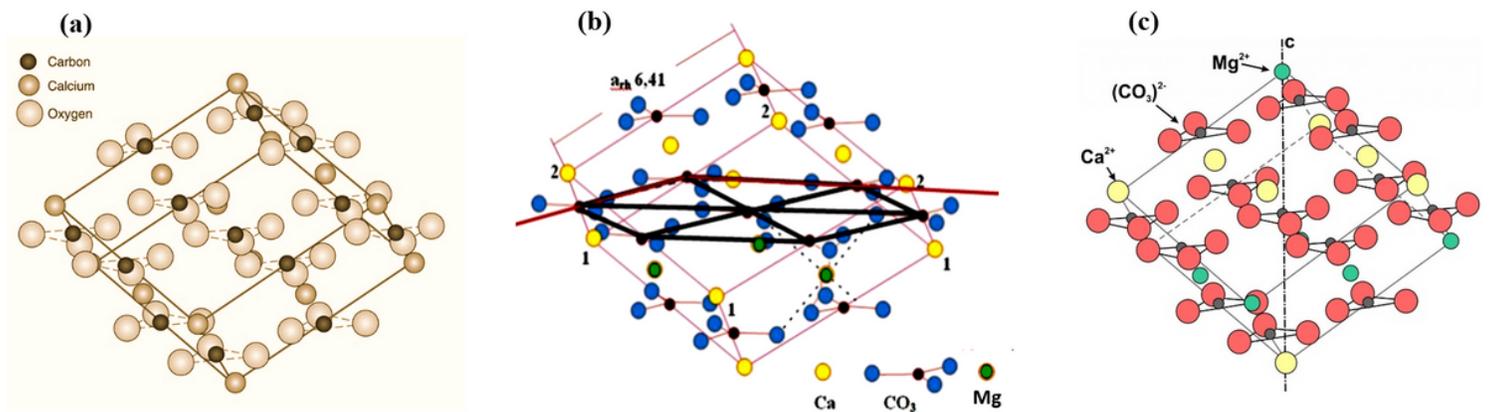


Figure 2

Crystal structures of analysed minerals: (a) low-Mg calcite (Shaffer, 2021); (b) high-Mg calcite (Stanienda, 2013a); (c) dolomite (Papeschi, 2021)

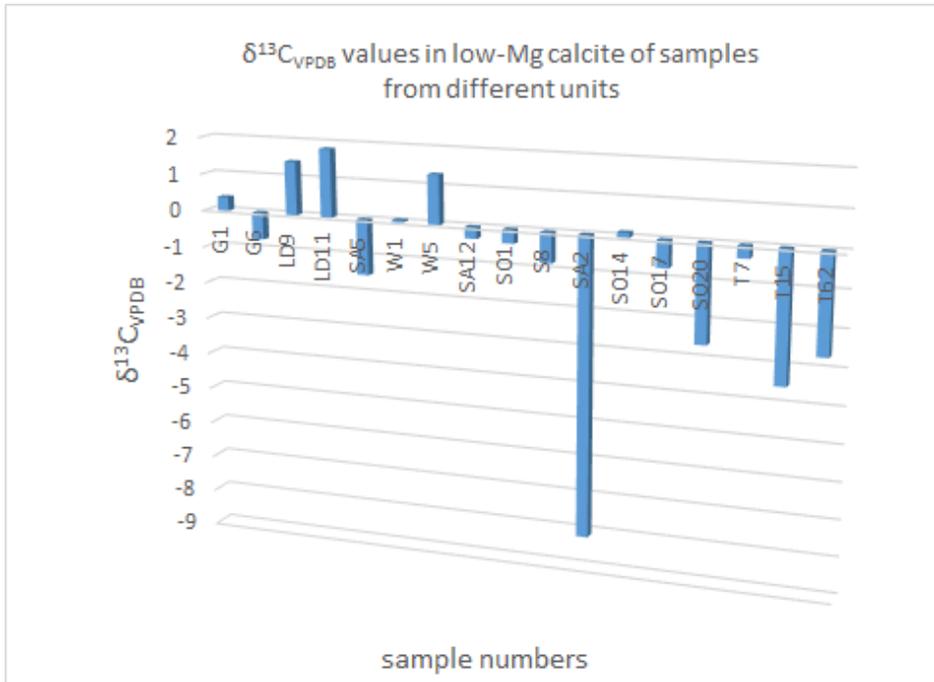


Figure 3

$\delta^{13}\text{C}_{\text{VPDB}}$ values in low-Mg calcite of samples from different units

