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THERMAL CHARACTERIZATION OF CARBONATE ROCKS
Kozani area, North-western Macedonia, Greece

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Abstract

Representative carbonate rock samples collected from the broader area of Kozani (NW Macedonia, Greece) are examined. The participation of constituents in the formations was determined combining three different methods of analysis, atomic absorption spectroscopy (AAS), X-ray diffraction analysis (XRD) and thermogravimetry (TG). The three methods are used in a complimentary way in order to specify the exact composition of the samples. Although the question about the composition can be answered by AAS, the percentage of the included calcite and dolomite can be determined with accuracy, only through TG analysis, under the appropriate conditions, regarding the gas carrier. The results of the analysis lead to a more complete view of the geological conditions that predominated in the studied area.

Keywords: AAS, calcite, carbonate rocks, dolomite, TG-DTA

Introduction

Naturally occurring carbonate rocks are extremely important natural resources finding widespread applications [1–10] and thus being placed among the most important raw materials. The main constituents of these formations are calcite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$), whereas other minerals (e.g. quartz, feldspars, micas, etc.) participate in minor amounts in their mineralogical composition. The physical and chemical characteristics as well as the formation conditions of these carbonate rocks are the subject of the work of many researchers throughout the years [11–16].

From reactions occurring in minerals or other chemical substances during thermal treatment (heating or cooling) for example during dehydration, or loss of CO_2, SO_3,

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etc., the mass loss which can be determined with thermogravimetry (TG), can be clearly identified and accurately measured. The quantitative determination of the percentage of dolomite, calcite [17, 18] or other carbonated salts with satisfying accuracy in carbonated rocks can be realized from the mass variations observed, when these can be attributed to specific compounds, through information from literature and XRD measurements. This quantitative determination combined with atomic absorption spectroscopy (AAS) measurements can give the complete composition of the rocks.

The thermal decomposition of dolomite shows peculiar characteristics depending on the atmosphere in which the experiments are carried out. The decomposition of dolomite in an inert nitrogen (N_2) atmosphere [19], in air [20] and at low partial pressures (below 200 Torr inside and/or around the sample) of carbon dioxide (CO_2) occurs in a single step [21] and can be depicted by the following reaction:

$$CaMg(CO_3)_2 \rightarrow CaO+MgO+2CO_2 \quad (1)$$

Higher partial pressures of carbon dioxide causes the decomposition and the process proceeds with a split into two stages [22, 23] as follows

$$CaMg(CO_3)_2 \rightarrow CaCO_3+MgO+CO_2 \quad (2)$$

$$CaCO_3 \rightarrow CaO+CO_2 \quad (3)$$

In this work, the above peculiar characteristics for dolomite's identification with TG are used, in samples from the carbonate formations of the broader area of Kozani (NW Macedonia, Greece). The participation of constituents in the formations was determined combining three different methods of analysis, AAS, X-ray diffraction analysis (XRD) and thermogravimetry (TG). The simultaneous use of these methods is necessary in order to specify the exact composition of these samples. Our aim is by taking advantage of the complementarity of these methods to investigate their declination areas. The results are contributing in the study of the geological conditions that predominated in the area.

Geological setting and samples

The studied samples were collected from the Kozani broader area (northwestern Macedonia, Greece), which geotectonically belongs to the Pelagonian zone (Fig. 1). Samples B-SE3, B-ME1, B-ME3 and B-ER5 were collected from carbonate formations of the Vermion mountain [24], samples K-RY1, K-AM1 and K-AM2 were collected from carbonate formations near the town of Kozani [25], samples BO-BI2, BO-SX1 and BO-PA2 belong to the quarried limestone formations of Vourinos [26] and samples BO-SE3, BO-PR3 belong to carbonate formations nearby the mountain of Vourinos. Additional petrological and geological data of the carbonate formations of the Kozani area are given in Dagounaki [27].

