

THERMAL METAMORPHISM BY COMBUSTION OF ORGANIC MATTER: ISOTOPIC AND PETROLOGICAL EVIDENCE

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ABSTRACT

New evidence is presented in support of the previously suggested hypothesis that combustion of organic matter in a Cretaceous bituminous sedimentary sequence supplied the heat for the high-temperature, low-pressure metamorphism of the Mottled Zone in Israel. Such a model is compatible with stable isotope data on carbonates from the Mottled Zone which are strongly enriched in C^{12} and O^{16} .

INTRODUCTION

The paradox manifested by rocks of the "Mottled Zone" in Israel (Bentor et al. 1963, 1972) is the occurrence of a sanidinite to pyroxene hornfels facies assemblage within a sequence of sedimentary rocks, without any apparent cause for thermal metamorphism.

It is the purpose of this paper to review the available data on this sequence and to show that the earlier suggested mechanism of spontaneous combustion of organic matter (Wellings 1934, Bentor and Vroman 1960) is compatible with stable isotope analyses of the carbonates involved. Thus, an unorthodox source of energy for thermal metamorphism is suggested.

PREVIOUS WORK

The sequence containing the high temperature minerals is known to crop out at nine separate basins in Israel as well as in Jordan (fig. 1), always in the same stratigraphic and structural position: synclines filled by Maestrichtian to Paleocene sedimentary rocks. The normal sedimentary sequence—the Ghareb and Taqiya formations—(fig. 2) consists of highly bituminous and phosphatic marls, chalks and limestones. Organic matter content ranges from 10–25% (Shahar and Wuerz-

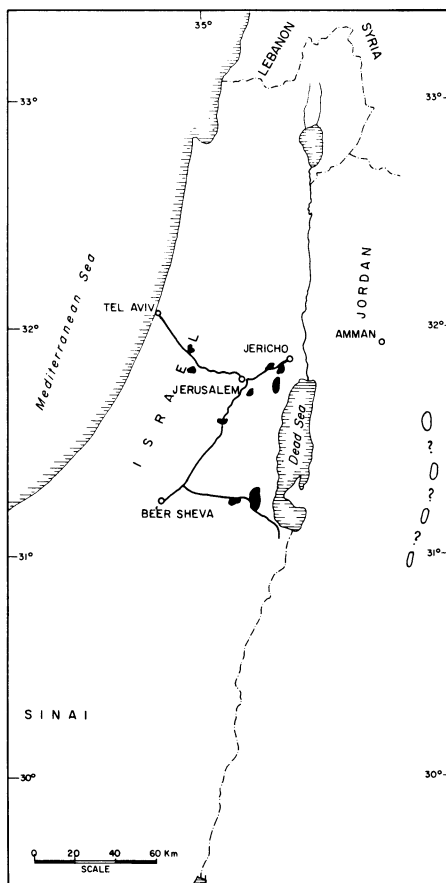


FIG. 1.— Outcrops of the "Mottled Zone" complex in Israel and Jordan. Approximate data for Jordan—from Bender (1968).

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burger 1967). The bituminous sequence is underlain by the cherty Mishash formation and overlain by Eocene limestones. A clastic formation of Neogene age—the

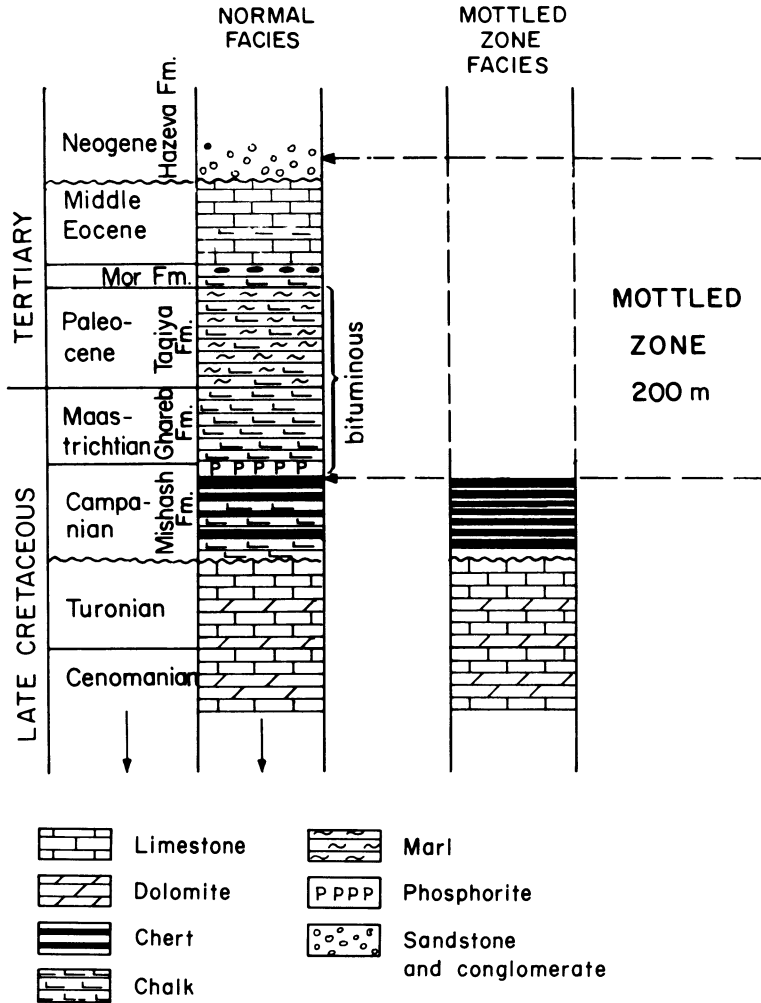


FIG. 2.—Schematic stratigraphic position of the Mottled Zone complex

Hazeva formation covers the stratigraphic column uncomformably (fig. 2). The normal sequence has been preserved over large areas in southern Israel, mainly in synclines, both cropping out and in the subsurface.

Where metamorphism took place, the rocks are "mottled" in color: red-green-yellow-black. The metamorphic sequence is also characterized by strong veining, disappearance of sedimentary bedding and appearance of foliated structures. Rocks of the Mottled Zone make a beautiful building stone and many of Jerusalem's buildings are ornamented by it.

That something rather drastic happened to the Mottled Zone rocks (hereafter abbreviated M.Z.) became apparent to many visiting geologists in Palestine as early as the middle of the nineteenth Century (see Avnimelech 1964 for a review). Explanations for its origin varied from volcanic through hydrothermal, diagenetic and tectonic.

The first evidence for a high temperature origin of the M.Z. assemblage was presented by Bentor et al. (1963a, b) who showed that it contained high temperature phases such as spurrite, gehlenite, and brownmillerite, as well as portlandite, volchons-

koite, ettringite, vaterite and others. The mineral assemblage most closely resembles that of some well-known contact metamorphic occurrences (Burnham 1959, Agrell 1965). In the case of the M.Z., contact metamorphism can be discarded as an explanation because: (a) no igneous body has been detected in its near vicinity, (b) the rocks underlying the M.Z. complex are normal marine calcareous and siliceous sediments lacking any sign of metamorphism.

