משרד האנרגיה והתשתית

K-Ar dating of clay fractions from Mesozoic sedimentary rocks in Israel

Kapusta Y., Sandler A., Kotlarsky P., Steinitz G.

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ABSTRACT

K-Ar age determinations have been performed on silicate fractions (clay minerals, feldspar) separated to size fractions from some 25 sedimentary rocks (shale, carbonate, sandstone) from Jurassic to Paleocene formations in Israel. The aim of the study is to identify the types of geologic events which can be dated using such fractions. The results show that:

1. In some cases the K-Ar ages are significantly higher than the assumed the stratigraphic age, portraying the age of mica and feldspar which accompanies the detrital kaolinite. The latter is the major clay mineral in such cases. It is concluded that the silicates in these samples are all, or to a large extent, of a detrital origin.
2. In some cases the K-Ar age of the separated fraction is equal to or close to the assumed stratigraphic age. The samples contain different clay mineral assemblages. All contain smectite or phases of illite/smectite. In some authigenic feldspar is also present. The fractions dated therefore represent mixtures (size, mineralogy) of components which are: a) detrital; b) reset (K-Ar clock) and/or authigenic.
3. Ages which are significantly younger than the assumed stratigraphic age have not been encountered, even in the finest ($<0.2\mu$) fractions. It is concluded that these clay minerals did not loose argon since their inclusion in the host rock.

The overall pattern of results indicates the potential in the dating of such clay fractions in terms of geochronologic-stratigraphic and paleogeographic aspects as well as the petrology of clay minerals in these depositional environments.

INTRODUCTION

The use of fine silicate fractions and minerals from sedimentary rocks as K-Ar chronometers recording sedimentary events has often been investigated in various locations. The conclusions as to the usefulness of these fractions as such chronometers range in the literature from trustworthy to dubious (e.g. Faure 1986, Weaver 1989).

K-Ar chronometry has generally been tried on clay fractions (mainly illites) from clastic sequences and from shale beds. Furthermore, much of the K-Ar study of fine grained mineral fractions has centered around burial diagenesis and anchimetamorphism. In other cases glauconite has been extensively studied, due to its clear authigenic origin, as well as its high K content (Odin, 1982).

Dating of clay minerals from the sedimentary sequence in Israel was performed by Segev (1986) and by Harlavan (1992). They used the K-Ar, Ar-Ar and Rb-Sr methods to date illites ($<2\mu$) separated from carbonates and micaceous sandstones of Early Paleozoic (Cambrian) age. They demonstrated that the K-Ar and Rb-Sr systems in the illites are reset by a Devonian (thermal ?) event.

This report presents the first results on the K-Ar systematics of the fine silicate fractions in Mesozoic marine sedimentary rocks. The main aim of the project is a survey as to the types of geologic events which can be dated using such fractions from these formations. In light of this aim two goals were set:

a) Trying to identify potential stratigraphic chronometers within the large variety of lithologies and clay mineral associations in the stratigraphic column.
b) Give insight as to the use of K-Ar isotope systematics in these fractions as a paleogeographic, an environmental (depositional) and a petrological tool in the study of these strata.

The Mesozoic strata were chosen for this investigation in light of the fact that ample continuous sections are developed and exposed in southern Israel as well as the fact that they were never deeply buried.

Overviews on the Mesozoic and Lower Tertiary stratigraphy and paleogeography in southern Israel are given in Bartov and Steinitz (1977) and Garfunkel (1978, 1988). The stratigraphic ages associated with the units investigated follow the conventions as used at the Geological Survey (Bartov et al., 1981). The age results obtained by the K-Ar method are compared with the assumed stratigraphic age of the samples using the numerical time scale of Odin and Odin (1990).

SAMPLING

The sites sampled in the first stage of the project were chosen to represent the Late Mesozoic and Early Tertiary section in Israel. Relevant features of the sampled sequence are:

1. The stratigraphic units, span a time interval of some 150 ma.
2. Within this interval mainly marine lithologies are developed having diverse facial aspects spanning from open marine (shelf) to coastal environments.
3. In many of the formations different lithologies are encountered, spanning from fine grained clastics (shales) to chemical precipitates (carbonates).
4. These formations are widely exposed in Israel.
5. The bio-stratigraphic correlation and control on the formations in this sequence is of high quality, being based on a large data set of paleontologic parameters (macro and micro fauna). As a result, these controls serve as a sound reference time framework for evaluating the analytical results obtained.
6. The stratigraphic, sedimentologic and petrologic attributes of these rocks are well known as a result of a series of investigations carried out in the last decades.

The samples analyzed (Table 1) represent a lithologic and stratigraphic variety from the exposed Mesozoic (up to Early Cenozoic) sequence in southern Israel. The sampling covers the Ardon, Mahmal, Hazera, Ora, Nezer, Menuha, Ghareb and Taqiye Formations. The lithologies sampled were mainly carbonates and associated shaly (clay rich) rocks.

Table 1: Sample location.

Sample	Location	Coordinates	Stratigraphy Formation	Stratigraphy age	Lithology sampled
GYP-9	En Mor	1286/0276	Taqiye	Paleocene	chalk
GYP-10	"	" / "	"	"	marl
GYP-11	"	1287/0282	Ghareb	Maastrichtian	chalk
GILT-9111	Massada Graben	1824/0804	Menuha	Senonian	shale
GILT-9027	" "	1821/0794	"	"	"
GILT-9033	" "	1822/0791	"	"	"
AG-1	" "	1832/0806	"	"	chalk
AG-2	" "	" "	"	"	shale
AG-3	" "	" "	"	"	chalk
GYP-12	Jerusalem	1723/1349	"	"	shale
GYP-13	"	" "	"	"	chalk
SA-107	Nahal Darga	1864/1104	Nezer	Turonian	dolomite
SA-109	" "	" "	"	"	shale
NB-5/2	Nahal Boker	1294/0360	"	"	sandstone
NB-2/7	" "	" / "	"	"	shale
SA-2	Har Zavo'a	1372/0491	"	"	sandstone
SA-11	" "	" "	"	"	"
HG-69	Ma'ale Shaharut	1515/9261	Ora	Turonian	shale
HG-74	" "	" "	"	"	"
GYP-7	Makhtesh Ramon	1324/0037	Hazera	Cenomanian	dolomite
GYP-8	" "	" / "	"	"	shale
GYP-4	" "	1345/0035	Mahmal	Jurassic	marl
GYP-5	" "	" / "	"	"	shale
GYP-6	" "	" / "	"	"	"
GYP-1	" "	1372/0015	Ardon	Liassic	limestone
GYP-2	" "	" / "	"	"	marl
GYP-3	" "	" / "	"	"	shale