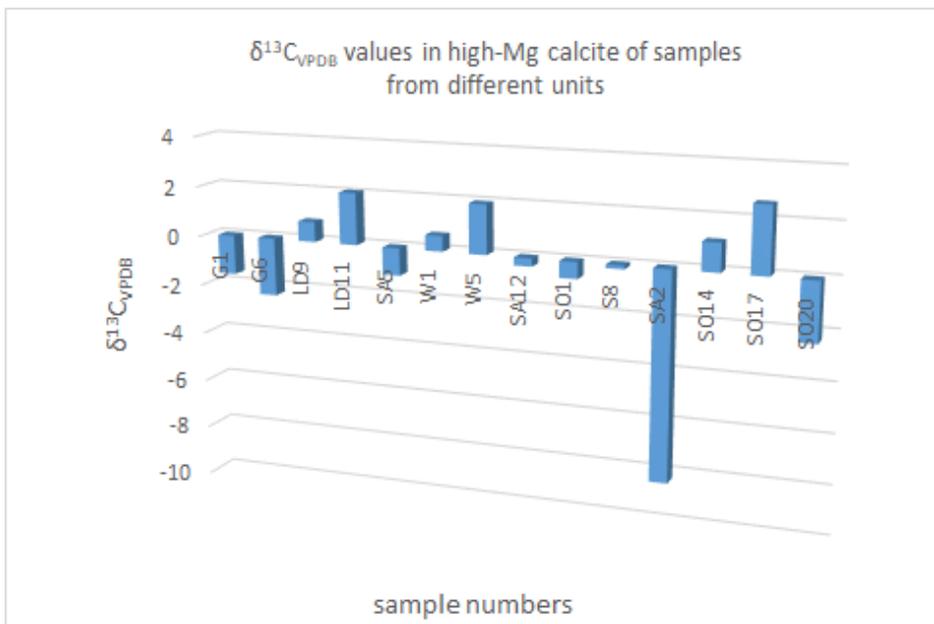


Figure 4

$\delta^{13}\text{C}_{\text{VPDB}}$ values in high-Mg calcite of samples from different units

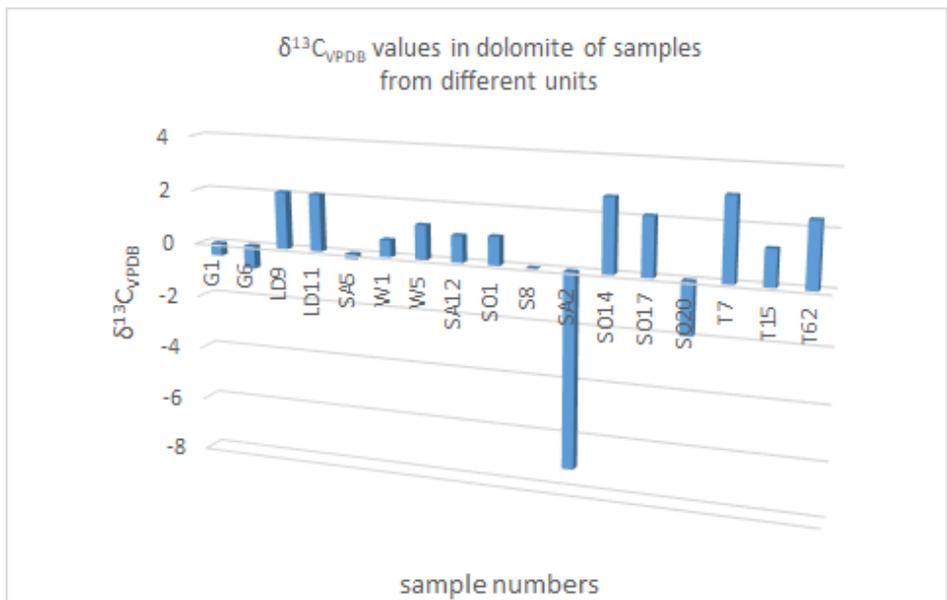


Figure 5

$\delta^{13}\text{C}_{\text{VPDB}}$ values in dolomite of samples from different units