The paradox of high temperature minerals occurring with no apparent source of heat has been explained by several authors in different ways. Both Avnimelech (1964) and Gross et al. (1967) stressed the stratigraphic position of the rocks and doubted the high temperatures indicated by their mineralogy. The former explained the phenomenon as a result of subaerial weathering under hot climate, whereas the latter followed Picard (1931), who suggested a diagenetic origin, and proposed "penecontemporaneous" formation of the sequence. Bentor and Vroman (1960) and later Bentor and his coworkers (1963 *a, b*) stressed the mineralogical evidence, and in order to explain it, revived the unpublished view of Wyllie et al. (1923) and Wellings (1934) who suggested spontaneous combustion of bituminous matter in the original rocks as a source of heat. Bentor and Vroman termed this phenomenon "autometamorphism." Reverdatto (1970, p. 87-89) summarized the literature on thermal metamorphism caused by burning of coal seams, oil, and gas. The temperatures thus attained can be extremely high, usually exceeding 1,000°C (Brady and Greig 1939 and Schreyer and Schairer 1961).

Fission track dating (Kolodny et al. 1971) yielded 13.6 ± 2.0 m.y. (Miocene) for the age of the thermal event. Thus the confinement of metamorphism to a defined stratigraphic sequence does not indicate the time of the event, which occurred some 50 m.y. later than deposition of the sedimentary rocks. The Miocene date of the M.Z. event was confirmed by

Kolodny et al. (1973) who found Neogene sediments of the Hazeva formation affected by metamorphism (see fig. 2).

Bentor et al. (1972) presented results of experiments in which most M.Z. minerals were synthesized from unmetamorphosed rocks by heating them in air in a furnace. Thus the essentially isochemical (except for decarbonation) character of the metamorphism was demonstrated. It is the aim of this work to analyze the conditions of formation of the M.Z. assemblage. An attempt is made to integrate mineralogical, chemical and petrographical results with stable isotope data and discuss their implications on various models of origin of this unusual occurrence.

METHODS OF STUDY

All samples were examined in thin sections, x-rayed, and several studied by DTA (Gross 1971). For chemical analysis, samples were fused with NaOH and analyzed for SiO₂ gravimetrically. Ca was determined by atomic absorption spectrophotometry, after HF—H₂SO₄ dissolution. CO₂ was determined on the vacuum line volumetrically in the course of preparation of gas for isotopic analysis.

Four minerals from the M.Z. are carbonate bearing: calcite, aragonite and vaterite which are polymorphs of CaCO₃, and spurrite which is a carbonate silicate of calcium. Whole rock samples of the M.Z. were reacted with 100% phosphoric acid, and the liberated CO₂ analyzed for the isotopic composition of carbon and oxygen (McCrea 1950). Measurements were performed on an M86 mass spectrometer at the Isotope Department of the Weizman Institute. Samples were measured by interpolation between standards of known isotopic composition (Zur et al. in preparation). The results are reported in the δ notation relative to PDB standard for both C and O (except where indicated that SMOW was used as the oxygen standard). Reproducibility of isotopic analysis is better than $\pm 0.2\%$ on the same gas and within $\pm 0.5\%$ on the same powder. Some of the analyzed rocks were practi-

TABLE 1
SOME CHARACTERISTIC MINERALS IN THE M.Z. AND THEIR NORMAL PARAGENESIS

Mineral and Composition	Lower Estimated Temperatures of First Appearance ($P = 1$ atm)
(a) High temperature-low pressure decarbonation assemblage:	
Diopside ^{b,c} ;	CaMg(SiO ₃) ₂
Periclase ^{a,c} ;	MgO
Wollastonite ^{b,c} ;	CaSiO ₃
Monticellite ^{a,c} ;	CaMg(SiO ₄)
Gehlenite ^{a,c} ;	Ca ₂ Al [(Si, Al) ₂ O ₇]
Spurrite ^a ;	Ca ₅ [CO ₃ , (SiO ₄) ₂]
	~ 200°C (Turner 1967)
	270°C (Turner 1967)
	~ 625°C (Burnham 1959);
	500°C (?) (Turner 1967)
	[$P_{\text{CO}_2} \approx 10\text{--}100$ bars
	(Burnham personal communication)]
Rankinite ^{a,c} ;	Ca ₃ Si ₂ O
Merwinite ^{a,c} ;	Ca ₃ Mg(SiO ₄) ₂
Larnite ^{b,c} ;	β -Ca ₂ SiO ₄
	450°C (Gross 1973);
	560°C (Turner 1967)
Grossular ^b ;	Ca ₃ Al ₂ [SiO ₄] ₃
Brownmillerite ^{a,c} ;	Ca ₂ (Al, Fe) ₂ O ₅
Mayenite ^{a,c} ;	Ca Al ₁₄ O ₃₃
	800-980°C (deKayser 1955)
	600°C (Gross 1973);
	750°C (Roy and Roy) 1962
Pseudowollastonite ^{a,c} ;	α -CaSiO ₃
(b) The lower temperature assemblage of hydration and recarbonation:	
Ettringite ^{d,e} ;	Ca ₆ [Al(OH) ₆] ₂ (SO ₄) ₃ · 26H ₂ O
Apophyllite ^{d,e} ;	KF Ca ₄ (Si ₈ O ₂₀) · 8H ₂ O
Tobermorite ^{d,e} ;	Ca ₄ H ₂ [Si ₃ O ₉] ₂ · 4H ₂ O
Portlandite ^{d,e} ;	Ca(OH) ₂
Bayerite ^e ;	Al(OH) ₃
Aragonite ^d ;	CaCO ₃
Vaterite ^{d,e} ;	μ -CaCO ₃

^a Sanidine facies. ^b Pyroxene-hornfels facies. ^c Portland cement clinker or slags (Taylor 1964).
^d Late hydration and carbonation phases of low temperature. ^e Hydrated Portland cement (Taylor 1964).

cally pure spurrite (e.g., samples SG 360 and SG 442), as evidenced by both their mineralogical analysis and the CO₂ yields. The fractionation factor for oxygen between H₃PO₄ liberated CO₂ and total CO₃²⁻ in spurrite is not known (compare Sharma and Clayton 1965). Description of the samples together with chemical and isotopic results is given in tables 2 and 3.

PETROGRAPHY AND MINERAL PARAGENESIS

Table 1 summarizes the major mineralogical characteristics of the M.Z. As evident from it, two major assemblages can be discerned.

THE HIGH TEMPERATURE-LOW PRESSURE PARAGENESIS OF DECARBONATED PHASES

The first nine minerals in Table 1 (assemblage a) are all members of Bowen's

(1940) classical decarbonation series. Their normal geological occurrence is associated with sanidine and hornblende-hornfels facies of contact metamorphism (Crestmore California, Scawt Hill in Ireland, Mayen-Laacher See in Germany, Ardnamurchan, Scotland and several localities in Mexico) (see Turner 1968 (p. 225-259), Agrell 1965, Temple and Heinrich 1964). In the M.Z. spurrite is the most abundant rock-forming mineral of this group. Eight of the minerals in this association (table 1) are normal phases in Portland cement clinker and in slags. In both cases, these minerals are indicative of high temperatures acting on siliceous carbonate assemblages at low pressure.