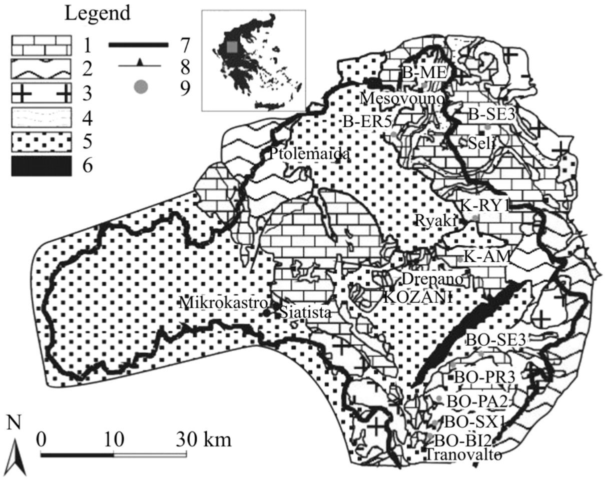

Fig. 1 Geological sketch map of the Kozani broader area and sample locations.1 – Limestones–marbles, 2 – Metamorphic rocks, 3 – Igneous rocks, 4 – Flysch, 5 – Alluvial deposits, 6 – Polyfytos lake, 7 – Kozani prefecture borders, 8 – Obduction, 9 – Sample locations. B-SE3, B-ME1 and B-ME3 Vermion (limestone from Axios zone and Upper Cretaceous dolomites, respectively), K-RY1, K-AM1 and K-AM2 Kozani (Triassic-Lower Jurassic dolomites), BO-BI2, BO-SX1, BO-PA2 Vourinos (Middle Triassic-Jurassic quarried limestones), BO-SE3, BO-PR3 Vourinos (limestones with no further information for their age)

Experimental

Chemical analysis of the rock samples was performed by AAS using a Perkin Elmer 5000 apparatus. The rock sample is crushed in an agate mill till it reaches a size <20 μm. Then it is dried for a whole night at 105°C. 200 mg of rock powder is weighed with a precision of ±0.03 in Teflon autoclaves. Sample dissolution is achieved with the addition of 10 mL HF, 2 mL H_2SO_4 and 1 mL $HClO_3$. The autoclaves are heated at 110°C for 60 min. After being cooled in tap water for about 30 min, 5 g of H_3BO_3 are quickly added along with 30 mL of warm distilled water. The solution is stirred for 5–15 min on a magnetic plate. After this stage the solution should be absolutely clear owing to complete dissolution. It is then transferred to a 250 mL volumetric flask, adjusted to volume and stored in a polyethylene container. From this solution Si, Al and Mn are determined with flame atomic absorption spectroscopy. 10 mL from the first solution is condensed in an open Teflon vessel until it is completely dry. Then 4 mL HCl 1:9 are added and left to evaporate (this procedure is done twice). Finally, after all the liquid has evaporated, 10 mL HCl 1:9 are added to the solid residue along with 1 mL dense HCl. The solution is transferred to a 100 mL volumetric flask along with 10 mL of 50 mg mL^{-1} $LaCl_3$ solution. The solution is adjusted to 100 mL volume and is used to determine K, Na, Ca, Mg and Fe with flame atomic absorption spectroscopy. P and Ti are determined with a Spekol, Carl Zeiss simple beam spectrophotometer, according to Terashima [28]. Loss of ignition (*LOI*) is determined by heating 0.5–1 g of rock powder for 2 h at 1050°C. Detection limits in solution are: Si 1.8 μg mL^{-1}, Al 1.0 μg mL^{-1}, Fe 0.12 μg mL^{-1}, Mn 0.055 μg mL^{-1}, Mg 0.007 μg mL^{-1}, Ca 0.08 μg mL^{-1}, Na 0.015 μg mL^{-1}, K 0.04 μg mL^{-1}.

For X-ray diffraction analysis and thermal analysis part of each carbonate sample was ground to size smaller than 125 μm (measured by sieving) in an agate mortar. Randomly oriented samples were scanned over the interval 3–63° of 2θ at a scanning speed of 1.2° min^{-1}, using a Phillips PW 1011 diffractometer with Ni-filtered CuK_{α} radiation.

A Setaram Setsys TG-DTA 1750°C system was used for the simultaneous thermogravimetric and differential thermal analysis. The samples, in powder form, were placed in an alumina crucible and an empty alumina crucible was used as reference. Samples were heated from ambient temperature to 1100°C at a constant rate of 10°C min^{-1} in a 50 mL min^{-1} flow of CO_2.