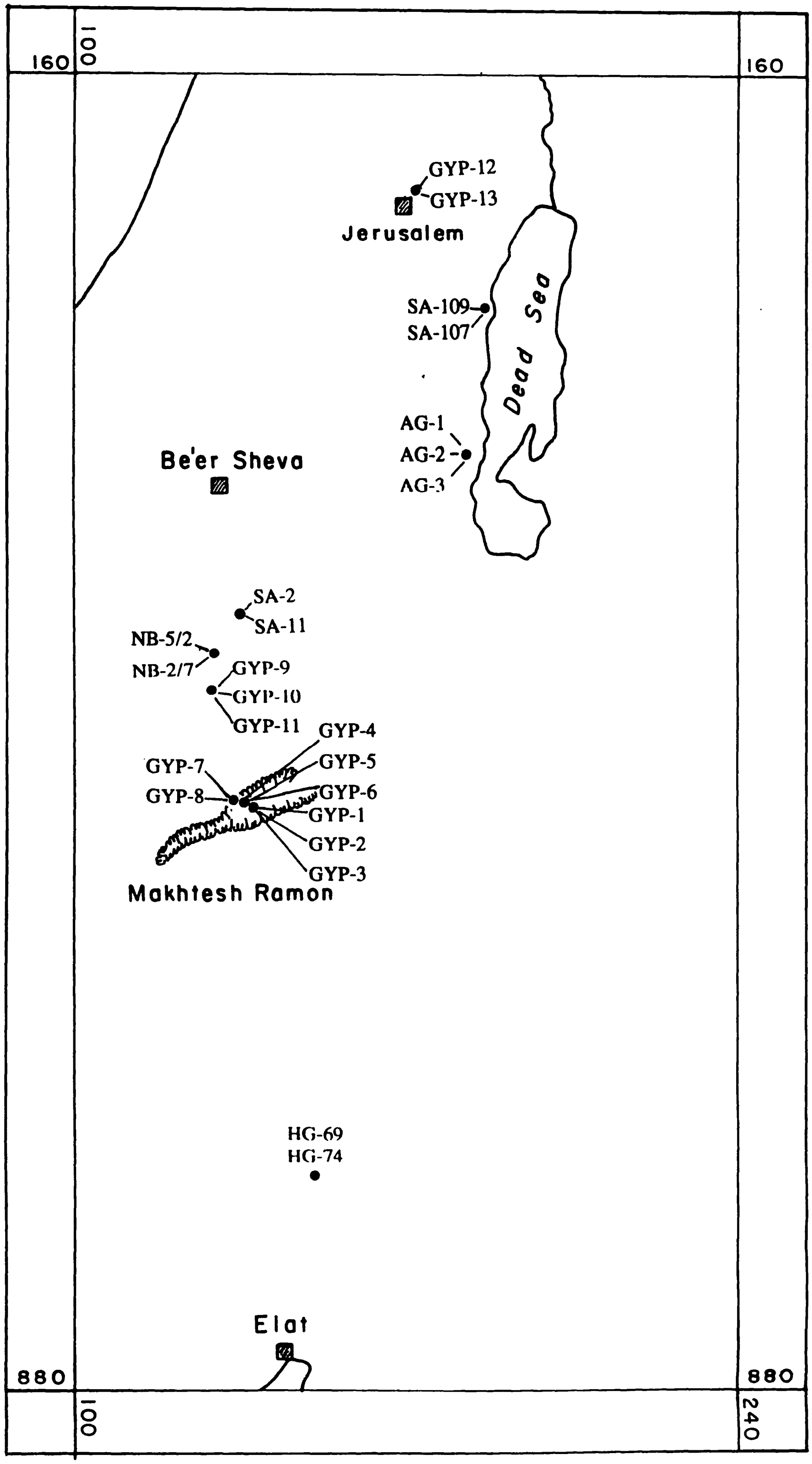

Figure 1: Location map and sampling sites.

METHODS

a. Sample preparation

Samples were dried at 100°C for 10-15 hours prior to crushing and grinding. The ground samples were disaggregated in distilled water. Carbonates were removed by acid digestion, using 2N HCl. The insoluble residue (IR) was rinsed to remove all chloride. Size separation followed using standard sedimentation methods. In most samples size fractions 0-0.2, 0.2-2 and $>4\mu$ were separated. The 0-0.2μ fraction was separated using a centrifuge. In the case of a K-feldspar rich IR the fraction $>4\mu$ was processed (at least three times) in an ultrasonic bath to disaggregate the clay particles from the feldspar surfaces during the size separation. All samples were dried in an oven at 70-80°C. The dry samples were disintegrated in a Spexmix mill using plastic balls.

Due to technical limitations, all clay-size separations were carried out once for each separation. Experience has shown that the resulting separations are incomplete to a certain extent.

b. Analytical

Mineralogical identifications were carried out using XRD (Philips 1730). Bulk IR, total and some coarse fractions were backpacked into aluminum holders or were smeared with methanol on glass. Clay fractions were sedimented from stable suspensions on glass or pumped onto filters. Identification of clay minerals was performed on glycolated samples. Mineral content is estimated qualitatively to semiquantitavely. In some cases observation by SEM (Jeol 840 equipped with a Link model 10000 EDS detector) was carried out.

The amount of potassium in the samples was determined by atomic absorption spectroscopy at the chemistry laboratory of the GSI, using a Varian Spectra 400 AA spectrometer. Samples were dissolved in a mixture of $HF+HNO_3+HClO_4$. All determinations were performed in duplicate.

The argon analysis was performed using the standard isotope dilution procedures of the geochronological laboratory at the GSI (Steinitz et al., 1983, Kotlarsky et al., 1992). Samples, packed in aluminum foil, were loaded into the glass arm of a metal extraction line. Argon was extracted in a molybdenum crucible using RF induction heating. Scrubbing of gases followed in two steps, using liquid nitrogen and ZrAl getters. Argon is concentrated on a charcoal finger and let into a MM-1200B mass spectrometer and measured under full computer control.

RESULTS

Some 25 carbonate, shale and sandstone samples from Middle Jurassic to Paleocene marine formations in central and southern Israel were analyzed. From these, an assortment of IR and clay sized mineral fractions were dated in some 70 K-Ar experiments. The mineralogical and K-Ar age results are presented below, based on the stratigraphic order of the formations sampled.

Ardon Formation (Nevo, 1963a,b) - Lias [205-201 ma]

The Liassic Ardon Formation was sampled in Makhtesh Ramon. The formation consists of shale, marl, limestone and dolomite, probably in part of lagunar origin and in part of shallow marine origin. Some sandstone beds occur in its upper part. The thickness of the Formation in Makhtesh Ramon is around 50 meters.

The three shaly and marly samples analyzed were collected from a stratigraphic interval of some 10 meters, at the upper part of the formation. This part of the formation consists of the red member (Bentor, 1966; locally also known as the "Chocolate Clay") which attains a thickness of up to some 30 meters. The average clay mineralogy of the shale units as given by Bentor (1966) is kaolinite (80%), illite (10%), mixed layer (7%) and traces of montmorillonite.

Table 2 summarizes the mineralogy of the samples insoluble residue. Kaolinite predominates with minor amounts of illite (mica) among the clay minerals.

Table 2: Mineralogy of IR in samples from the Ardon Formation.

Sample	Lithology	%IR	K	I+M	I/S	Q	F	G+H	Others
GYP-1 IR	limestone	18	xxx	tr	-	x(x)	tr	(x)	Anat
GYP-2 IR	marl	53	xx(x)	tr	(x)?	x(x)	(x)	(x)	-
GYP-3 IR	shale	81	xxx	?	-	x	(x)	(x)	-

x ≈ 20%, (x) ≈ 10%, tr - <5%;
K - kaolinite, I - illite, M - mica, I/S - illite/smectite, Q - quartz,
F - feldspar, G - goethite, H - hematite, Anat - anatase

At the present stage only total IR samples have been subjected to the K-Ar analysis. The results are summarized in Table 3.

Table 3: K-Ar analytical results for samples from the Ardon Formation.

Sample	Lithology	%K	$^{40}Ar_{rad}$ 10^{-5}cc/gr	%$^{40}Ar_{rad}$	^{36}Ar 10^{-8}cc/gr	Age ma
GYP-1 IR	limestone	0.69	0.926	85.2	0.545	315.9±6.5
GYP-2 IR	marl	1.33	1.957	90.8	0.669	343.6±7.1
GYP-3 IR	shale	1.64	2.435	92.7	0.649	346.5±7.2
					mean age:	335.3±16.8

From a mineralogical point of view the high kaolinite content of the three marine samples indicates a detrital source for the clay fractions. This is based on the prevalent notion that the source of kaolinite, as a major component of the silicate fraction in such rocks, is from continental sources and could not have been formed in marine conditions.

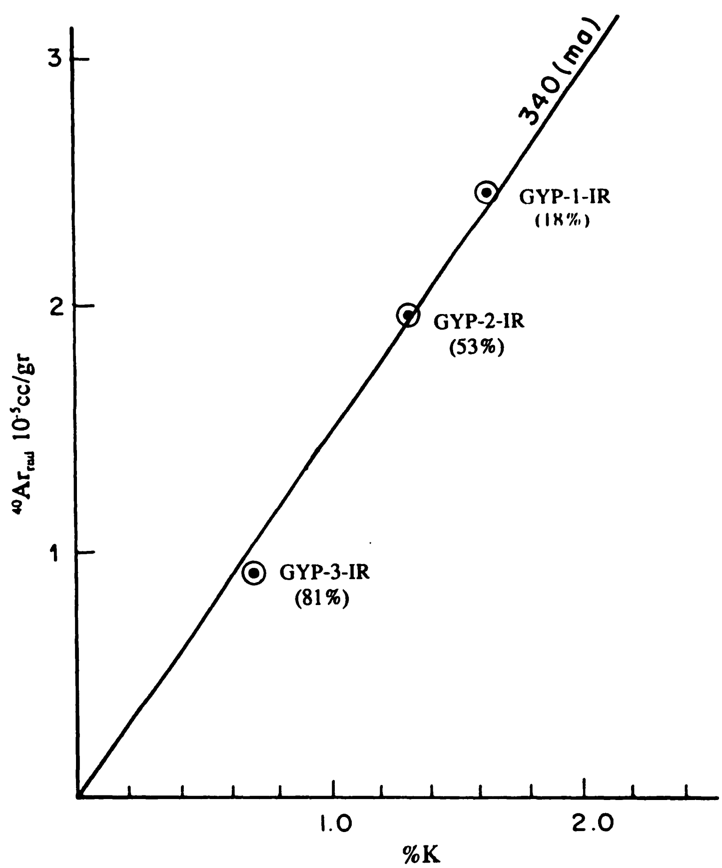

Figure 2: K-Ar correlation diagram for Ardon Formation samples. A reference isochron of 340 ma is indicated. Insoluble residue (IR) content in rock sample is given in brackets.