The general conditions for the stability of a calcite-spurrite association, and the practical elimination of tilleyite (which is

TABLE 2

DESCRIPTION AND STABLE ISOTOPE COMPOSITION OF CARBONATES FROM THE MOTTLED ZONE

Sample	Description of Mineralogy and Texture	δC^{13}	δO^{18}	Carbonate Type*
<i>a:</i>				
SG395...	Calcite, micrite, Maestrichtian fauna	- 1.2	- 6.1	a
SG567...	Calcite, micrite (marl)	- 1.2	- 4.6	a
SG568...	Calcite, micrite (marl)	- 1.2	- 4.5	a
SG569...	Calcite, micrite (marl)	+ 0.5	- 5.4	a
SG570...	Calcite, micrite (marl)	+ 0.8	- 5.2	a
MK103...	Calcite, (slightly recrystallized limestone)	- 0.6	- 4.1	a
MK116...	Calcite, micrite (oil shale)	+ 1.5	- 4.9	a
<i>b:</i>				
SG181....	Calcite, brownmillerite, portlandite, ettringite, larnite	- 8.0	- 4.6	b (d)
SG204....	Calcite (recrystallized) diopside, garnet	- 5.4	- 3.5	b
SG244....	Calcite (relict) garnet, ettringite, minor aragonite	- 16.5	- 11.8	b (d)
SG257....	Calcite (granular)	- 12.1	- 13.3	b
SG299....	Calcite (recrystallized, equigranular) garnet	- 16.1	- 11.1	b
SG301....	Calcite (recrystallized) spurrite, mayenite, quartz, apatite	- 19.8	- 16.1	b
SG305....	Calcite (recrystallized, preferred orientation), brownmillerite	- 21.2	- 10.7	b
SG331....	Calcite (recrystallized), lizardite, garnet, brownmillerite	- 15.2	- 7.4	b
SG333....	Calcite (large crystals, recrystallized + ameboidal; foram. ghosts) hydrogarnet, isotropic matter	- 3.6	- 7.4	b (d)
SG340....	Calcite (recrystallized) garnet, zeolite, diopside	- 6.0	- 4.3	b
SG364....	Calcite (dedolomite), lizardite	- 7.1	- 7.1	b
SG390....	Calcite (recrystallized, in places replaces ettringite), spurrite, ettringite	- 23.4	- 8.3	b (d)
SG391....	Calcite (fine grained) hydrogarnets, tobermorite, Ca-Si-hydrates	- 20.1	- 8.4	b (d)
SG425....	Calcite (large crystals, recrystallized)	- 14.2	- 9.9	b
SG441....	Calcite (micritic, partly recrystallized), garnets	- 9.6	- 8.8	b
SG463....	Calcite (in part replacing spurrite) brownmillerite, ettringite	- 16.6	- 11.2	b (d)
SG504....	Calcite (microsparite), garnets	- 6.7	- 9.3	b
MA1....	Calcite (recrystallized, preferred orientation), apatite	- 18.4	- 11.8	b
MA3....	Calcite (sparitic, strongly recrystallized)	- 15.4	- 9.4	b
MK99....	Calcite (recrystallized, prismatic jointing)	- 23.3	- 8.8	b
MK100...	Calcite in bituminous phosphorite (recrystallized)	- 12.4	- 7.9	b
MK102...	Calcite (strongly recrystallized)	- 16.7	- 9.3	b
MK104...	Calcite (recrystallized), apatite	- 13.7	- 10.1	b
MK105...	Calcite (strongly recrystallized), apatite	- 18.6	- 13.5	b
MK106...	Calcite (recrystallized), brownmillerite	- 19.6	- 12.6	b
MK109...	Calcite (recrystallized), spurrite	- 19.5	- 10.1	b
MK110...	Calcite, spurrite, brownmillerite, pyrite	- 14.0	- 15.6	b
MK126...	Calcite (recrystallized), brownmillerite, spurrite	- 15.1	- 13.8	b
MK127...	Calcite (recrystallized), brownmillerite, spurrite	- 18.7	- 15.3	b
MK129...	Calcite (recrystallized), spurrite, garnet	- 18.1	- 12.7	b
MK130...	Calcite (recrystallized), brownmillerite	- 16.5	- 13.6	b
MK131...	Calcite ("augen" structures, preferred orientation), brownmillerite	- 11.3	- 12.1	b
MK142...	Calcite (prismatic jointing)	- 22.3	- 7.4	b
MK143a..	Calcite (micritic, prismatic jointing, poorly preserved microfauna)	- 22.0	- 10.5	b
<i>c:</i>				
SG329....	Spurrite, brownmillerite, calcite	- 19.6	- 8.0	c
SG346....	Spurrite, calcite, garnet (augen structures)	- 20.6	- 10.1	c
SG359....	Spurrite, fine grained, cloudy, veins of ettringite, calcite	- 18.3	- 4.6	c (b)
SG360....	Spurrite, brownmillerite; calcite/spurrite = 1/40†	- 17.6	- 14.0	c
SG427....	Spurrite, laminated, fine grained, brownmillerite, mayenite; calcite/spurrite = 1/75†	- 14.5	- 11.4	c
SG442....	Spurrite, calcite, portlandite; calcite/spurrite = 1/21†	- 18.1	- 11.2	c
SG442r...	Sample SG442 recarbonated in laboratory atmosphere (see text)	- 21.0	- 4.7	
SG464d ..	Spurrite, (fine grained) calcite, gehlenite; calcite/spurrite = 1/10†	- 19.1	- 10.0	c

TABLE 2 (Continued)

Sample	Description of Mineralogy and Texture	δC^{13}	δO^{18}	Carbonate Type*
SG4641 . . .	Spurrite, calcite (light colored margin of 464d, calcite/spurrite = 1/12†)	-18.9	-9.1	c (d)
SG497	Spurrite, calcite, gehlenite; calcite/spurrite = 1/29†	-18.7	-9.8	c
BT6000 . .	Spurrite, calcite; (calcite/spurrite = 1/12†)	-20.7	-9.5	c
R-4D	Spurrite, calcite; (calcite/spurrite = 1/7†)	-17.5	-11.3	c
R-4L	Spurrite, calcite; (light colored margin of R-4D)	-17.2	-8.0	c (d)
MK128 . . .	Spurrite, calcite	-17.6	-10.5	c
<i>d:</i>				
SG277	Calcite, (large symplectic crystals) gehlenite; weathering crust	-5.2	-0.1	d
SG341	Calcite, (both micritic and symplectic)	-7.9	-2.2	d (b)
SG344	Calcite, vaterite, isotropic matter	-12.5	-1.4	d
SG345	Calcite (partly recrystallized, partly symplectic) garnet, aragonite, tobermorite	-10.5	+0.5	d (b)
SG447	Calcite, aragonite (symplectic), isotropic matter	-11.2	-1.4	d
SG572	Calcite, aragonite, chromatite	-19.5	-4.8	d, b
SG573	Calcite, gypsum, brownmillerite	-12.8	-1.3	d, b
SG576	Calcite (brownmillerite)	-14.7	-1.7	d, b
MK107	Calcite, aragonite, garnet, zeolite	-10.6	-6.5	d, b
MK108	Calcite, aragonite, garnet	-9.5	-2.7	d, b
MK138	Calcite (symplectic) aragonite, garnet, zeolite (?) diopside	-6.9	-0.7	d, b
<i>e (Metamorphic Hazeva sediments):</i>				
SG210	Tobermorite, apophyllite, clear sparry calcite	-17.8	-12.6	b
SG192	Calcite (recrystallized replacing sand grains), apophyllite	-15.7	11.8	b
MK134	Calcite, apophyllite, hydrogarnets	-8.4	-7.5	b
MK136	Calcite, vaterite, apophyllite (replaces quartz, carbonate replaces apophyllite)	-13.5	+3.4	d
MK137	Calcite, quartz, apophyllite	-9.3	-8.0	b
MK146	Calcite, quartz, apophyllite	-11.0	-7.0	b
MK147	Calcite, quartz, apophyllite, tobermorite (calcite replaces both quartz and apophyllite)	-8.4	-6.2	b
MK150	Strongly recrystallized calcite, limestone fragment from conglomerate	-9.9	-9.2	b

* See four groups of carbonate in text.

† See Gross 1971, for method of calculation.

the only member of the decarbonation series missing in the M.Z.) were summarized by Zharikov and Shmulovich (1969, fig. 10). These require excess Ca, high temperature, low pCO_2 .