Results and discussion

AAS and XRD measurements

The results of chemical analysis are summarized in Table 1. The main contribution in all studied samples is from Ca and Mg and the amount of impurities that ranges between 0.91 and 3.22% is attributed to the low grade of metamorphism (greenschist face) of the rocks. AAS gives reliable results about the presence of different impurities, especially in the case of very small quantities. However, by atomic absorption the chemical composition of a material expressed in the form of oxides, and therefore only in combination with XRD measurements and thermogravimetry, quantitative results can be received concerning the composition of the rocks.

In a typical XRD pattern (sample BO-PA2) is shown the presence of dolomite, calcite and quartz (Fig. 2). The results are collected in Table 2 – for all examined

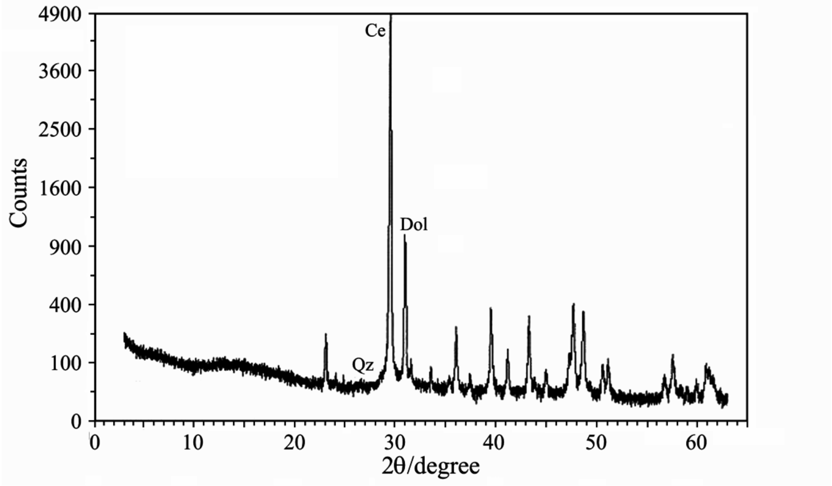

Fig. 2 Typical XRD pattern showing the presence of dolomite (Dol), calcite (Cc) and quartz (Qz) in sample BO-PA2

Table 1 Chemical analysis of carbonate rocks from Kozani area using AAS

mass%	B-ME3	B-ME1	K-RY1	K-AM1	K-AM2	BO-PA2	B-SE3	BO-SX1	BO-BI2	BO-PR3	B-ER5	BO-SE3
SiO_2	0.48	0.69	0.37	0.70	0.21	2.14	2.41	0.70	0.75	0.88	0.45	0.59
Al_2O_3	0.18	0.03	0.08	0.17	0.08	0.00	0.12	0.13	0.16	0.10	0.10	0.16
TiO_2	0.165	0.077	0.154	0.055	0.121	0.000	0.016	0.110	0.060	0.165	0.036	0.055
MnO	0.006	0.000	0.000	0.000	0.000	0.004	0.010	0.000	0.000	0.000	0.000	0.007
Fe_2O_3	0.00	0.00	0.00	0.00	0.00	0.00	0.13	0.00	0.00	0.00	0.00	0.00
CaO	28.58	32.37	31.66	33.08	35.07	49.80	51.25	55.08	54.40	53.82	54.70	56.46
MgO	25.05	20.65	21.60	19.90	18.70	4.62	2.08	1.34	0.96	0.50	0.59	0.55
K_2O	0.20	0.16	0.14	0.26	0.18	0.05	0.19	0.17	0.18	0.13	0.12	0.09
Na_2O	0.27	0.28	0.25	0.33	0.28	0.12	0.30	0.16	0.32	0.27	0.30	0.23
P_2O_5	0.000	0.030	0.030	0.042	0.036	0.025	0.040	0.045	0.025	0.000	0.030	0.066
LOI	44.83	45.43	45.36	45.22	45.30	45.36	43.36	45.30	42.82	42.33	42.85	41.52

Table 2 Participation of constituents of the Kozani carbonate rocks using TG and XRD