In the three analyzed samples the K content of the IR fraction increases inversely with the IR content in the rock. The K-Ar age results span from 316 to 346 ma. Such ages are significantly higher than the stratigraphic age of the Ardon Formation (205-201 ma). It is noticeable that the age of the samples varies somewhat with the K content. Considering the mineralogy of the samples it must be concluded that the K is probably enclosed mainly in feldspar and partly in mica (which can even be noticed in hand samples).

On a $^{40}Ar_{rad}$-^{40}K correlation diagram (Fig. 2) the three points align along a line which passes through the origin. The simplest explanation for this plot, at this stage based on three points only, is that we are probably dealing with only one K-Ar system. Still, such a correlation on the $^{40}Ar_{rad}$-^{40}K plot can be due to another situation: the samples are mixtures of two mineral phases in different proportions, one of them with a relatively higher K content. Taking into account the IR content in the rocks it is probable that the distribution reflects a relatively high proportion of K-feldspar in the limestone (GYP-1).

Assuming a single source we can suppose the age of 340 ma to be the minimum age of the source rocks for the detrital fraction in the Ardon Formation. It has been demonstrated that K-Ar ages of illites in the Early Paleozoic (Cambrian) sediments in Israel are reset to around 370-380 ma (Harlavan 1991, Segev 1986). Further analysis should help to clarify the significance of the ages and the genesis of the various phases. In this context it should also be mentioned that zircon fission track ages (307-355 ma), from boreholes in southern Israel, have been attributed to an Early Carboniferous uplift (Feinstein et al., 1989).

Mahmal Formation (Nevo, 1963 and Katz, 1968) - Middle Jurassic, [176-167 ma].

The Middle Jurassic (Bajocian) Mahmal Formation was sampled in Makhtesh Ramon. The formation is composed mainly of sandstone, calcareous sandstone, shale, as well as sandy limestone and dolomite, all presumed to be of marine origin. It attains a thickness of some 80 meters. According to Bentor (1966) kaolinite predominates in the clay fractions of this formation.

The three shale and limestone samples analyzed were collected from a zone of calcareous beds from the "Brown Questa". One shale sample (GYP-5) originates some 2 meters below the marl sample (GYP-4). The shale sample is located some 40 meters lower in the section.

The mineralogical composition of the analyzed samples is presented in Table 4.

Table 4: Mineralogy of IR in samples from the Mahmal Formation.

Sample	Lithology	%IR	K	I	I/S	Q	F	G/H	Others
GYP-4 IR	marl	54	tr	-	-	xxxx	-	-	-
GYP-5 IR	shale	69	xx(x)	?	-	x(x)	-	x(x)	-
GYP-6 IR	shale	83	x(x)	-	x?	xx	?	tr	

x ≈ 20% (x) ≈ 10% tr - <5%
K - kaolinite, I - illite, M - mica, S - smectite, Q - quartz,
F - feldspar, G - goethite, H - hematite.

At the present stage, only IR (total) samples have been subjected to the K-Ar analysis. The results are summarized in Table 5 and Fig. 3.

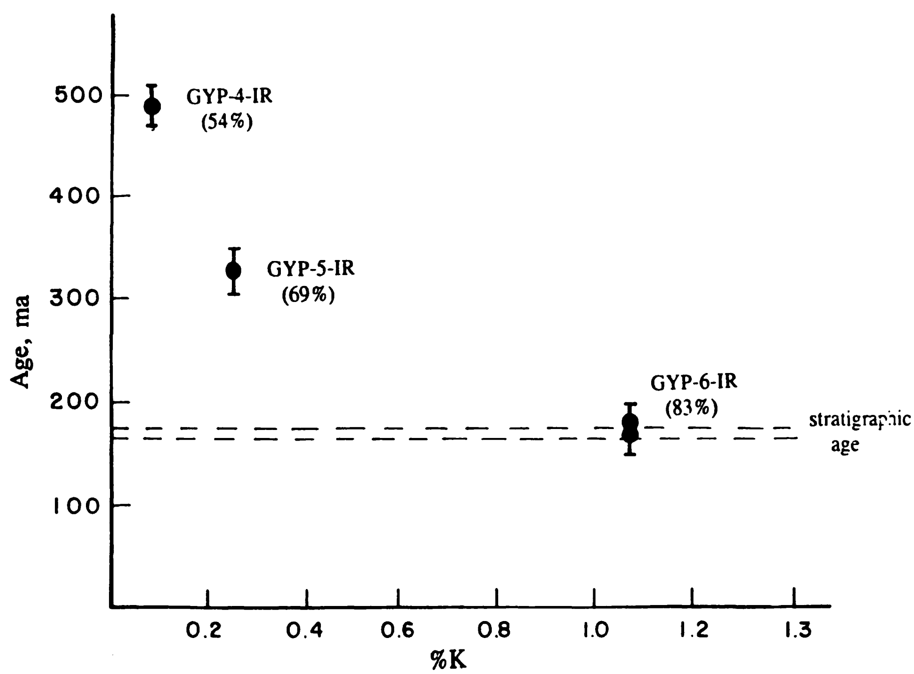

Figure 3: K-Ar age as a function of the K content in the samples from Mahmal Formation. The mean chronometric age of the formation is indicated. IR content in rock sample is given in brackets.

Table 5: K-Ar analytical results for samples from the Mahmal Formation.

Sample	Lithology	%K	$^{40}Ar_{rad}$ 10^{-5}cc/gr	%$^{40}Ar_{rad}$	^{36}Ar 10^{-8}cc/gr	Age ma
GYP-4	Marl	0.074	0.164	78.5	0.152	496.9±10.3
GYP-5	Shale	0.25	0.343	61.3	0.733	322.4± 7.0
GYP-6	Shale	1.09	0.792	79.8	0.680	178.4± 3.7
GYP-6	"	1.09	0.773	77.0	0.783	174.4± 3.6

One shale sample (GYP-6), with a K content of >1%, yielded a K-Ar age of 176 ma which conforms with the stratigraphic age of the Mahmal Formation. The second shale sample (GYP-5) yielded an age which is similar to the age indicated by the samples analyzed from the Ardon Formation (Table 3).

The IR of the marl sample has a much lower K content and it yields a "Pan African" age (cf. Bentor, 1985) of 497 ma. This age is probably a lower estimate for the age of the source rocks of the detrital fraction.

Hazera Formation (Arkin and Braun, 1965) - Cenomanian [96-91 ma].

The Cenomanian Hazera Formation is composed mainly of limestone, dolomite and shale which were deposited in a shallow open marine environment. Clay-rich rocks are relatively abundant in the lower part of the formation. The thickness of the formation in the Makhtesh Ramon area is around 250 meters. The overall average clay mineralogy of Early and Late Cenomanian rocks in Israel was found to be: montmorillonite - 17% & 31%; illite - 56% & 56%; kaolinite - 21% & 9%, respectively (Bentor, 1966).

One shale and one dolomite were sampled at the northern flank of Makhtesh Ramon. The two samples originate from the "bentonite" beds at Ma'ale HaAtzmaut (cf. Bentor 1966, p. 79). These beds, attaining there a thickness of some 3 meters, belong to the Hevyon Member (Late Albian to Early Cenomanian - cf. Bartov et al., 1981), which is the lowermost member of the Hazera Formation.

The mineralogy of the IR samples and the separated fractions are presented in Table 6.

Table 6: Mineralogy of IR in samples from the Hazera Formation.