THE LOW TEMPERATURE PARAGENESIS OF HYDRATED AND CARBONATED PHASES

Here (table 1, assemblage b) various complex calcium silicate hydrates and calcium aluminium hydrates occur, together with several hydroxides and metastable carbonates. The most abundant among these are ettringite, tobermorite and aragonite. These minerals occur usually in veins, but in some cases are rock forming. Elsewhere in nature, these minerals are related to late phases of meta-

morphism, typified by a drop of temperature, hydration and carbonation (Jas-mund and Hentschel 1964, Agrell 1965). The two above-mentioned assemblages suggest the following general sequence of events for the formation of the M.Z.

Parent rock heating \rightarrow decarbonation, formation of assemblage (a) cooling \rightarrow recarbonation and hydration, formation of assemblage (b). The two stages may not have been contemporaneous for the entire M.Z.: whereas decarbonation was going on in one place recarbonation might have already taken place in another.

Accordingly, we distinguish five rock types related to the M.Z. event.

1. *Non-metamorphic rocks.*—These can be recognized in thin section by well-

TABLE 3
CHEMICAL COMPOSITION OF CARBONATES FROM THE MOTTLED ZONE

Sample	CaO (%)	SiO ₂ (%)	CO ₂ (%)	Ca/CO ₂ (Equiv. ratio)	Ca/SiO ₂ (Equiv. ratio)
SG395.....	42.89	8.5	32.0	1.0	5.3
SG567.....	44.43	5.66	38.5	0.9	8.4
SG568.....	44.45	5.17	39.6	0.9	9.2
SG569.....	45.65	5.22	38.6	0.9	9.4
SG570.....	49.67	4.52	39.7	1.0	11.8
MK103.....	53.20	2.75	41.7	1.0	20.8
SG204.....	24.67	34.18	9.1	2.1	0.8
SG244.....	39.84	15.68	20.2	1.6	2.7
SG257.....	44.96	5.02	36.5	1.0	9.6
SG299.....	46.95	7.60	30.0	1.2	6.6
SG301.....	49.41	6.96	24.8	1.6	7.6
SG305.....	48.85	8.38	24.3	1.6	6.3
SG333.....	33.95	19.59	21.6	1.2	1.9
SG340.....	25.03	34.13	5.7	3.5	0.8
SG364.....	43.80	3.93	35.0	1.0	12.0
SG390.....	44.02	14.88	13.5	2.6	3.2
SG391.....	35.44	21.04	8.0	3.5	1.8
SG425.....	43.84	12.26	23.8	1.5	3.8
SG441.....	37.52	13.69	28.6	1.0	2.9
MA1.....	55.31	1.76	29.7	1.5	33.7
MA3.....	51.41	1.26	41.0	1.0	43.8
MK100.....	33.17	22.41	20.1	1.3	1.6
MK102.....	49.97	1.90	44.0	0.9	28.1
MK105.....	44.60	9.92	29.6	1.2	4.9
MK106.....	41.49	9.01	28.8	1.2	5.3
MK109.....	44.56	10.14	23.4	1.5	4.7
MK110.....	47.31	7.22	23.9	1.6	7.1
MK126.....	49.40	4.45	27.6	1.4	11.9
MK127.....	53.42	4.21	30.4	1.3	13.6
MK129.....	50.43	6.56	25.3	1.6	8.3
MK130.....	49.22	10.98	18.0	2.2	4.8
SG329.....	41.23	13.44	9.4	3.4	3.3
SG346.....	49.76	6.02	14.4	2.7	8.9
SG360.....	50.17	16.77	7.3	5.4	3.2
SG442.....	48.29	15.93	7.7	4.9	3.3
SG442r.....	40.61	11.18	26.5	1.2	3.9
SG464d.....	49.26	17.46	9.0	4.3	3.4
SG464l.....	43.20	15.69	6.9	4.9	2.7
SG497.....	46.78	18.15	9.9	3.7	2.8
BT6000.....	50.43	16.42	10.8	3.7	3.3
R-4d.....	42.32	13.21	10.4	3.2	3.5
R-4l.....	33.27	11.64	14.7	1.8	3.1
MK128.....	45.43	14.18	9.4	3.8	3.3
SG277.....	36.16	15.41	19.0	1.5	2.5
SG341.....	32.31	27.30	13.7	1.9	1.3
SG344.....	31.87	21.38	18.1	1.4	1.6
SG345.....	35.69	19.24	13.5	2.1	2.0
SG447.....	32.81	20.10	16.7	1.5	1.8
SG573.....	36.50	6.76	10.1	2.8	5.8
SG576.....	45.89	5.62	33.2	1.1	8.8
MK107.....	29.94	19.26	15.0	1.6	1.7
MK108.....	35.40	23.66	20.3	1.4	1.6
SG210.....	29.86	39.35	2.3	10.2	0.8
SG192.....	43.86	12.00	30.3	1.1	3.9

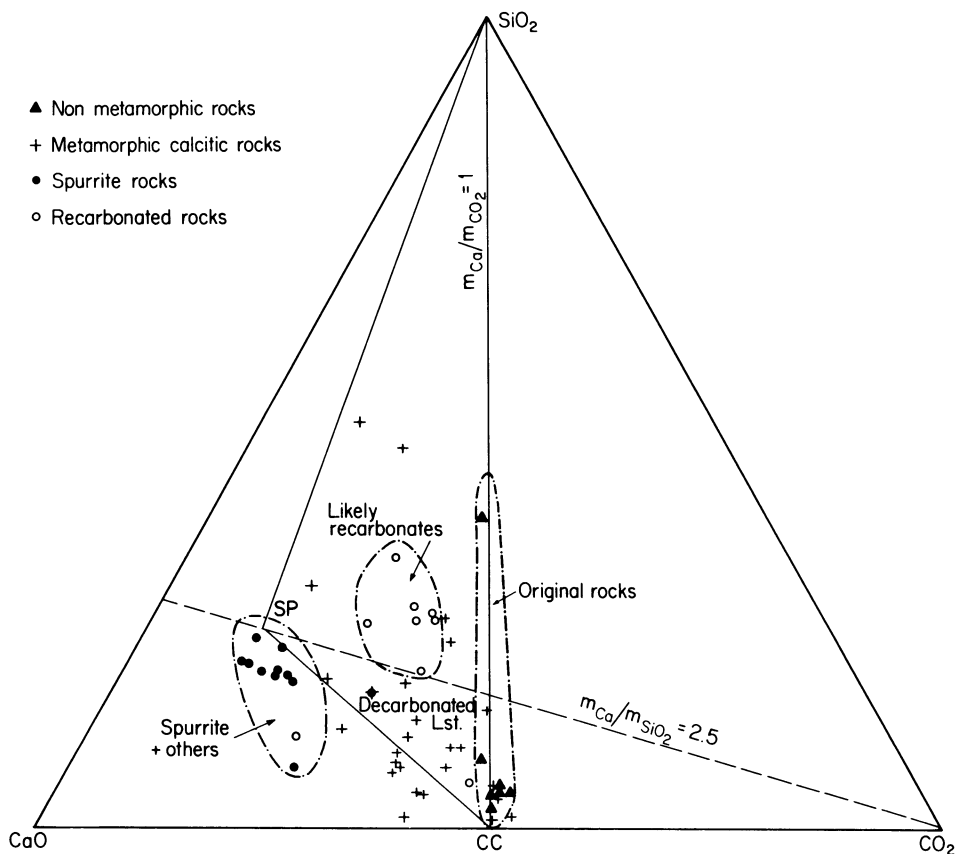


FIG. 3.—CaO—SiO₂—CO₂ triangular plot for whole rock chemical analyses. The sum for the three oxides was taken as 100%. Clastic Hazeva sediments are not included.

preserved microfauna and by the absence of metamorphic minerals. This group represents the parent material. Chemically, these rocks are characterized by a molar ratio of $\text{Ca}/\text{CO}_2 = 1$ (neglecting the presence of gypsum, apatite or other Ca bearing non-carbonate). On a triangular diagram with CaO—SiO₂—CO₂ as apices their compositions fall generally in the vicinity of the calcite—SiO₂ line (fig. 3).