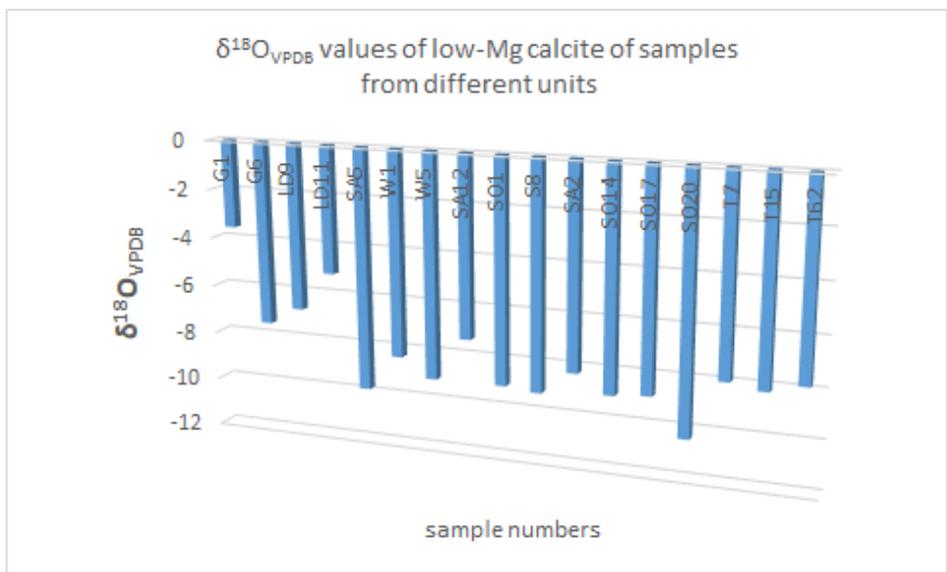


Figure 6

$\delta^{18}\text{O}_{\text{VPDB}}$ values in low-Mg calcite of samples from different units

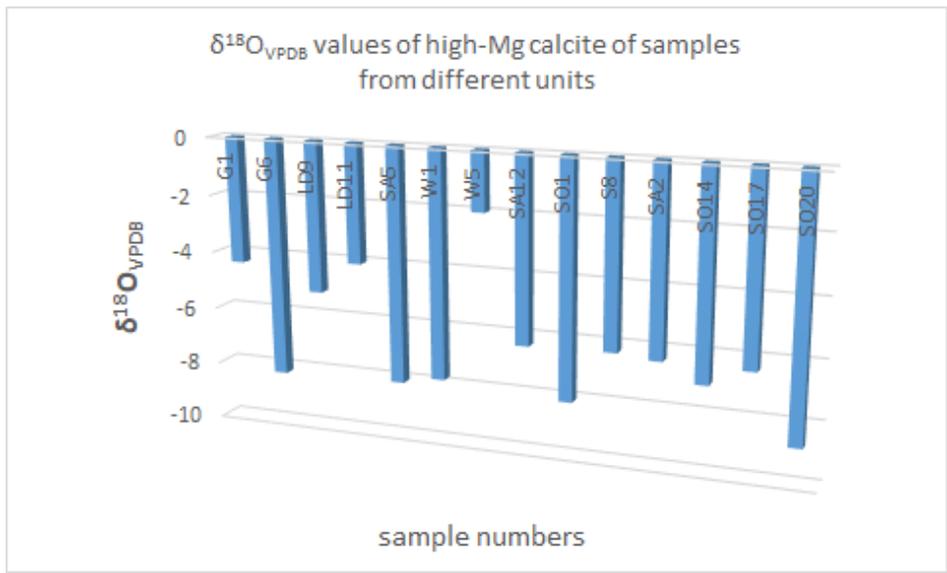


Figure 7

$\delta^{18}\text{O}_{\text{VPDB}}$ values in high-Mg calcite of samples from different units