Sample	Lithology	%IR	K	I	I/S	Q	F	G/H	Others
GYP-7 IR	dolomite	8	?	x	x?	?	xxx	-	-
GYP-7 >4μ	"		-	-	-	-	xxxxx	-	-
GYP-7 0.2-2μ	"		-	[xxx	]	-	tr?	x	ber
GYP-7 0-0.2μ	"		-	[xxx(x)	]	-	-	(x)	-
GYP-8 IR	shale	76	x	(x)	xxx	x	(x)	-	
GYP-8 >4μ	"		-	-	-	xxx(x)	x		
GYP-8 0.2-2μ	"		x(x)	(x)	xxx	-	-	-	-
GYP-8 0-0.2μ	"		x	(x)	xxx(x)	-	-	-	-

x ≈ 20%, (x) ≈ 10%, tr - <5%
K - kaolinite, I - illite, M - mica, S - smectite,
Q - quartz, F - feldspar, G - goethite, H - hematite,
ber - berthierine

Table 7: K-Ar analytical results for samples from the Hazera Formation.

Sample	Lithology	%K	$^{40}Ar_{rad}$ 10^{-5}cc/gr	$\%^{40}Ar_{rad}$	^{36}Ar 10^{-7}cc/gr	Age ma
GYP-7 IR	dolomite	8.62	3.305	82.4	0.239	96.1±2.0
GYP-7 IR	"	8.83	3.491	88.7	0.151	99.0±2.0
GYP-7 >4μ	"	11.97	4.668	95.3	0.078	97.6±2.0
GYP-7 "	"	"	4.669	95.7	0.071	97.7±2.0
GYP-7 "	"	"	4.629	93.8	0.102	96.8±2.0
GYP-7 0-0.2μ	"	4.25	1.630	56.5	0.424	96.1±2.1
GYP-7 0.2-2μ	"	4.26	1.807	65.0	0.329	105.9±2.3
GYP-8 IR	shale	3.30	1.403	76.8	0.143	106.2±2.2
GYP-8 >4μ	"	5.35	2.560	84.0	0.164	119.3±2.5
GYP-8 0.2-2μ	"	2.48	0.963	64.0	0.184	97.2±2.1
GYP-8 0-0.2μ	"	2.54	0.923	64.7	0.171	91.2±1.9

The K-Ar age results are summarized in Table 7 and Fig. 4. The ages of the various fractions separated from these two adjacent samples - a dolomite and a shale - span from 119 to 91 ma, all within the Albian-Cenomanian time scale (108-91 ma). This result, obtained on two different lithologies, implies the K-Ar system in the various silicate fractions is basically controlled by a syn-sedimentary event. The syn-sedimentary event is recorded and retained in the finest size fractions, indicating their retentivity in these lithologies.

The clay fraction of the shale sample (GYP-8) is composed predominantly of I/S (mixed layer illite-smectite) and about 20% kaolinite. No clear mineralogical differentiation is noticed between the $<2\mu$ separated size fractions. In this sample the highest age is the age of the $>4\mu$ fraction. The fine fractions yield younger ages, with the smallest fraction ($0\text{-}0.2\mu$) yielding the youngest age, and the total IR fraction with an intermediate age. These age relations, as well as the relatively higher K content of the $>4\mu$ fraction, suggest that K-feldspar having an older age is present in the coarse fraction. XRD patterns indicate the presence of circa 20% K-feldspar in the $>4\mu$ fraction. Still, such an amount cannot account for the 5.35% K in this fraction and another K-bearing phase must be assumed. The finest fraction separated from the shale has, relative to the stratigraphic age, a somewhat younger (10%) age. This may either be the result of some argon loss or due to a late diagenetic effect. Such questions cannot be resolved without additional data.

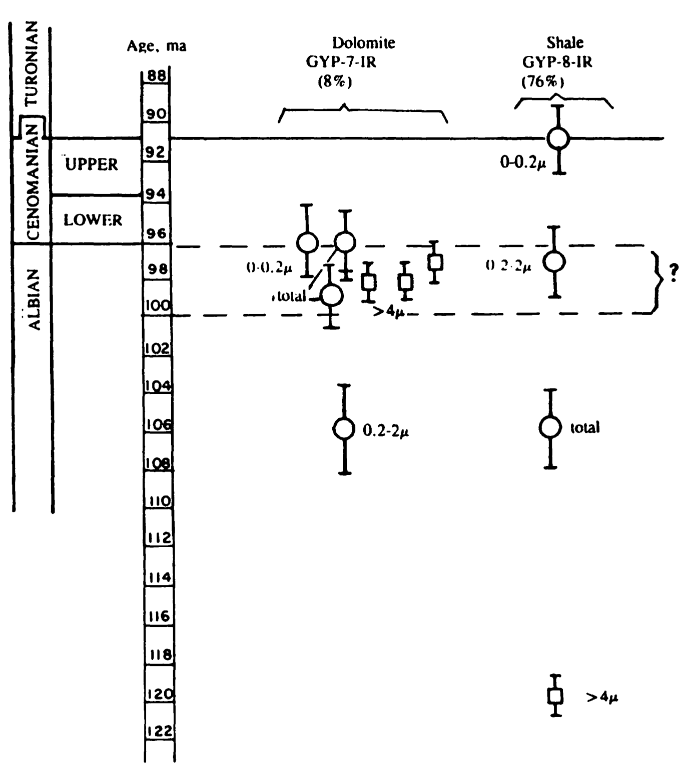

Figure 4: Distribution of size fraction ages in the Hazera Formation (Hevyon Member) relative to its chronometric age. IR content in rock sample is given in brackets.

The IR fraction of the dolomite sample (GYP-7) is rich in K-feldspar associated with minor amounts of illite and illitic I/S. The different size fractions yield (semi) pure mineral separates, with the clay minerals predominating in the $<2\mu$ fraction. Pure K-feldspar was separated from the coarser ($>4\mu$) fraction. SEM investigation shows it to be crystals with idiomorphic forms (Fig. 5), mostly in the size range of 4-15μ. Based on these criteria it is assumed that the K-feldspar in the dolomite is authigenic. Authigenic K-feldspar in Cenomanian carbonates has been reported from localities in Israel and Lebanon (Goldman-Teitel, N., M.Sc. thesis, in prep.; Huckel, 1974).

The 0.2-2μ clay mineral fractions in the dolomite yield an age which coincides with the IR age of the adjacent shale sample (Fig. 4). The age of the K-feldspar, which clearly governs the age of IR age, is similar to the age of the finest fraction. The Late Albian age of the various fractions are in accordance with the petrographic observations as to an authigenic origin of the K-feldspar and imply that the illitic phase in these samples is an early diagenetic product. The somewhat older age of the 0.2-2μ fraction is probably a result of a detrital component within it.