Sample	Dolomit/ mass%	Calcite/ mass%	Other/ %	XRD results/ assessment of quantity
B-ME3	95.5	3.9	0.6	D>>>C
B-ME1	89.6	9.7	0.7	D>>>C
K-RY1	89.5	10.2	0.3	D>>>C
K-AM1	86.6	13.2	0.2	D>>>C
K-AM2	85.8	14.0	0.2	D>>C
BO-PA2	19.4	80.2	0.4	D<<C, D>>Q
B-SE3	7.7	90.8	1.5	D<<<C, D>>Q
BO-SX1	2.0	97.8	0.2	D<<<C, D>Q
BO-BI2	1.6	97.9	0.5	D<<<C, D>Q
BO-PR3	1.0	98.4	0.6	D<<<C, D≥Q
B-ER5	0.0	98.4	1.6	C
BO-SE3	0.0	99.8	0.2	C>>>Q

samples –, as relative quantities, being a qualitative estimate of dolomite, calcite and quartz present. From XRD patterns it is clear that the main constituents of all the samples are dolomite and calcite and there is a participation in very small quantities in some of them, of quartz, clays and feldspars.

TG and DTA measurements

TG-DTA measurements were performed for the determination of the calcite's and dolomite's participation percentage in the rocks studied and the critical point is the mass loss. The influence of procedural variables e.g. heating rate, sample weight, particle size, on the shape of the DTG and DTA peak is not presented as the mass loss is independent of these variables. The gas used as carrier in all thermal experiments was CO_2, at higher partial pressures. As it is known from literature, under these conditions the analysis of dolomite decomposition proceeds in two stages. The first stage of mass loss allows the direct determination of the percentage of dolomite present in the samples, while the second stage of decrease gives quantitative information about the existence or not of calcite as independent constituent.

Thermogravimetric (TG) and derivative TG (DTG) plots from the thermal analysis of two characteristic samples (K-AM2, B-SE3) from that listed in Table 2, are presented in Figs 3, 4. The heating rate of the samples was preserved in all experiments stable at 10°C min^{-1} as it is known from literature [23] that increase in the heating rate causes increase in the peak temperature and height of the DTA peak. Consequently, partial or total mass variations remain uninfluenced and this is the reason that we are not including in the present work results with different heating rates. In

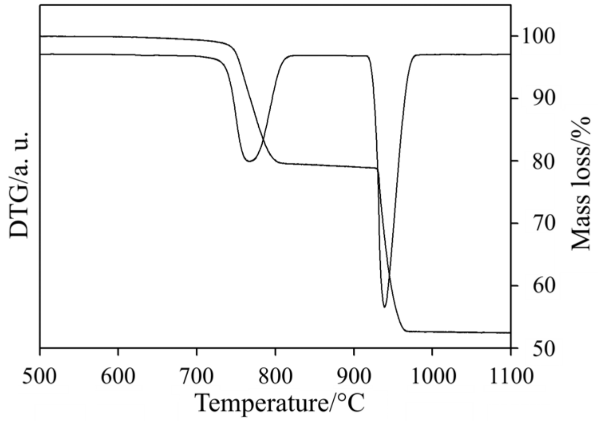

Fig. 3 TG and DTG curves for sample K-AM2

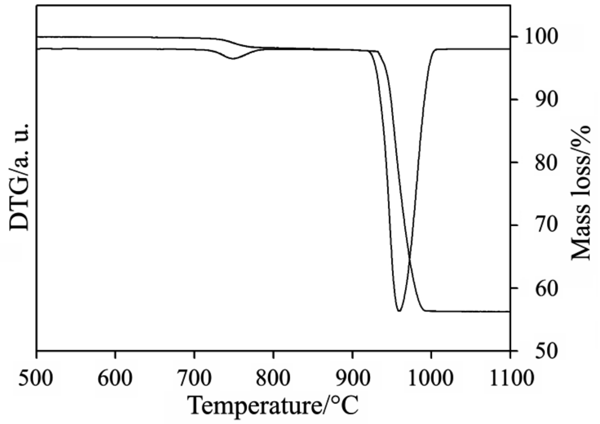

Fig. 4 TG and DTG curves for sample B-SE3

almost all the studied samples (except B-ER5, BO-SE3) the mass variation is observed only in two characteristic temperature ranges, where the two stages of the decomposition take place. The first stage occurs at around 750°C and it is due to the decomposition of $MgCO_3$ from the dolomite. Thus, the amount of dolomite can be calculated. At around 950°C any $CaCO_3$ quantity present, decompose and the total amount of $CaCO_3$ present at this stage can therefore be determined. Subtracting the amount corresponding to the dolomite present, the remaining $CaCO_3$ may count for the amount of calcite present as independent constituent.

