MINERALOGICAL CHANGES UPON HEATING CALCITIC AND DOLOMITIC MARL ROCKS

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ABSTRACT

The formation of new minerals upon heating marl rocks containing kaolinite, montmorillonite and illite, together with calcite or dolomite is described. The process and minerals are determined with thermal analysis, X-ray diffraction and IR spectroscopy. The minerals which were formed upon heating the calcitic marl were metakaolinite, calcium oxide, gehlenite, and anorthite, and those formed upon heating the dolomitic marl were metakaolinite, calcite, periclase, calcium oxide, gehlenite and diopside.

INTRODUCTION

Thermal analysis of mixtures of clays and calcite or dolomite were investigated in ceramics (West [1]), cements (Ba'rta [2]), building materials (Webb and Kruger [3]) and oil shales (French et al. [4]). Most studies were carried out with mixtures of kaolinite and calcite, recently by Heller-Kallai et al. [5] and Mackenzie et al. [6, 7].

This work describes the formation of new minerals upon heating marls which contain natural mixtures of clays and calcite or dolomite. The marls were collected from the Cenomanian age Moza formation, near Jerusalem. The Moza marls were used as a raw material for ancient ceramics (Porat [8]), and their thermal analysis is important for archaeological studies (Heimann et al. [9]). It is also relevant for a geological study of contact metamorphism of marl rocks (Mason [10]).

EXPERIMENTAL

Methods

Simultaneous DTA, TG, and DTG measurements were carried out in a Stanton Redcroft apparatus (STA 780). Platinum crucibles were used both for the specimen and for the calcined alumina reference. The samples (50 mg of powdered marl) were heated from room temperature to $1300°C$. The heating rate was $10°C$ and $25°C$ per minute Measurements were performed in flowing N_2. The temperature was measured near the sample holder.

Samples of the thermally treated marl were taken from the DTA furnace for X-ray and IR study of the minerals formed. X-ray diffractograms were recorded with a Philips PW 1050/80 diffractometer. Slides were prepared by sedimenting the mineral powder from alcohol. Infrared spectra were recorded in KBr disks (1%) with a Nicolet ZDX FT-IR spectrometer.

Minerals

The mineralogical composition of the Moza marl was determined by Goldman [11]. X-ray diffraction showed the presence of kaolinite, montmorillonite, illite and mixed layers. IR spectra showed that kaolinite was the principal clay mineral. The calcite or dolomite content were 30% and 40%, respectively. According to X-ray data the dolomite was enriched with Ca. Both samples contained traces of K-feldspar and quartz.

RESULTS AND DISCUSSION

Fig. 1 shows the DTA, TG and DTG curves of the calcitic and dolomitic marls. The peak maxima are summarized in Table 1. The mineralogical composition (determined by X-ray and IR) of samples taken from the DTA furnace at various stages of the thermal analyses are shown in Table 2. Representative X-ray diffractograms and IR spectra are shown in Figs. 2 and 3.

The heating processes can be divided into two stages: decomposition of the original minerals in the marl rocks and the formation of new silicates.

Decomposition of the Original Minerals

At the decomposition stage the DTA peaks are accompanied by thermal weightloss in the TG, DTG curves. As one would expect from decomposition reactions, which are accompanied by gas evolution, the locations of the peak · maxima are affected by the heating rate.

Formation of Metakaolinite

An intense endothermic peak appearred at 510°C in the calcitic marl, and at 505°C in the dolomitic marl at a heating rate of 10°C per minute (Table 1). These peaks are mainly due to the dehydroxylation of the kaolinite in the marls to form metakaolinite, since the dehydroxylation of montmorillonite and illite occurs at higher temperatures [12]. After heating to almost the end of these peaks, both marl samples showed by X-ray that the characteristic diffractions of the kaolinite disappeared and the baseline shifted (Fig 2a), a phenomenon characteristic for metakaolinite. The IR spectra of these samples showed that the OH bands which characterize kaolinite [13] disappeared (Fig. 3a).

Table 1. Peak maxima (°C) in the DTA curves of calcitic and dolomitic marl at heating rates of 10°C and 25°C per minute.