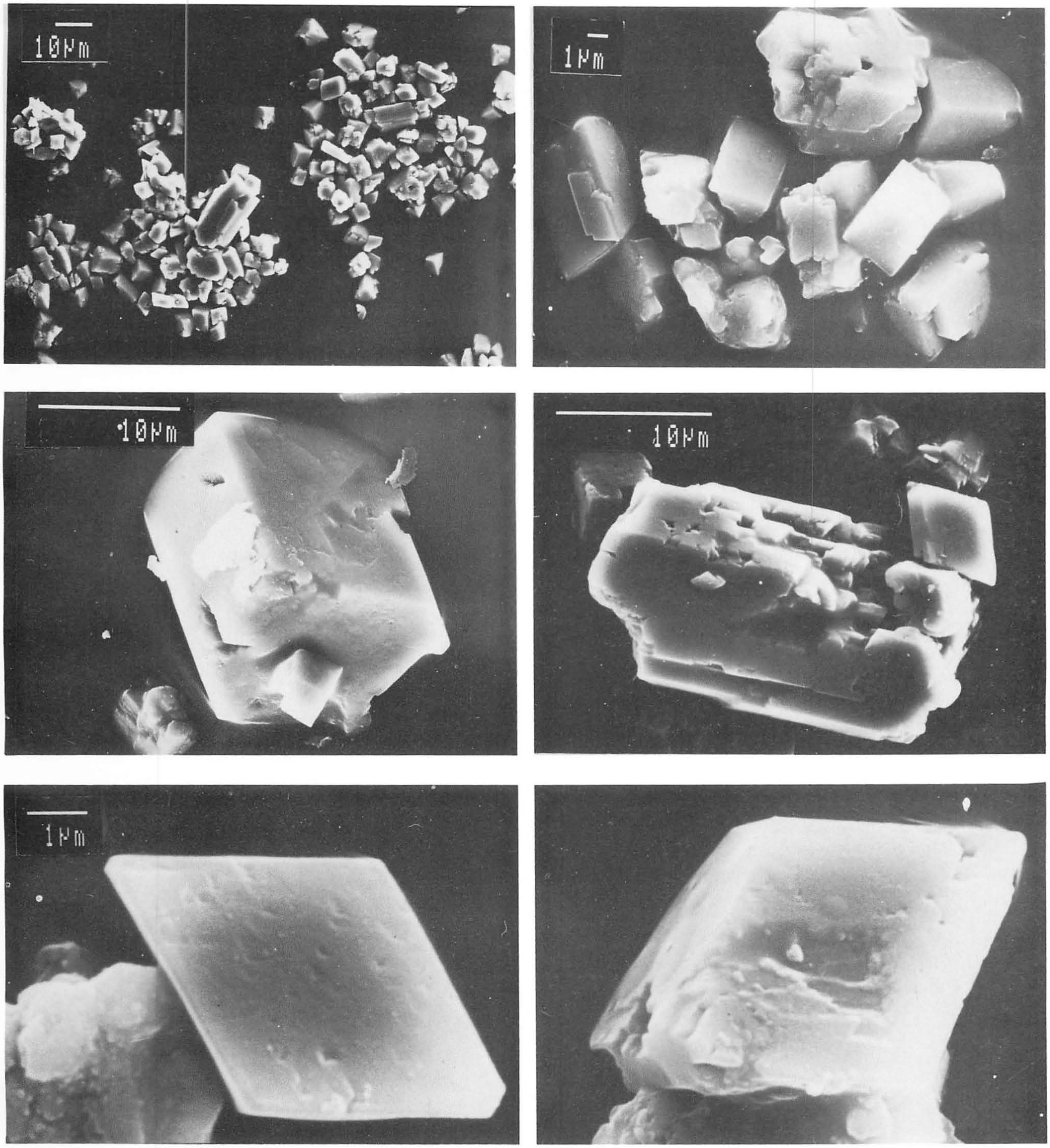

Figure 5: SEM picture of idiomorphic K-feldspar crystals separated from dolomite sample (GYP-7; Hazera Fm.)

Ora Formation (Freund, 1962) - Turonian [91-88 ma].
Nezer Formation (Bentor and Vroman, 1963) - Turonian [91-88 ma].

The Ora (Shale) Formation was defined in the southern and central Negev and its age is Latest Cenomanian to Middle Turonian. The Nezer Formation was defined in the northern Negev and its age is Middle to Late Turonian. Since the samples from the Ora Formation originate from its Upper Member they are time equivalents of the samples from the Nezer Formation, all sampled from its clastic unit.

The Ora Formation is composed of shale, dolomite, limestone, and locally of sandstone, gypsum and anhydrite. The environment of deposition is assumed to be shallow marine, from open to partially restricted (lagoonal). In the southern Negev the formation attains a thickness of around 100 meters. The general clay mineral composition of the Turonian strata was given by Bentor (1966) as: montmorillonite (40%), illite (30%) and kaolinite (30%).

The two samples analyzed (HG-69, HG-74) originate from an anhydrite and dolomitic shale party exposed at Ma'ale Shaharut, in a section which is similar to that exposed at Ma'ale Gerofit. The clay mineralogy of the shale layers along a 20 meter section at this outcrop varies from illite dominance with some kaolinite in the lower beds to different proportions of montmorillonite, illite and kaolinite in higher beds (Bentor, 1966).

The Nezer Formation consists of open marine limestones and marls attaining a thickness of several tens of meters.

The samples analyzed are shale and sandstone from the clastic unit at Nahal Boqer and Har Zavo'a, and a two dolomite and dolomitic shale samples (SA-107, SA-109) from the same stratigraphic level at Nahal Darga in the Judean Desert. Sample SA-109A is a new separation of the $<2\mu$ fraction from the same sample. A trace of quartz is detected in this separation (relative to the first).

The mineralogical composition of the separated samples from the Ora and Nezer formations is given in Table 8. K-Ar age determinations are presented in Table 9 and Fig. 6.

The ages of the various separated fractions, 140 to 76 ma, spread around the stratigraphic age of the sampled formations.

The analyzed samples can be grouped to a continental shale and sandstone facies (NB-5/2, SA-2, SA-11 & NB-2/7) and to a restricted marine dolomite-anhydrite and shale facies (SA-109, SA-107, HG-74 & HG-69). The ages of the $<2\mu$ fractions of the first group are close to 100 ma and those of the second group around 78 ma. The I/S compositions of the latter group are more illitic (higher K) and were suspected to be early diagenetic products (Sandler, in prep.).

The result obtained implies that the analytically significant age difference of the two groups of $<2\mu$ fractions may be controlled by facies parameters. The only $>4\mu$ fraction analyzed from a sample from the latter group resulted in a higher age. From these results it can be concluded that:

a) A major syngenetic K-Ar signal is present in the analyzed fractions;

b) A diagenetic signature (circa 10 ma younger relative to expected age) is recorded in the K-Ar systems of relatively high K illitic phases.

Table 8: Mineralogy of clay fraction in samples from the Turonian formations.

Sample	Lithology	%IR	K	I	I/S	P	Ch	Anh	Q	F
NB-5/2 $<2\mu$	sandstone		tr	(x)	xxxx	tr	-	-	-	
SA-2 $<2\mu$	sandstone	97	x	(x)	xxx(x)	tr	-	-	tr	
SA-11 $<2\mu$	sandstone	96	tr	tr	xxxx	-	-	-	tr	
NB-2/7 $<2\mu$	shale		tr	(x)	xxx	x(x)	-	-	-	
SA-109 $<2\mu$	shale	52	(x)	[xxxx]		-	tr	tr	(tr)	
SA-107 $<2\mu$	dolomite	13	(x)	x	xxx	-	-	-	-	
SA-107 $>4\mu$	"		tr	tr	(x)	-	-	-	xx(x)	x
HG-74 $<2\mu$	shale	77	-	[xxxxx]		-	-	-		
HG-69 $<2\mu$	shale	61	-	[xxxxx]		-	-	-	-	

x≈20%, (x)≈10%, tr-<5%.
K-kaolinite, I-illite, S-smectite, P-palygorskite,
Ch-chlorite Anh-anhydrite Q-quartz F-feldspar

Table 9: K-Ar analytical results for samples from the Turonian formations.

Sample		Lithology	%K	$^{40}Ar_{rad}$ 10^{-4}cc/gr	%$^{40}Ar_{rad}$	^{36}Ar 10^{-7}cc/gr	Age ma
NB-5/2	<2μ	sandstone	3.17	0.133	66.7	0.224	104.6±2.2
SA-2	<2μ	sandstone	2.55	0.097	62.7	0.196	95.7±2.1
SA-11	<2μ	sandstone	1.69	0.066	66.7	0.112	98.4±2.1
NB-2/7	<2μ	shale	2.86	0.162	72.7	0.206	140.0±2.9
SA 109	<2μ	shale	5.00	0.152	61.0	0.328	76.5±1.7
SA-109A	<2μ	shale	4.28	0.136	64.2	0.256	79.7±1.7
SA-107	<2μ	dolomite	3.64	0.113	58.1	0.276	78.3±1.7
SA-107	>4μ	"	3.44	0.135	78.1	0.128	98.4±2.0
HG-74	<2μ	shale	4.91	0.164	80.3	0.136	84.3±1.8
HG-74	<2μ	"	4.71	0.146	64.4	0.273	78.1±1.7
HG-69	<2μ	shale	4.21	0.134	60.1	0.301	79.9±1.7