For pure dolomite, the theoretical mass losses in the first and second stage are 23.87% in each step, while for pure calcite the expected mass decrease in the one step (at 950°C) is 43.97%. Values different from these, are an indication for the presence of other constituents in the samples. According to the results, the studied samples can be divided in two groups. The first group includes samples B-ME3, B-ME1, K-RY1, K-AM1, K-AM2 with high dolomitic content (mass variation at the first step 20–23%), while in the second group are included samples BO-PA2, B-SE3, BO-SX1, BO-BI2, BO-PR3, B-ER5, BO-SE3 containing almost mainly calcite, in which the first step of mass variation is 0–4.4%. From the mass loss diagram of Fig. 5 (sample BO-PR3) it is easily concluded that minimum mass loss about 0.2% can be reliably used for the quantitative determination of dolomite as for mass decrease with smaller value the calculation results in uncertain conclusions. On the contrary, the mass loss observed in sample B-ER5 – in the same temperature area – can not be attributed with certainty to the decomposition of $MgCO_3$ as this loss is continuous.

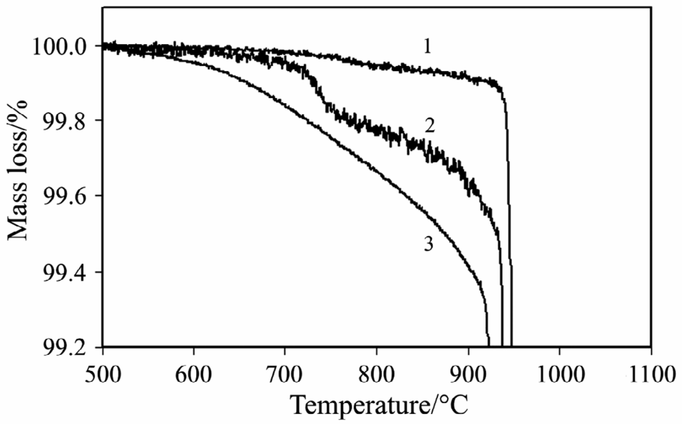

Fig. 5 Part of TG curves for samples 1 – BO-SE3, 2 – BO-PR3, 3 – B-ER5

No other endothermic or exothermic peaks apart from those that coincide in temperature with the areas in which each sample exhibits its corresponding mass variation can be noticed in the heat flow diagram of Fig. 6. Additionally, in the case of quartz that is present in some samples, as this is observed in XRD and AAS measurements, the small peak attributed to its endothermic transition at 573°C [29] is not verified due probably to the small amount present. The combination of DTA and TG measurements, leads to the conclusion that all the samples are composed basically of dolomite and calcite in different ratios and the existence of other thermally traceable constituents is not verified. The peak shape, the number of peaks in the heat flow diagrams and the peak position in the DTG diagrams are also, possibly, connected to the presence of impurities in the host materials [30]. From the atomic absorption measurements it is clear – Table 1 – that there are some very small amounts of elements which could be considered as impurities in our materials. As it concerns the thermal analysis, the sharp decomposition peak of a pure crystal in the DTA curve, in the case of the same mineral that is impure or disordered, is only broadened and lowered in intensity, being without a distinct endothermic minimum. Therefore, the shape of decomposition peak indicates whether substitutions or crystal physical defects are present in the crystal structure. Their influence can not be estimated analytically, as the