Range	Peak	Reaction	Calcitic marl		Dolomitic marl	
			10°C.min⁻¹	25°C. min⁻¹	10°C.min⁻¹	25°C.min⁻¹
Dehydr-ation		Endothermic	105	135	110	135
		"	170	190		
		"	275	295		
Dehydroxy-lation	A	"	510	540	505	530
Decarbon-ation	B	"	-	-	770	790
	C	"	790	810	800	830
Formation of .new silicates	D	Exothermic	945	950	915	925
	E	"	1090	1090	1090(w)	1100(w)
	F	"	-	-	1160	1160
Melting	G	Endothermic	1165		-	
		"	1200(w)		1205	

N.D. = Not detected
w   = Week

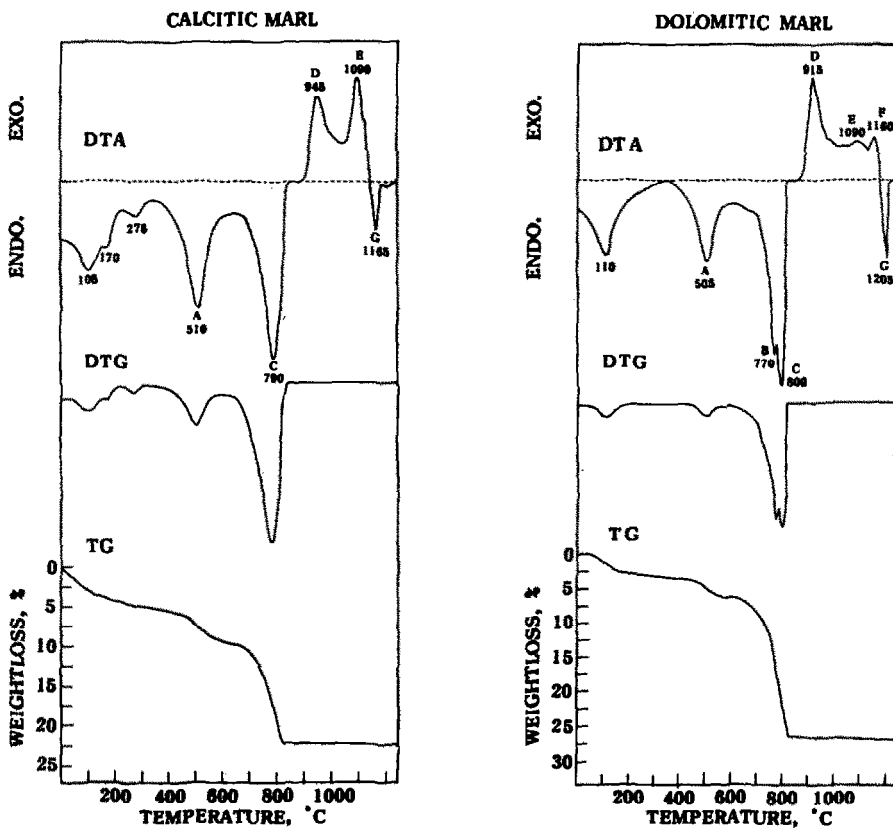**CALCITIC MARL**   **DOLOMITIC MARL**

Fig. 1   DTA curves of calcitic and dolomitic marls (Heating rate 10°C per minute).

Table 2. Mineralogical composition of samples taken from the DTA furnace at almost the end of the various peaks, Heating rate 25°C per minute.