2. *Metamorphic calcitic rocks.*—These are recognized by strong recrystallization of calcite, and the first appearance of metamorphic minerals (commonly garnets and diopside, rarely spurrite and brownmillerite).

Where the parent rocks were pure limestones recrystallization is the major criterion of metamorphism. Some admixture

of silicate is necessary for the commencement of decarbonation at temperatures lower than the decomposition temperature of CaCO₃. Upon decarbonation each bulk composition will move away from the CO₂ apex on the triangular diagram.

3. *Spurrite rocks.*—In these rocks spurrite is the major mineral. Calcite is relict. There is a minimum amount of SiO₂ necessary for spurrite to become the major mineral ($m_{\text{Ca}}/m_{\text{SiO}_2} = 2.5$). With progressive metamorphism the Ca/CO_2 ratio increases. It reaches 5 in spurrite which is the last carbonate containing mineral. Further decarbonation will lead to the formation of larnite which although present in the M.Z. will not be considered here, since it does not contain any CO₂ which we could analyze isotopically.

4. *Recarbonated rocks.*—Mineral assemblages from recarbonation during a late, retrograde stage of metamorphism are recognized by the following criteria: a. The presence of unstable carbonates. The inversion of aragonite (and vaterite) to calcite at several hundred degrees centigrade is so rapid (Turner 1968, p. 166) that these phases could not have survived the heating event. b. Textural relationships which indicate hydration and carbonation: such as the replacement of brownillerite, spurrite and larnite by calcite or by hydrates. In this group, the carbonates exhibit a very distinct symplectic texture, often showing fibrous growth and forming spherulites. Recarbonation of silicates often results in the formation of two symplectically intergrown phases, a calcium carbonate, usually forming large, optically-continuous crystals, and an isotropic phase consisting mainly of silica with some Al-serpentine.

Recarbonated rocks must by definition be relatively high in CO_2 but they must also contain sufficient SiO_2 to have undergone decarbonation in the first place below the decarbonation temperature of CaCO_3 (fig. 3).

5. *Metamorphosed sandstones.*—Rocks belonging to the Neogene Hazeva formation are calcite-cemented, poorly-sorted sandstones and conglomerates. Where affected by the M.Z. event, apophyllite and tobermorite appear in the calcitic matrix, and replace rims of the sand grains. In one case garnets were also observed in the matrix. (Kolodny et al. 1973).

The field relations of the M.Z. rock types are extremely complex and no detailed map of the M.Z. is yet available. The rocks of the M.Z. generally preserve the compositional characteristics of the parent rocks: whereas the lower part of the sequence is rich in Ca-silicates, inherited from the calcareous Ghareb Formation, the upper part derived from the shaley Taqiya Formation contains higher amounts of Ca-Al silicates (Bentor et al. 1972).

Figure 3 shows the distribution of the analyzed samples on a $\text{CaO-SiO}_2\text{-CO}_2$ triangular diagram. The chemical criteria of division as outlined above are in fairly good agreement with the mineralogical-petrographic division.

CONDITIONS OF FORMATION OF THE M.Z. ASSEMBLAGE

The high temperature-low pressure environment of formation of the prograde M.Z. assemblage is indicated not only by sanidinite facies mineral paragenesis but by non-mineralogical criteria as well:

(a) A steep temperature gradient must be responsible for the formation of prismatic columnar shaped jointing structures (Avnimelech 1964) all along the contact of the M.Z. with the underlying unmetamorphosed rocks. Similar prisms resembling basaltic columnar jointing are common at contacts of igneous intrusions with sandstones, clays and limestones (Ramdohr 1972).

(b) A lower limit on the temperatures which prevailed during the M.Z. event is placed by the disappearance of fluid inclusions, which are abundant in unmetamorphosed sand grains in Hazeva Formation sandstones. The three-phase inclusions are absent whenever metamorphic minerals are present which are in this case minerals of relatively low thermal grade—apophyllite, tobermorite, and garnet. Dolgov (1954) showed that decrepitation of fluid inclusion in quartz sand grains occurs in the range of 380–620°C; crude experiments with Hazeva sandstones in this laboratory indicate 200–400°C as decrepitation temperatures. Thus even the “coolest” rocks of the M.Z. were apparently heated above 300°C.

(c) Field evidence places an upper limit on the possible pressure. As noted already by Wellings (1934) “the metamorphosed beds are always the youngest strata . . .” Where the bituminous sequence is conformably overlain by younger rocks it is unmetamorphosed. In the case of the metamorphosed Hazeva Formation sedi-

ments, there is good evidence that these were never covered by any overburden (Kolodny et al. 1973). Thus, any evolved CO₂ could have escaped immediately, limiting total pressure and $p\text{CO}_2$ to essentially atmospheric pressure.

There is, however, no way to translate uniquely the extremely variable mineralogy of the M.Z. into temperature-pressure terms, due to the large variability in the chemical composition of the parent rocks.

SOURCE OF ENERGY FOR THERMAL METAMORPHISM

In its most fully developed occurrence the M.Z. complex is about 220 m thick and covers an area of 50 km². Following the approach of Jaeger (1957) the igneous body which heated such a volume of sediments to temperatures as deduced from the M.Z. mineralogy would have been about 2-km thick. A body of this size is unlikely to be overlooked in the field.

By elimination of contact metamorphism and diagenetic explanations for the origin of the M.Z., and because the non-metamorphic equivalents of the M.Z. rocks are extremely rich in bituminous matter whereas the organic carbon content of the metamorphic equivalents ranges between 0.02 and 0.25%, we tend to accept the model of internal combustion of organic matter as the major source of energy for the M.Z. Such an event was compared by Bentor et al. (1963a) with the "spontaneous combustion of artificial slag heaps also known as coal tips." It may also be visualized as resembling the colossal peat fire which imperiled large areas in the Soviet Union in the summer of 1972 (Stern 1972. See satellite photographs there). The major problem which such a mechanism raises is that of oxygen supply to sustain the "burning" of a 200 m thick sequence of rocks.

It might be speculated that the ignition of the rocks was triggered by intense cracking in Miocene times, possibly related to Rift Valley tectonics. Recent fission-track dating indicates that epidote min-

eralization, apparently related to faulting, has taken place in the Late Miocene along the Rift Valley. Such cracking would create the channels of oxygen supply necessary for combustion. It is visualized that the burning was pulsating—starting, reaching its peak, then being extinguished locally due to lack of oxygen supply. Upon cooling, contraction and collapse would take place, new channels of oxygen supply open, and the fire would start again. It is interesting to note that the only cases, where relict unmetamorphosed sediments are found in the M.Z., are lenses of bituminous rocks at the *bottom* of the section, directly overlying the chert. These are the locations most likely to suffer from oxygen deficiency.

The probability of producing the necessary metamorphic energy from the organic matter of bituminous limestone *in situ*, is best demonstrated by Quennell's (1951, p. 112) report on the possible economic uses of this limestone. He mentioned that "the material is burnt for the production of quick-lime. It is mixed and built into rough kilns and fired. There is sufficient fuel in the limestone to complete the process of burning".