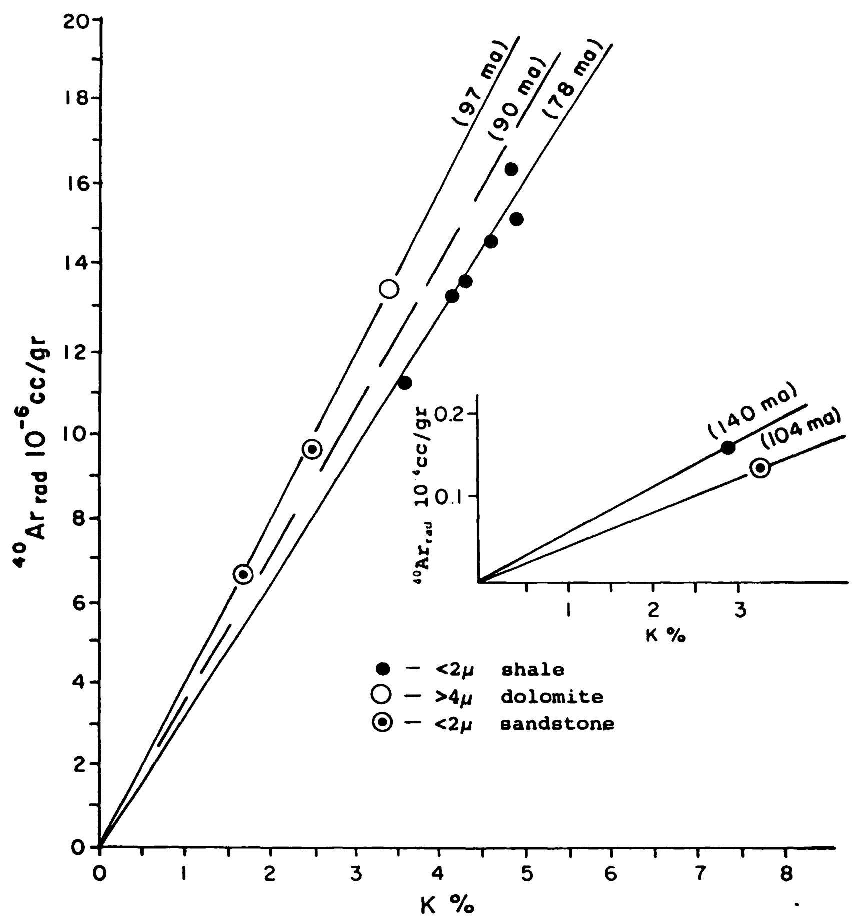

Figure 6: K-Ar correlation diagram of Turonian samples. Insert: NB5/2 and NB2/7 samples, analyzed in 1987.

Menuha Formation (Shaw, 1947; Bentor and collab., 1960) - Santonian-Campanian [87-83 ma].

The Menuha Formation consists of massive chalks of Santonian and Campanian age. In the Negev its thickness may attain some 80 meters, but in many areas it is less. In some areas (southern Negev, Judean Desert) a clayey unit is developed which contains shale, phosphoritic marls and chert. The environment of deposition is marine.

The samples analyzed were collected from this unit in the Judean Desert and in Jerusalem. Three samples (GILT - analyzed in 1985) are from shale beds occurring in the central part of the section as developed in the Massada Graben. Their mineralogical composition was not determined at the time but it is assumed to be similar to that of the additional samples (AG) originating from the same area and to other samples from the same stratigraphic level (Sandler et al., 1992). The samples collected in Jerusalem are a shale and an adjacent chalk, at a stratigraphic position which is similar to that of the samples from the Massada Graben.

The mineralogical composition of the analyzed fractions are presented in Table 10.

Table 10: Mineralogy of IR and clay fractions in samples from the Menuha Formation.

Sample		Lithology	%IR	K	I,M	S	Q	F	G	Ap
GYP-12	IR	shale	50	[	xxx	]	x	(x)	(x)	-
GYP-12	0.2-2μ	"		x(x)	tr	xxx	-	-	(x)	-
GYP-12	0-0.2μ	"		x	-	xxxx	-	-	tr	-
GYP-13	IR	chalk	2	[	xx	]	xx	(x)	?	-
GYP-13	0.2-2μ	"		x(x)	x	xx	tr	-	(x)	-
GYP-13	0-0.2μ	"		x	x	xx(x)	tr	-	(x)	-
AG-1	<2μ	chalk	7	tr	tr	xxx	xx	-	-	-
AG-1	>4μ	"		-	tr	-	xxx	x(x)	-	tr?
AG-2	<2μ	shale	75	(x)	tr	xxx(x)	(x)	-	?	-
AG-2	>4μ	"		tr	tr	-	xx(x)	xx	-	(x)
AG-3	<2μ	chalk	14	(x)	tr	xxx(x)	(x)	-	-	-
AG-3	>4μ	"		tr	tr	-	xxx	xx	-	tr?

x≈20%, (x)-10%, tr-<5%.
K-kaolinite, I,M-illite, mica S-smectite, Q-quartz,
F-feldspar, G-goethite, Ap-apatite.

The K-Ar age results are summarized in Table 11.

Table 11: K-Ar analytical results for samples from the Menuha Formation.

Sample	Lithology	%K	$^{40}Ar_{rad}$ 10^{-5}cc/gr	%$^{40}Ar_{rad}$	^{36}Ar 10^{-8}cc/gr	Age ma
GILT 9027 <2μ	shale	2.72	0.906	76.3	0.953	83.7±1.7
GILT 9027 <2μ	"	2.19	0.755	78.3	0.708	86.5±1.8
GILT 9033 <2μ	"	1.65	0.499	79.5	0.435	76.2±1.6
GILT 9111 <2μ	"	2.09	0.777	79.3	0.685	93.5±1.9
GYP-12 0-0.2μ	shale	0.53	0.221	57.0	0.563	104.0±2.3
GYP-12 0.2-2μ	"	0.62	0.398	68.1	0.630	157.9±3.3
GYP-12 IR	"	0.66	0.495	77.5	0.495	183.4±3.8
GYP-13 0-0.2μ	chalk	1.56	0.724	74.3	0.868	118.5±2.5
GYP-13 0.2-2μ	"	1.76	0.920	76.1	0.982	129.8±2.7
GYP-13 IR	"	1.68	0.759	72.2	0.760	112.7±2.3
AG-1 <2μ	chalk	1.02	0.433	51.0	1.411	106.6±2.4
AG-1 >4μ	"	4.74	1.961	85.0	1.169	103.4±2.1
AG-2 <2μ	shale	1.47	0.552	58.7	1.314	94.2±2.1
AG-2 >4μ	"	6.52	2.458	80.2	2.047	94.5±2.0
AG-3 <2μ	chalk	1.53	0.682	66.1	1.185	111.2±2.4
AG-3 >4μ	"	8.24	2.350	90.5	0.832	71.9±2.4
AG-3 "	"	8.24	2.355	89.1	0.976	72.0±1.5

The results are displayed on a K-Ar distribution diagram (Fig. 7). Overall, the K-Ar ages tend to be near the stratigraphic age of the Meunuha Formation. A partially systematic variation is observed for the different samples.

The shale samples analyzed from the Judean desert have a relatively high K content. For these first three samples (GILT) only $<2\mu$ fractions were analyzed. They yield ages which are close to the stratigraphic age. The additional set of three samples (AG) from a nearby locality includes two chalk samples and one shale sample from which the $<2\mu$ and the $>4\mu$ fractions were analysed. The ages are all between 111 to 72 ma. The younger ages are observed in the $>4\mu$ K rich fraction in which K-feldspar was identified. This result implies a diagenetic age for the K-feldspar.

The different size fractions of the shale and chalk samples from Jerusalem yield somewhat higher ages. Both the age of the fraction as well as its K content vary with the size. This probably indicates that the fractions are mixtures of an authigenic component and a detrital one. This relationship is also demonstrated on the K-Ar distribution diagram where each set of sub-samples forms a separate linear array which is steeper than the reference isochron.