| Range	Peak	Temperature at the end of the peak	Calcitic marl		Dolomitric marl	
			Formation	Destruction	Formation	Destruction
Dehydroxylation	A	620	Meta-kaolinite	Kaolinite	Meta-kaolinite	Kaolinite
Decarbonation	B	800			Calcite and Periclase	Dolomite
	C	850	Calcium oxide	Calcite	Calcium oxide	New Calcite
Formation of new silicates	D	975	Gehlenite	Part of Calcium oxide	Gehlenite	Part of Calcium oxide
	E	1120	Anorthite	Calcium oxide	some Anorthite	Calcium oxide
	F	1180			Diopside	Periclase and new Anorthite
Melting	G	1230		Gehlenite		Gehlenite
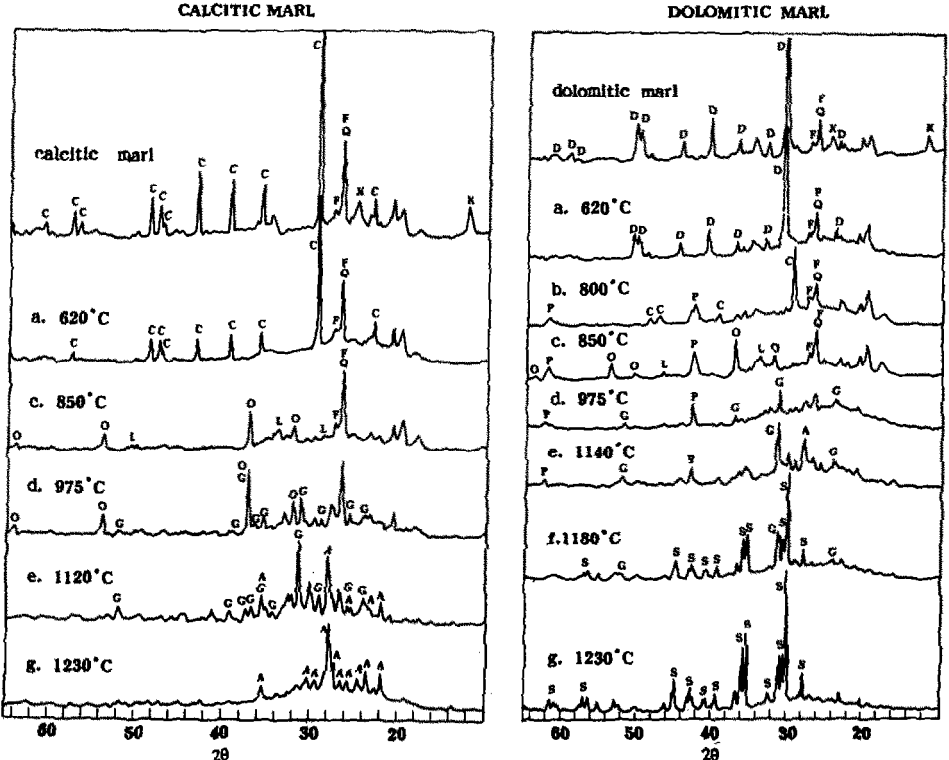
Fig. 2. X-ray diffraction of thermally treated calcitic and dolomitic marls (samples taken from the DTA furnace). K=Kaolinite, C=Calcite, D=Dolomite, Q=Quartz, F=K-Feldspar, P=Periclase, O=Calcium oxide, L=Portlandite, G=Gehlenite, A=Anorthite, S=Diopside.
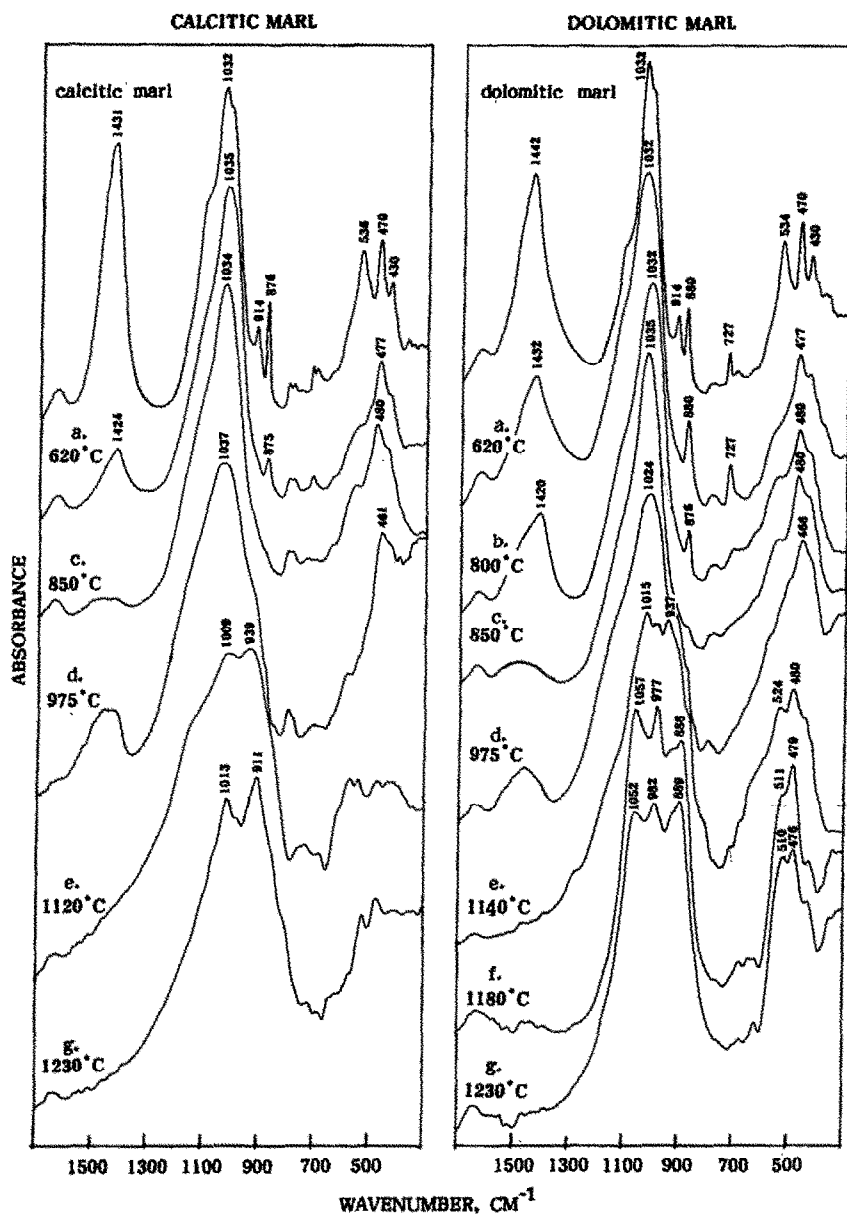
Fig. 3. IR spectra of thermally treated calcitic and dolomitic marls.