Recarbonation and hydration processes probably accompany the cooling stages of the event. Moreover, temperatures during these last stages might have risen considerably due to the strong exothermic effect of most hydration reactions as known from hydration of Portland cement clinkers. (Copeland and Kantro 1964). The occurrence of minerals such as apophyllite which are often found in hydrothermal environments is therefore not surprising.

STABLE ISOTOPES IN M.Z. CARBONATES

Figure 4 is a plot of δO^{18} versus δC^{13} . It shows that the isotopic composition correlates well with the mineralogical petrographic classification of our rocks. In particular it should be noted:

(a) The unmetamorphosed sediments show both carbon and oxygen isotopic compositions in the range of normal

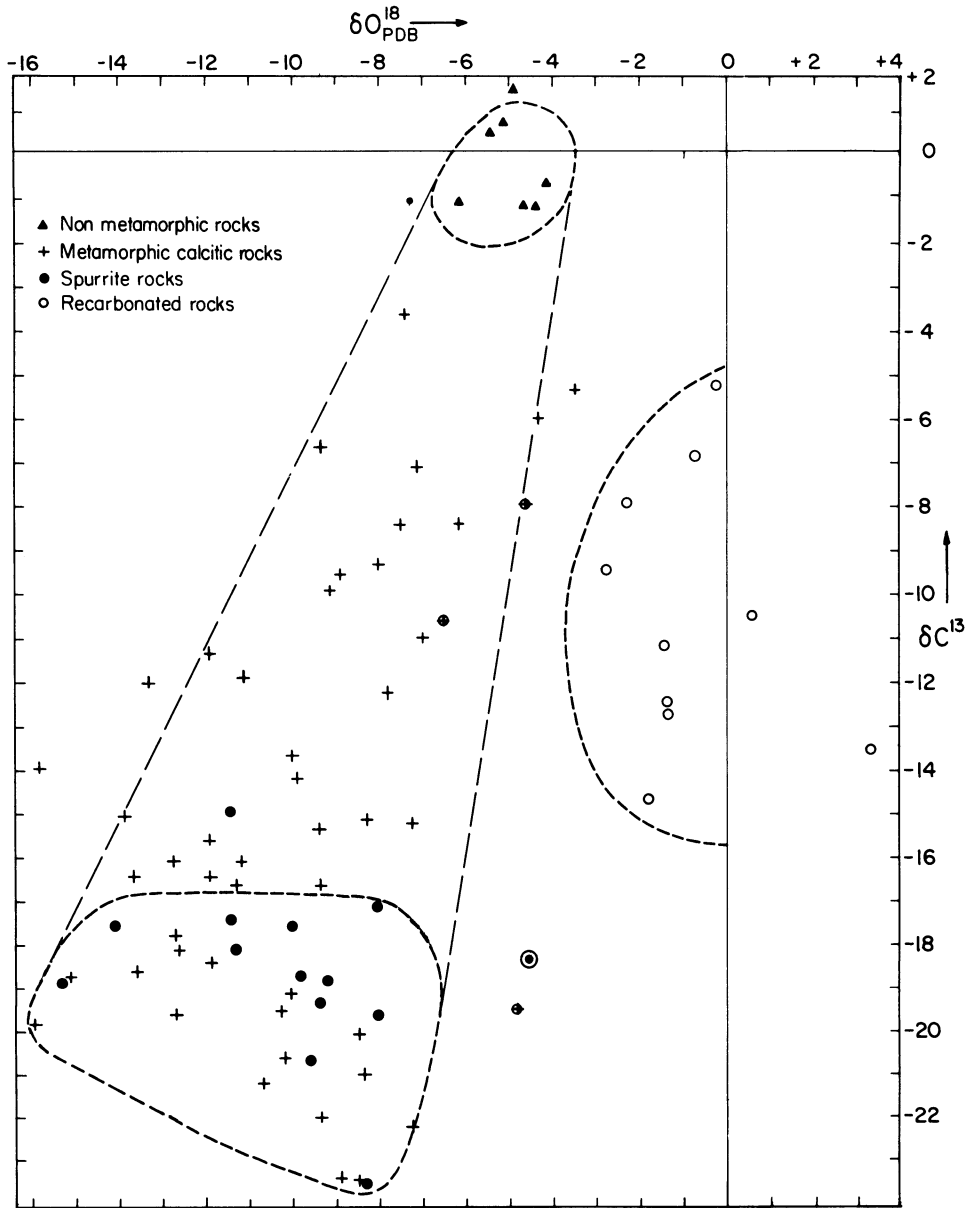


FIG. 4.—Isotopic composition of oxygen and carbon in carbonates from the M.Z.

marine carbonates, in which oxygen has apparently undergone some later isotopic modification ($\delta C^{13} = -1.2\text{‰}$ to $+1.5\text{‰}$; $\delta O^{18} = -4.1\text{‰}$ to -6.1‰).

(b) The spurrite rocks are strongly enriched in C^{12} and O^{16} (δC^{13} varying between -14‰ and -21‰ , δO^{18} be-

tween -4‰ and -14‰). [Compare these to three unpublished analyses of Crestmore spurrites by S. Lambert which averaged $\delta C^{13} = -3.53\text{‰}$, $\delta O_{PDB}^{18} = -14.90\text{‰}$].

(c) The isotopic composition of most metamorphosed calcite rocks is inter-

mediate between types (a) and (c), the non-metamorphosed and the spurritic rocks.

(d) The recarbonated rocks are characterized by a significant enrichment in O^{18} even in comparison with the unmetamorphosed sediments.

Accepting the suggested model for the origin of the M.Z. rocks, two processes could have determined the isotopic composition of carbon and oxygen in the prograde metamorphic assemblage.

1. *Decarbonation.*—It has been shown by Bottinga (1968) that at comparatively high temperatures (500–1,000°K) carbon dioxide has C^{13}/C^{12} and O^{18}/O^{16} ratios which are higher than those of the calcite with which it is in equilibrium. Shieh and Taylor (1969) showed that decarbonation reactions result in lowering the O^{18}/O^{16} and C^{13}/C^{12} ratios of rocks.

2. *Interaction with CO_2 derived from organic matter combustion.*—Such CO_2 is strongly depleted in C^{13} , and carbonates with strongly negative δC^{13} have usually been interpreted as resulting from participation of organic matter carbon in their formation. In some cases, oxidation of organic matter has been invoked (Hodgson 1966; Hoefs 1970; Sass and Kolodny 1972), in others methane gas has been suggested as the carbon source (Hathaway and Degens 1968).

The isotopic composition of oxygen in the M.Z. rock may probably also have a strong imprint of interactions with groundwater.

It is difficult to evaluate the relative importance of each of the two processes in establishing the present isotopic composition of the M.Z. rocks.

Decarbonation alone cannot however account for two aspects of the observed results:

(a) The isotope effect during decarbonation in the relevant temperature range should be equal for oxygen and carbon or more marked for oxygen (Shieh and Taylor 1969). Thus points on a $\delta O^{18} - \delta C^{13}$ diagram should plot on a line with a slope

of unity or smaller. Figure 4 shows that our results fall on a trend whose slope is considerably larger than unity. The enrichment in C^{12} is almost twice as large as that in O^{16} . Thus, if decarbonation is operative, and additional process must be invoked, the result of which would be either enrichment of oxygen in its heavy isotope or of carbon in its light one. One possible process of such nature could be interaction with groundwater. If one accepts the isotopic composition of oxygen in the unmetamorphosed rocks ($\delta O^{18} = -4.1\%$ to -6.1%) as a result of isotopic exchange with groundwater, one could by the same token accept late-metamorphic low temperature, or post-metamorphic exchange of groundwater with decarbonated, hence strongly O^{16} enriched rocks, resulting in a relative enrichment in O^{18} . The alternative process (i.e., enrichment in C^{12} will be discussed below.