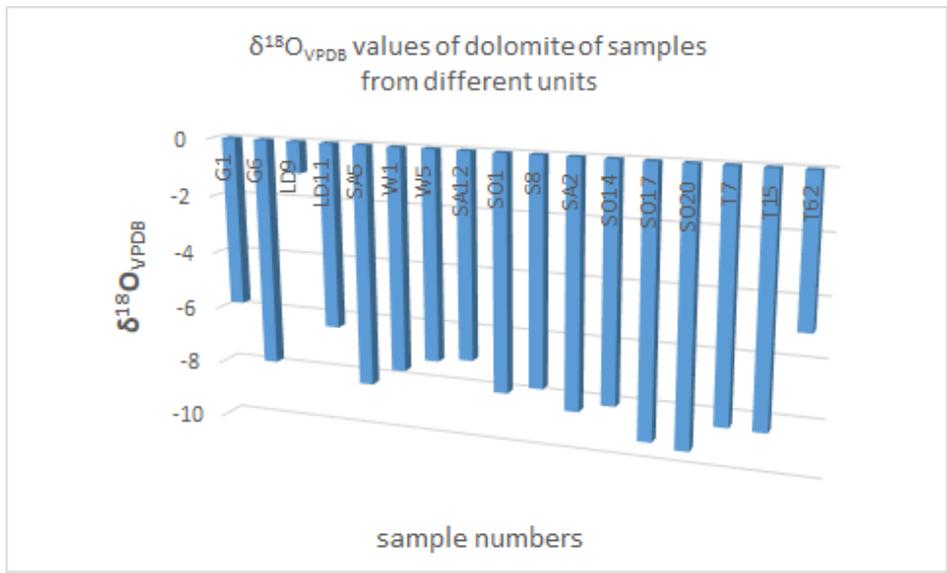


Figure 8

$\delta^{18}\text{O}_{\text{VPDB}}$ values in dolomite of samples from different units

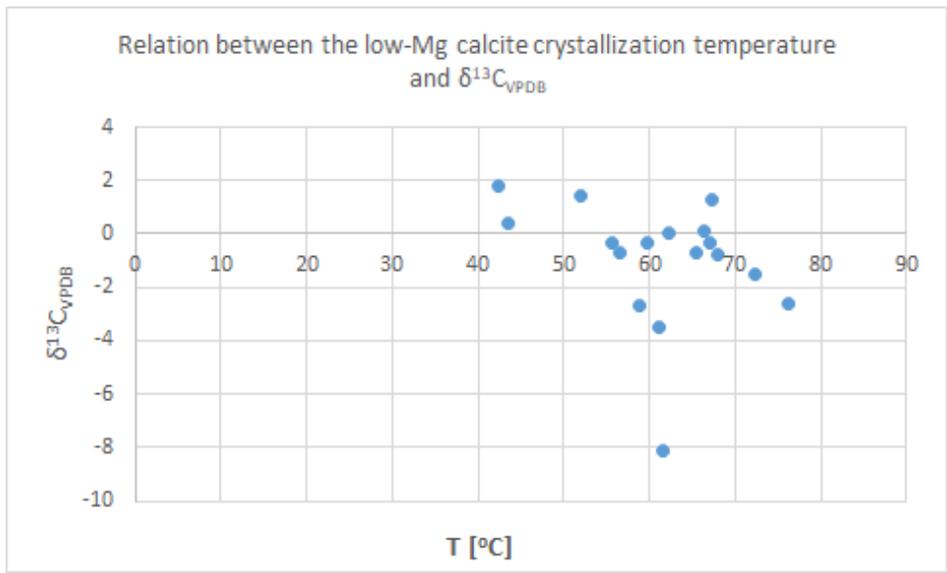


Figure 9

Relation between the low-Mg calcite crystallization temperature and $\delta^{13}\text{C}_{\text{VPDB}}$

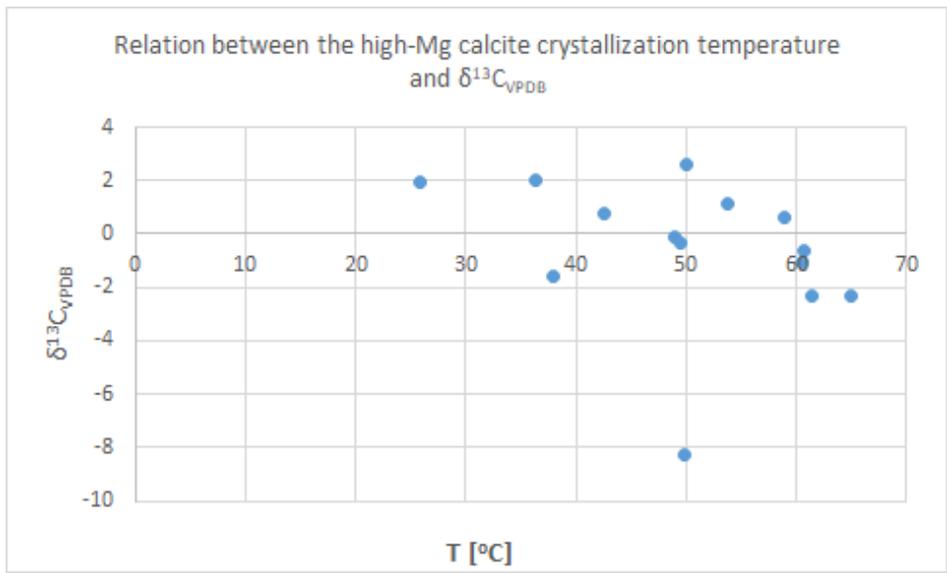


Figure 10

Relation between the high-Mg calcite crystallization temperature and $\delta^{13}\text{C}_{\text{VPDB}}$