Formation of Calcite and Periclase

The dolomitic marl showed two endothermic peaks at 770°C and at 800°C, due to the thermal dissociation of the dolomite. In pure dolomite, the first peak is attributed to the decomposition of the carbonate ions associated with magnesium and the second peak to the decomposition of those associated with calcium [14]. A dolomitic marl sample that was examined by X-ray after heating to almost the end of the first peak, showed that the diffractions of dolomite disappeared and calcite and periclase (MgO) were obtained (Fig. 2b). CaO was not identified at this stage. IR spectra of these samples showed that the CO_3 bands became weak and the main CO_3 peak shifted from 1442 cm^{-1} (typical for dolomite) to 1420 cm^{-1} (typical for calcite) (fig. 3b). The results indicate that at this stage calcite is formed directly from dolomite by heating. Alteration of dolomite to calcite is known from contact metamorphism [10].

Formation of Calcium Oxide

The calcitic marl showed an asymmetric endothermic peak at 790°C. As previously mentioned, the dolomitic marl has a second endothermic peak in this temperature region at 800°C. These peaks are due to the thermal dissociation of the original and new calcite in the calcitic and dolomitic marls, respectively. Both marl samples examined by X-ray, after heating to almost the end of this peak, showed that the diffractions of the calcite disappeared and CaO was obtained (Fig. 2c). Gehlenite was not identified at this stage. Some of CaO interacted with water to form portlandite ($Ca(OH_2)$), during the preparation of the samples. Broad peaks of the latter appear beside those of CaO in the diffractograms. IR spectra of these samples showed that the CO_3 bands disappear and OH bands of portlandite appear at 3643 cm^{-1} (not shown in the figure 3). The reaction of portlandite with atmospheric CO_2 to form calcite is slow, and no X-ray diffractions of the latter were observed even after being exposed to air for a month.

The thermal dissociation of calcite in both marls appears in the DTA curves at lower temperatures than that of pure calcite. This distortion of the calcite peak is known in mixtures of kaolinite and calcite [4-7]. The relatively early dissociation of calcite, in the dolomitic marl, causes the two decarbonation peaks of dolomite to be close to one another.

Formation of New Silicates

At the silicate transformation stage the DTA peaks are not accompanied by thermal weightloss in the TG curves, and consenquently, their locations are scarcely affected by the heating rate.

Transformations in the Clay Component and Formation of Gehlenite

A first broad exothermic peak appears at 945°C in the calcitic marl and at 915°C in the dolomitic marl. The exothermic peaks are attributed to transformations in the clay component of the marls. Pure kaolinite has a sharp exothermic peak at about 980°C when metakaolinite transforms to a cubic, very poorly crystallized phase that is described as Al-Si spinal [15]. Pure montmorillonite and illite have small s-shape endothermic-exothermic peaks at about 850°C-950°C [12]. The appearance of the exothermic peaks in the marls, at lower temperature than the pure kaolinite, may be caused by the carbonate residue. Its broad character may be due to the overlapping of the three clay minerals peaks in the marls.