(b) If decarbonation were the major effective process, a positive correlation should be observed between enrichment in C^{12} and the degree of decarbonation which can be estimated by the increase in the Ca/CO_2 ratio. Figure 5 shows that indeed for rocks with sufficient silica ($m_{Ca}/m_{SiO_2} = 2.5 - 3.5$) to be strongly affected by decarbonation, a decrease in δC^{13} accompanies the increase in Ca/CO_2 ratio. On the other hand, pure limestones which underwent little or no decarbonation are in many cases strongly depleted in C^{13} . It is noteworthy that the "lightest" carbon found in this study is that of the limestones with prismatic jointing (table 2).

Thus, the stable isotope composition of M.Z. carbonates cannot be explained as the result of decarbonation only. The additional process of interaction with organic matter derived CO_2 is therefore necessary. The isotopic composition of such CO_2 would be approximately that indicated on figure 6, namely $\delta C^{13} = -28\%$ (analysis of organic matter from unmetamorphosed Ghareb fm. marl by A. Nissenbaum; see also Epstein 1968), $\delta O^{18} = -7.2\%$ (O^{18} SMOW = 23‰,

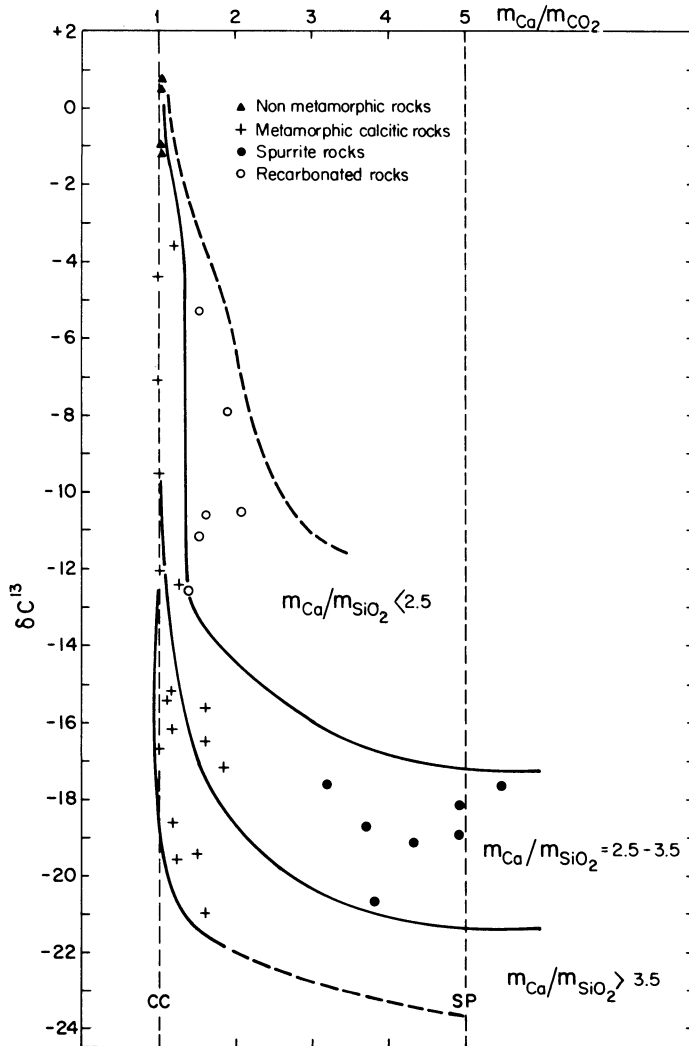


FIG. 5.—Isotopic composition of carbon in the M.Z. carbonates as a function of the degree of decarbonation. Various ratios of calcium to silica are indicated; see text.

atmospheric O_2 in which the organic matter is combusted). Isotopic exchange between carbonate and CO_2 is strongly temperature dependent. It has been shown by Anderson (1969) that it would take about 10^8 years to exchange 50% of carbon or oxygen in calcite by equilibrium with CO_2 gas at room temperature; the same result could be achieved in 10^6 years at $450^\circ C$, and 100–1,000 years at $700^\circ C$. Mass balance considerations limit the

extent to which isotopic exchange with organic matter derived CO_2 could have altered the isotopic compositions of M.Z. carbonates. Taking for instance 20% by weight as the value for organic matter content in the parent rocks, the approximate ratio of organic matter carbon to calcite carbon is 1. The size of the CO_2 reservoir being limited, the final isotopic composition of carbon in calcite or spurrite would depend on the amount of organic

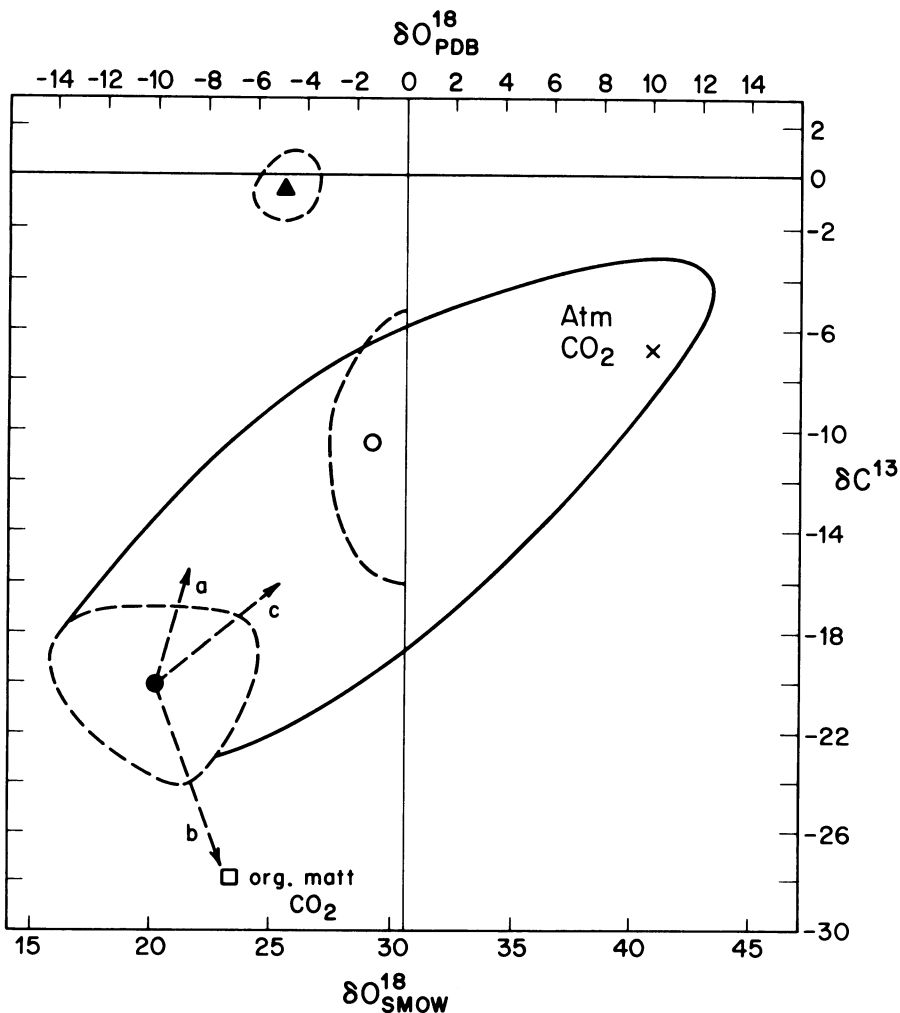


FIG. 6.—Mixing relationships of non-metamorphic, spurrite and recarbonated rocks with different hypothetical CO_2 reservoirs (see text).

matter available, on the length of burning time, and on the temperature reached. Obviously, if the mere operative process was equilibrium exchange with CO_2 , then isotopic compositions like those of samples MK 99, MK 143 or SG 305 ($\delta\text{C}^{13} = -23.3\text{‰}$, -22.0‰ , -21.0‰ , respectively) can be reached only if about 80% of the carbonate carbon is of organic matter origin. As an alternative to such an extreme requirement, participation of reduced species such as CH_4 or CO which are strongly enriched in C^{12} may be postulated. If these are subsequently completely

oxidized, extremely "light" carbon values can be reached. Non-equilibrium processes should also not be excluded. One could explain all our isotope data for prograde rocks involving only interaction with organic matter derived CO_2 and variable extents of exchange with hot meteoric water (see fig. 6).