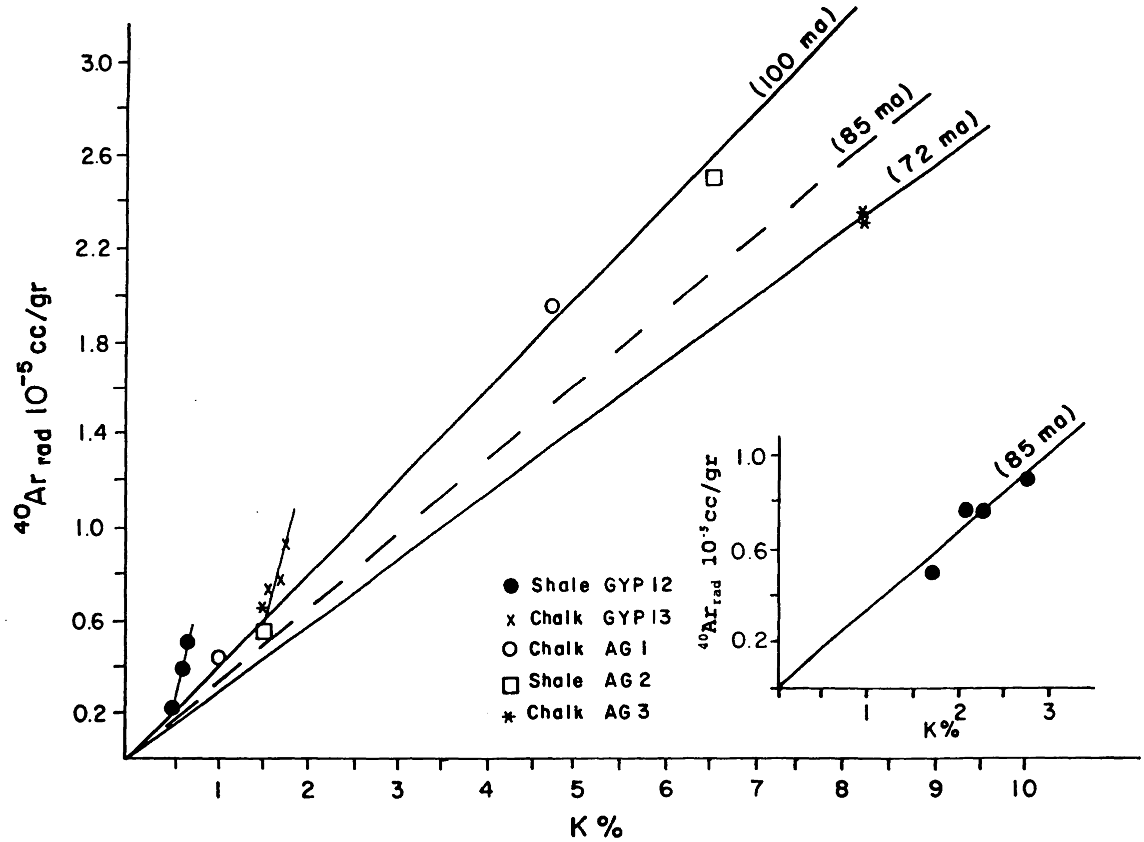

Figure 7: K-Ar correlation diagram for Menuha Formation samples and their clay fractions. The mean chronometric age of the formation is indicated by a reference isochron. Insert: GILT samples (shale) analyzed in 1985.

Ghareb Formation (Shaw, 1947) - Maastrichtian [72-65 ma].

The Ghareb Formation is composed of chalk and marl, of marine origin, in part probably of a restricted environment. Its thickness in the northern Negev is several tens of meters. A Maastrichtian age is attributed to it.

One chalk sample, collected at the classical outcrops of the Zin Valley, was analyzed.

The mineralogy of the samples is given in Table 12.

Table 12: Mineralogy of IR in samples from the Ghareb Formation.

Sample	Lithology	%IR	K	I,M	S	Q	F
GYP-11 IR	chalk	11	[	xxx(x)	]	x	(x)
GYP-11 >4μ	"			tr	x	xxx	x
GYP-11 0.2-2μ	"		tr	tr	xxxx	tr?	-
GYP-11 0-0.2μ	"		-	tr	xxxx(x)	tr?	-

x ≈20%, (x) ≈10%, tr -<5%
K -kaolinite, I,M -illite, mica S -smectite, Q -quartz, F -feldspar.

The K-Ar age results are summarized in Table 13 and presented in Fig. 8.

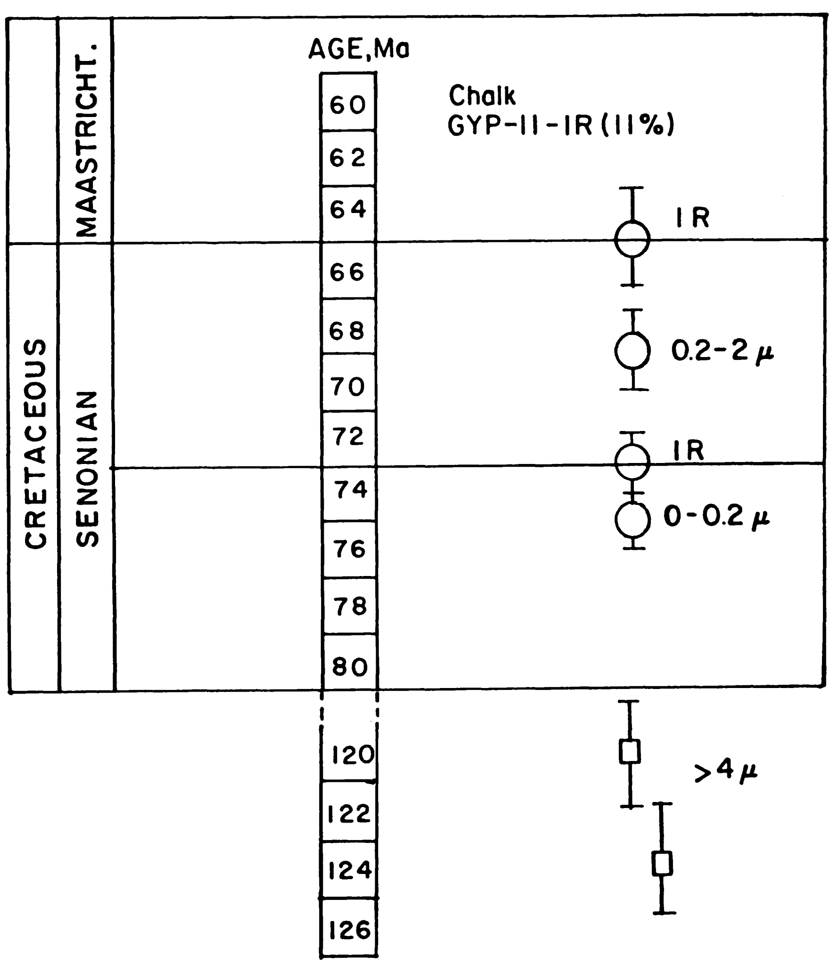

Figure 8: Distribution of the clay fraction ages in the Ghareb Formation relative to its chronometric age. IR content in rock sample is given in brackets.

Table 13: K-Ar analytical results for a sample from the Ghareb Formation.

Sample	Lithology	%K	$^{40}Ar_{rad}$ 10^{-5}cc/gr	%$^{40}Ar_{rad}$	^{36}Ar 10^{-8}cc/gr	Age ma
GYP-11 IR	chalk	1.82	0.532	71.4	0.722	73.3±1.5
GYP-11 IR	"	1.72	0.433	63.1	0.858	63.8±1.4
GYP-11 0-0.2μ	"	0.850	0.251	45.2	1.030	74.5±1.8
GYP-11 0.2-2μ	"	1.42	0.391	57.3	0.983	69.6±1.5
GYP-11 >4μ	"	2.38	1.148	81.6	0.876	120.0±2.5
GYP-11 >4μ	"	2.38	1.208	64.1	2.286	126.1±2.7

Total IR and the fine clay fractions separated from the chalk sample yield K-Ar ages (74-64 ma) which are very close to the stratigraphic age (72-65). The result implies a major authigenic component in the K-Ar system of these fractions. The higher K content in the >4μ fraction is accompanied by an increase in the age, probably a consequence of the higher feldspar content and/or detrital quartz. Still, even this fraction contains a significant authigenic K-Ar component.

Taqiye Formation (Browne et al., 1941; Shaw, 1947) - Paleocene [65-53 ma]

The Taqiye Formation, deposited under restricted marine conditions, is composed of marl and shale.

The paleogeography of the Taqiye Formation in the northern Negev was described in detail by Arkin et al. (1972). Samples were collected from the well known outcrop at En Mor (Zin Valley). In this area a prominent chalk unit is developed in the upper part of the formation - the Hafir member (Late Landenian). One sample comes from the marl just below the Hafir member and the other from the Hafir chalk.

The clay mineralogy of this formation, and especially the occurrence of palygorskite was studied in detail by Nathan (1970): In the lower part kaolinite and montmorillonite dominate, and only minor amounts of illite are encountered. The content of montmorillonite increases upwards and dominates the clay fraction just below the Hafir chalk. The clay just below and above the Hafir chalk consists of montmorillonite and palygorskite. These variations in the clay mineralogy have been ascribed to paleogeographic factors.

The mineralogy of the samples is presented in Table 14.

Table 14: Mineralogy of IR in samples from the Taqiye Formation.