X-ray of both marl samples after heating to almost the end of this peak, showed that the sample is poorly crystalline. In addition, diffractions of gehlenite ($Ca_2Al_2Si_1O_7$) appeared (Fig. 2d). The CaO diffractions became weaker in the dolomitic marl, due to the formation of gehlenite, but they were still strong in the calcitic marl. IR spectra of these samples showed that the broad band, assigned to SiO and AlO stretching and bending, broadened after the exothermic reaction (Fig. 3d).

More gehlenite was formed at higher temperatures and its characteristic X-ray diffractions become more intense (Fig. 2e). According to Mackenzie [6], the first exothermic peak in the DTA curves of kaolinite and calcite does not characterize the formation of gehlenite.

Formation of Plagioclase Anorthite

A second exothermic peak appears at 1090°C in the DTA curve of calcitic marl, but it is weak in the dolomitic marl. The calcitic marl sample, that was examined by X-ray after heating to almost the end of this peak, showed the appearance of anorthite ($CaAl_2Si_2O_8$) (Fig. 2e). Although the diffractions of anorthite in the calcitic marl were strong, the dolomitic marl shows, at this temperature, only a broad peak that is probably due to the presence of this mineral. These observations are in agreement with the intensities of the second endothermic peaks in the two marls, and indicate that it is related to the formation of anorthite.

Pure koalinite mostly shows an additional small exothermic peak at 1200°C-1300°C which is attributed to the rapid crystallization of mullite and/or cristabolite [16]. In the marls the second exothermic peak appears at relatively lower temperatures and the X-ray diffractograms show that anorthite is formed at its temperature region. This indicates that the nature of the second exothermic peak in the marl differs from that of the second exothermic peak in the pure kaolinite.

As mentioned, at this stage the diffractions of CaO disappear due to the formation of the new silicates. The amounts of anorthite which were formed in the two marls correlate with the amounts of CaO present during the previous stage. IR spectra of the calcitic marl at this stage show that the broad stretching band of SlO and AlO split into two distinct bands due to the crystallization (Fig. 3e).

Anorthite is known in high temperature potteries [9].

Formation of Pyroxene Diopside

A weak exothermic peak appears at 1160°C in the dolomitic marl, but not in the calcitic marl. The dolomitic marl sample, which was examined by X-ray after heating to almost the end of this peak, showed strong diffractions of diopside ($CaMg(S_1O_3)_2$) (Fig. 2f). Another sample, which was examined at the beginning of this peak, showed probable traces of diopside, indicating that this peak is related to the formation of diopside. The peak does not appear in the DTA curve of the calcitic marl, the latter does not have magnesium to form diopside. The diffractions of MgO in the dolomitic marl almost disappear due to the formation of diopside. The broad diffraction of new anorthite also disappear indicating that this mineral may be alterated to diopside. The diffractions of gehlenite were still strong. IR spectra of the dolomitic marl at this stage show that the broad stretching band of SiO and AlO split into three distinct bands due to the crystallization (Fig. 3f).

Diopside is known in high temperature potteries [9] and in contact metamorphism of carbonate-rich sediments [10].

Melting

A sharp endothermic peak appears at 1165°C in the calcitic marl and at 1205°C in the dolomitic marl. These peaks attributed to melting of components of the system. A parallel exothermic effect appears in the cooling curves and they are attributed to solidification. The main melting temperature in the calcitic marl is located at a relatively lower temperature, close to that of the exothermic peak that is related to the diopside formation in the dolomitic marl. After cooling, both marl samples had a glassy appearance. X-ray diffractograms of these samples showed that the gehlenite disappeared but the anorthite and the diopside were stable in the calcitic and dolomitic marls, respectively (Fig. 2g).

CONCLUSIONS

The formation of new minerals when the calcitic and the dolomitic marls are heated can be divided into two main stages:

I. The decomposition of the original minerals followed by endothermic peaks:

- Dehydroxylation of the kaolinite to form metakaolinite in both marls.
- Formation of calcite and periclase directly by the dolomite decomposition in the dolomitic marl.
- Formation of calcium oxide from the calcite in both marls.

II. The formation of new silicates followed by exothermic peaks:

- Transformations of the clay component in both marls are accompanied by the formation of gehlenite.
- Formation of anorthite occurs mainly in the calcitic marl, together with increases of gehlenite content and destruction of calcium oxide.
- Formation of diopside occurs in the dolomitic marl, together with destruction of periclase and anorthite and presence of gehlenite.

ACKNOWLEDGEMENTS

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