The isotopic composition of carbonates in recarbonated rocks will strongly depend on the source of CO_2 for recarbonation. Three sources can be suggested:

(a) Recarbonation could have occurred with organic matter derived CO_2 as the

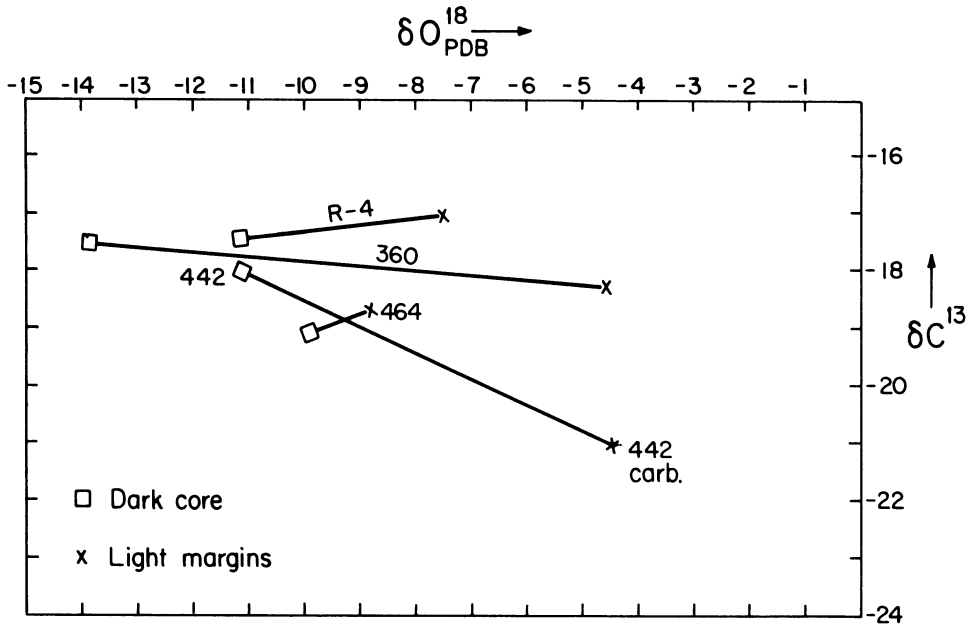


FIG. 7.—Relation between the isotopic composition of unweathered, dark spurrite rocks and their light colored weathered, carbonate margins. Sample 442 was re-carbonated in the laboratory by suspension in an open vessel in water for two years.

re-carbonating agent. Such CO_2 should have been marked by "light" carbon and an atmospheric value of the oxygen isotopic composition (line *b* on fig. 6).

(*b*) CO_2 evolved during decarbonation could have been reabsorbed on other decarbonated phases. This process should have resulted in carbonates whose isotopic composition on a $\delta C^{13} - \delta O^{18}$ diagram shows a trend along line *a* on figure 6, (i.e., the trend of enrichment in C^{12} and O^{16} expressed upon transition from non-metamorphic to extremely decarbonated rocks is reserved).

(*c*) If the re-carbonation agent is atmospheric CO_2 , the resultant carbonates should lie more or less along a mixing line between composition of atmospheric CO_2 ($\delta C^{13} = -7\%$ and $\delta O^{18}_{SMOW} = 41\%$) and the decarbonated phases. Figure 6 shows that our results are in accordance with the third interpretation. Furthermore it implies that re-carbonation occurred in a fairly dry environment, since otherwise CO_2 would have equilibrated with any

abundant groundwater present, resulting in an enrichment in O^{16} .

The only decarbonated phase which we could analyse was spurrite. Obviously, the isotopic composition of oxygen in completely decarbonated minerals will (when obtained), be crucial to the subject. Absorption of CO_2 on alkali hydroxides was studied by Baertchi (1952) and Craig (1953). They showed that this process is accompanied by a strong kinetic fractionation effect. Thus one could hardly expect the points which represent re-carbonated rocks to adhere strictly to the mixing line on figure 6.

Additional evidence on the re-carbonating process can be obtained by comparing the isotopic composition of C and O in spurrite rocks with that of light colored rims of these rocks which are products of weathering (and re-carbonation). Figure 7 shows such comparison, as well as the results for laboratory re-carbonation of sample SG 442 which was exposed in a water suspension to laboratory air for two

years. The isotopic composition of this water has not been measured, but is estimated as $\delta O^{18}_{SMOW} = -5\text{‰}$ to -6‰ (Jerusalem tap water). In all cases, recarbonation resulted in enrichment in O^{18} . Material balance calculation yields different values for the isotopic composition of the recarbonation agent for different samples, which in view of the reasons mentioned above are not surprising, and are not presented here.

SUMMARY AND CONCLUSIONS

1. The M.Z. rocks are the result of an event of intense heating of a marine carbonate-clay sequence.

2. The event occurred in the Late Miocene, i.e., some 50 m.y., after deposition of most of the parent rocks.

3. Metamorphism in the M.Z. was essentially isochemical; decarbonation and dehydration were the major chemical changes. The resultant rocks are of the sanidinite and pyroxene-hornfels facies.

4. The Mottled Zone Event was characterized by high temperature (600–800°C), low (about atmospheric) pressure and low pCO_2 . The end products also reflect a low Mg, silica deficient carbonate sequence as a starting material.

5. The energy for metamorphism was supplied by combustion of organic matter contained in the original sedimentary rocks.

6. Following the main prograde metamorphic event was a second low temperature stage. Recarbonation and hydration were the major results of this stage.

7. Whereas mineral parageneses are the best witnesses to the net *results* of the M.Z. event, analysis of the stable isotopes of carbon and oxygen reveals much of the *causes* of this event; specifically it fingerprints carbon dioxide of different sources which participated in the processes. Combustion of organic matter resulted in a strong enrichment of carbonates in C^{12} .

Interaction with meteoric water caused depletion in O^{18} . Decarbonation *per se* might have also enriched the metamorphic rocks both in C^{12} and O^{16} . The strong enrichment of recarbonated rocks in O^{18} is evidence of atmospheric CO_2 being the recarbonating agent. Thus, recarbonation is more closely related to weathering than to retrograde metamorphism in its classical sense.

8. The factors postulated here, which are necessary to start the combustion process, are extremely simple. In view of the abundance of bituminous sediments in the world the uniqueness of the M.Z. occurrence is puzzling. It may be speculated that only the combination of a carbonate rich bituminous sequence, exposed for a sufficient time at the surface but occurring in relatively young sediments and arid climate will result in a high probability of being both metamorphosed and preserved in the geologic record.

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