Sample	Lithology	%IR	K	P	I	I/S	Q	F	CT	Clin	B	Sep
GYP- 9 IR	chalk	12	[	(x)		]	x(x)	?	x	x	x?	-
GYP- 9 0.2-2μ	"		-	x	tr?	x	x	-	x(x)	(x)	-	-
GYP- 9 0-0.2μ	"		-	xx	tr?	xx	-	-	x	-	-	-
GYP- 9 2-8μ	"		[	x(x)		]	x(x)	?	x	x	-	-
GYP- 9 8-16μ	"		[	x(x)		]	x(x)	?	x(x)	(x)	-	-
GYP- 9 16-32μ	"		[	x		]	?	x	xx	(x)	x?	-
GYP- 9 32-64μ	"		[	x		]	?	x	xx	(x)	x?	-
GYP- 9 5-64μ	"		[	(x)		]	x(x)	x	xx	x	-	-
GYP- 9 >64μ	"		[	tr		]	x(x)?	?	xxx	tr	x?	-
GYP-10 IR	shale	24	[	xxx		]	x(x)	?	-	-	x	-
GYP-10 0.2-2μ	"		-	xx	-	xx	x	-	-	-	-	?
GYP-10 0-0.2μ	"		-	xx	tr?	xx(x)	tr	-	-	-	-	tr?
GYP-10 2-8μ	"		[	xx(x)		]	x(x)	x	-	-	-	-
GYP-10 8-16μ	"		[	xx(x)		]	x(x)	?	-	-	(x)	-
GYP-10 16-32μ	"		[	xxx		]	x(x)	?	-	-	x?	-
GYP-10 32-64μ	"		[	xxx		]	x(x)	?	-	-	x?	-
GYP-10 5-64μ	"		[	xxx		]	x(x)	?	-	-	x?	-
GYP-10 >64μ	"		[	xxx		]	x	?	-	-	x	-

x ≈20%, (x) ≈10%, tr -<5%.
K -kaolinite, I -illite, P -palygorskite, S -smectite, Q -quartz,
F -feldspar, CT -opal, Clin -clinoptilolite, B -barite, Sep-sepiolite

The K-Ar age results are summarized in table 15 and Fig. 9.

Table 15: K-Ar analytical results for samples from the Taqiye Formation.

Sample	Lithology	%K	$^{40}Ar_{rad}$ 10^{-5}cc/gr	$\%^{40}Ar_{rad}$	^{36}Ar 10^{-7}cc/gr	Age ma
GYP- 9 0-0.2μ	Chalk	0.777	0.270	18.5	0.401	87.9±4.3
GYP- 9 0-2μ	"	0.736	0.304	32.3	0.216	103.4±3.1
GYP- 9 2-8μ	"	0.846	0.345	39.6	0.178	102.0±2.6
GYP- 9 8-16μ	"	0.918	0.353	39.8	0.181	96.4±2.5
GYP- 9 16-32μ	"	0.782	0.229	28.3	0.197	73.9±2.4
GYP- 9 32-64μ	"	0.708	0.322	32.8	0.223	113.5±3.3
GYP- 9 >64μ	"	0.558	0.221	22.7	0.226	99.4±4.0
GYP- 9 5-64μ	"	0.770	0.318	23.6	0.347	103.2±4.0
GYP-10 0-0.2μ	Shale	1.14	0.398	25.7	0.389	87.6±3.1
GYP-10 0-2μ	"	1.08	0.511	42.1	0.238	118.5±2.9
GYP-10 8-16μ	"	1.24	0.666	74.8	0.076	133.1±2.8
GYP-10 16-32μ	"	1.27	0.652	74.8	0.074	127.0±2.7
GYP-10 32-64μ	"	1.24	0.618	70.2	0.087	123.8±2.6
GYP-10 >64μ	"	1.25	0.661	70.6	0.093	131.0±2.8
GYP-10 5>64μ	"	1.28	0.719	51.3	0.231	139.1±3.2

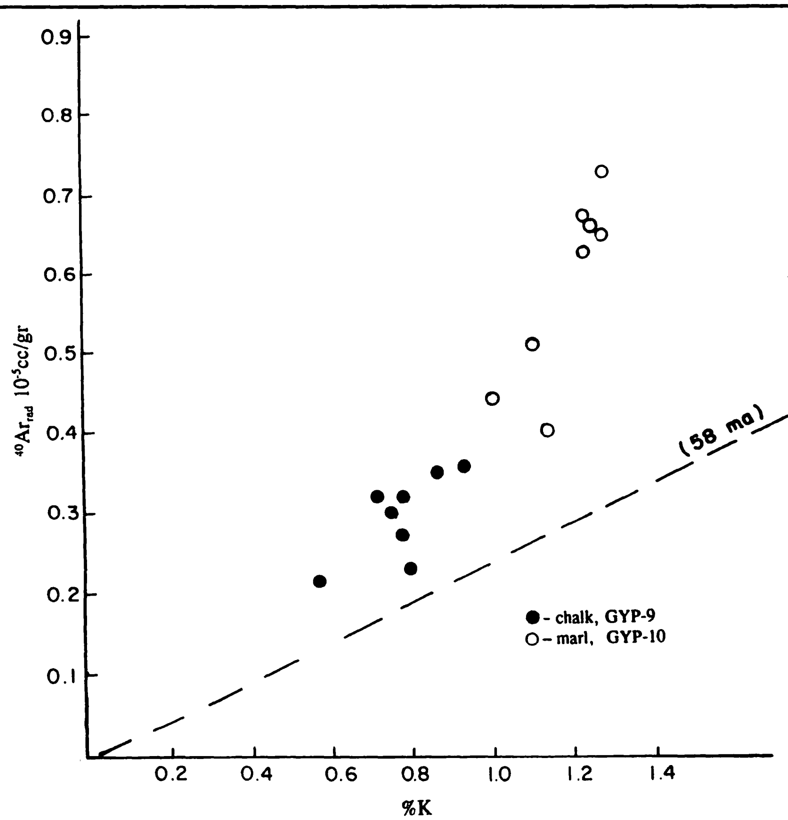

Figure 9: K-Ar correlation diagram for Taqiye Formation samples. The mean chronometric age of the formation is indicated by a reference isochron.

The K-Ar ages of all size fractions, from both samples, range from 139 ma to 74 ma - tending to the lower chronometric age [58 ma] of the paleocene. The tendency of some of the fractions to yield ages close to the chronometric age of the formation indicates that an authigenic K-bearing clay fraction is present (Fig.9).

DISCUSSION

In the present survey, clay fractions from major lithologies (carbonate, marl and shale) of formations, ranging in age from the Jurassic to the Early Tertiary, were dated with the K-Ar method. The range of formations investigated constitutes a significant part of the Mesozoic and Lower Tertiary marine sequence of Israel.

The prevailing approach in the literature is that the clay fractions in marine sedimentary sequences, and especially in shales, are primarily of a detrital origin (*c.f.* Weaver, 1989). However, from the K-Ar ages obtained in the present work we conclude the following:

a) Significant proportions of the K-bearing clay fractions are synchronous with the time of deposition, which means either detrital supply of land-derived authigenic K bearing clays, or syn-sedimentary diagenetic authigenesis, or both. The significance of this result is to be valued in light of the number of stratigraphic units surveyed as well as the two end member lithologies (carbonate, shale) investigated.

b) Mixing patterns between "authigenic" ages and "detrital" ages have been demonstrated in several cases. Two types of processes can lead to such mixing patterns:

1) Co-existence of authigenic and detrital minerals;

2) Partial to complete sedimentary (primary, diagenetic) resetting of inherited (detrital) K-Ar systems. Differentiating between these processes is difficult. Furthermore, it may well be that both can occur in the same sample.

c) Even the finest clay fractions ($<0.2\mu$) are probably retentive as to radiogenic argon. This retentivity is to be appreciated in light of the geologic history in the time elapsed, the exposure to erosion of the outcrops as well as the analytical processing which included acid leaching and bakeout (circa 150°C, 10 hours) on the extraction line.

d) In some cases it is possible to isolate a pure authigenic component in the $<2\mu$ silicate fraction.

e) Authigenic K-feldspar is probably quite abundant in shales and carbonates from the investigated sequence. K-Ar ages of such K-feldspar formation are indicative of diagenetic events.

f) K-Ar patterns differ among the various stratigraphic units investigated and between the different lithologies. Facies parameters (depositional and/or diagenetic) may be a controlling factor.

The results so far obtained demonstrate that the detailed investigation of the K-Ar isotopic system in the clay fractions of an assortment of associated lithologies (carbonate and shale), having the same depositional age, can yield significant information on parameters such as:

- source of detritus
- syngenesis of clay minerals
- diagenesis of K-bearing silicates

Information on these parameters shows that such K-Ar investigations, in conjunction with detailed mineralogical ones, can serve as a significant paleogeographic and petrological tool in the study of the marine carbonate shelf sequence in Israel. This sequence has not been subjected to deep burial.

The demonstrated retentivity of the clay fractions further suggests that it may be possible to date late epigenetic events which may have reset these phases in these rocks. The large scale dolomitization of Judea and Mount Scopus Group carbonates along the western scarp of the Dead Sea and the hydrothermal alteration of Cretaceous carbonates along the Paran lineament serve as examples.

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