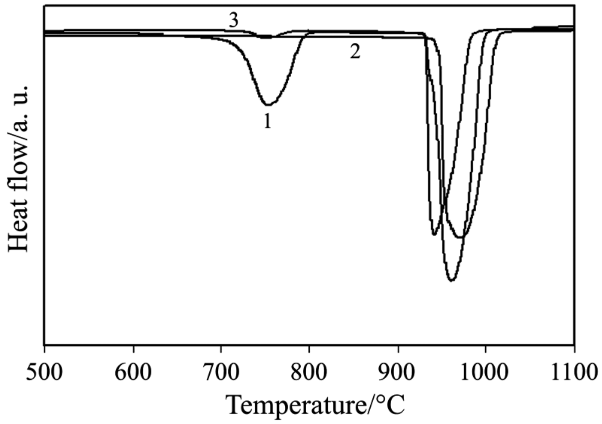

Fig. 6 DTA curves for samples 1 – K-RY1, 2 – BO-SE3, 3 – B-SE3

study of samples with the same stoichiometry and different content of impurities is required. Another reason for the peak broadening is the sample mass. From measurements with different sample mass in sample B-ER5 – that presents a characteristic broadening at the first steps of mass loss, in a wide temperature area –, it is found that the influence is at the final steps [31]. Also, the broadening is influenced by the particle size [32]. In any case, these do not affect either the partial or the total mass variation and consequently, there is no effect on the quantitative estimation of the components forming our materials.

One critical point, in the procedure of measurements processing for the quantitative determination of the samples composition, is the consideration of the end of the first step and the beginning of the second. In the temperature range between the two decompositions there is no mass stabilization, there is a small but continuous mass decrease. This loss is smaller, 0.1% (sample BO-PR3 Fig. 5), in the case of samples with low dolomite participation and ranges to 0.5% for higher dolomite content (sample B-ME3). The point that has been finally used is the one corresponding to the middle of that temperature range and, as a result, the dolomite and calcite percentages in these samples are calculated with maximum error of ±1%. The quantitative evaluation of our samples' chemical composition that results from the estimation of the mass decrease is presented in Table 2.

In Table 3 is given a comparison of atomic absorption values and results from TG measurements. The values of TG have been expressed to percentage in CaO and MgO. It is noticed that the observed divergences are small, within the resolution limits of the different methods. It must be taken into account that in carbonate rocks, the elements of Ca and Mg are possibly present not only in the form of dolomite and calcite but also in the constituents of the impurities or as aggregates. Therefore, the results obtained from the method of AAS do not discriminate the part participating in dolomite or calcite. In the TG-DTA method this determination is direct and consequently the results are accurate.

Table 3 Comparison of atomic absorption values and mass variation measurements

Sample	MgO		CaO	
	thermal	AAS	thermal	AAS
B-ME3	20.9	25.05	31.2	28.58
B-ME1	19.6	20.65	32.7	32.37
K-RY1	19.6	21.60	32.9	31.66
K-AM1	18.9	19.90	33.7	33.08
K-AM2	18.7	18.70	33.9	35.07
BO-PA2	4.2	4.62	50.8	49.80
B-SE3	1.7	2.08	53.2	51.25
BO-SX1	0.4	1.34	55.4	55.08
BO-BI2	0.3	0.96	55.3	54.40
BO-PR3	0.2	0.50	55.4	53.82
B-ER5	0.0	0.59	55.1	54.70
BO-SE3	0.0	0.55	55.9	56.46

As far as the composition of the studied samples is concerned, it can be said that they reflect the palaeo-conditions of the area. During the movement and emplacement of ophiolitic complexes in the area, fluids rich in Mg^{2+} ions were released and circulated into the carbonate rocks of the region because of the enormous strain forces that released at that time. The area where the formations of the samples K-RY1, K-AM1 and K-AM2 are now located, was a deep sea. The conditions for replacement of Ca^{2+} ions were convenient resulting in the appearance of the dolomitic rocks. The formations of the samples B-ME were straightly attached to the region where the ophiolites were abducted. The tectonic impact was tremendous and resulted in the generation of multiple joints, which were the passage for the fluids into the pre-existent rocks. The calcitic samples remained untouched, either due to their origin from another tectonic zone or due to their distance from this tectonic event.

Conclusions

The results of the methods confirm the fact that the two main carbonate phases coexist to the studied rocks. This coexistence is attributed to the geological conditions that predominated in the area, as during the metamorphic episodes fluids rich in magnesium ions found passage through the pores of the original limestones and replaced the calcium ions in the crystal lattice in a great extent, even completely in several cases. The identification of dolomite and calcite present can be realized through the XRD and TG-DTA measurements, but quantitative results with increased accuracy can be obtained only with TG-DTA analysis. These results combined with the AAS ones, complete the compositions analysis of the examined rocks.

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