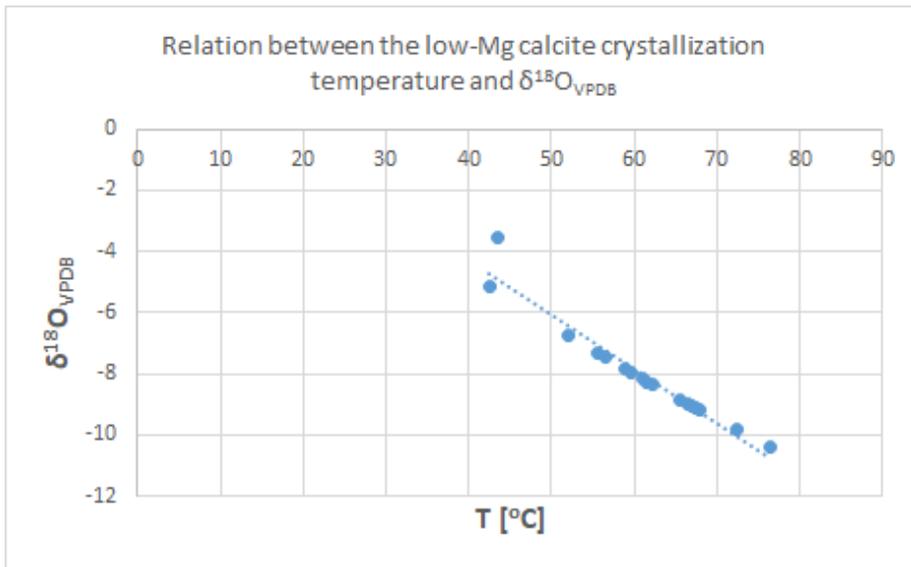


Figure 11

Relation between the low-Mg calcite crystallization temperature and $\delta^{18}\text{O}_{\text{VPDB}}$

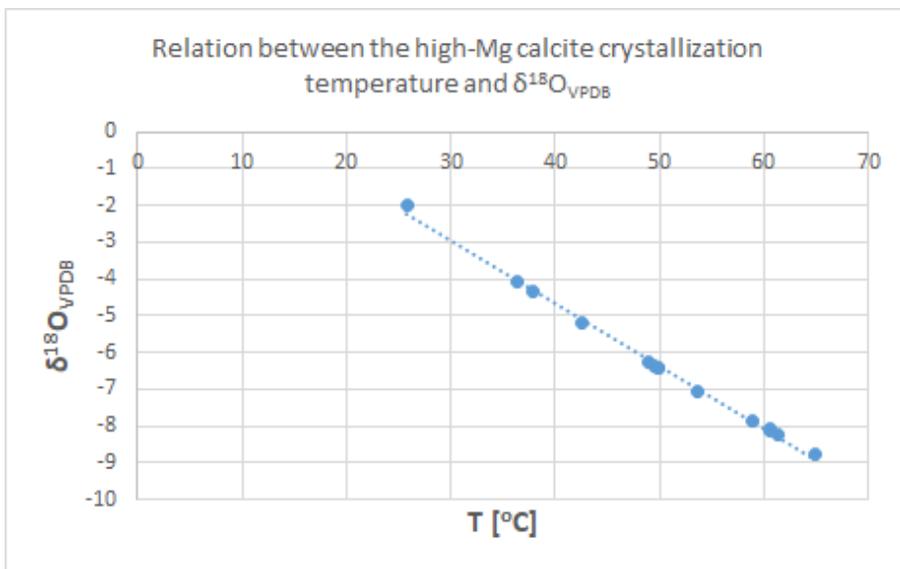


Figure 12

Relation between the high-Mg calcite crystallization temperatures and $\delta^{18}\text{O}_{\text{VPDB}}$