Canadian Mineralogist
Vol. 20, pp. 29-39 (1982)

FORMATION AND PROPERTIES OF AUTHIGENIC MINERALS IN BITUMINOUS CALCAREOUS SHALES, GHAREB FORMATION, ISRAEL**

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ABSTRACT

An assemblage of authigenic silicate minerals including microcline, heulandite, quartz and opal-CT, along with detrital quartz, kaolinite, montmorillonite and illite, occurs in calcareous shales, locally bituminous, in the Ghareb Formation (Maestrichtian age) in Israel. The microcline is of pure composition, disordered, mostly idiomorphic, showing a variety of forms and *tracht*. The mineralogical features of the microcline and the sedimentological properties of the calcareous shales suggest slow crystallization at low temperature under disequilibrium, where microcline forms within the stability field of albite. As microcline is less soluble than albite, this mineral is preserved in the sediment. Both quartz in idiomorphic crystals of low crystallinity index and opal-CT are probably byproducts in the formation of microcline. Illite is probably the weathered phase that provides, in addition to silica and alumina, titanium and iron. Titanium occurs in authigenic idiomorphic anatase. The iron-containing minerals, amorphous oxides and hydroxides probably act as a substrate for precipitating silicate minerals at low concentrations of silica and alumina. Pyrite occurs as single crystals, as framboids and in a microcrystalline variety. The organic matter raised the pH of the interstitial water during decomposition, thus increasing the solubility of illite. The hydrophylic–hydrophobic properties of the organic matter affect diffusion processes and, therefore, the crystal growth of authigenic minerals.

Keywords: authigenic, microcline, quartz, opal-CT, heulandite, anatase, disequilibrium, substrate, organic matter.

SOMMAIRE

Un assemblage de minéraux silicatés authigènes (microcline, heulandite, quartz et opale-CT) et détritiques (quartz, kaolinite, montmorillonite et illite) caractérise les shales calcaires et localement bitumineux de la formation Ghareb (d'âge Maestrichtien) en Israël. La microcline est pure et désordonnée; les cristaux, en majorité idiomorphes, montrent plusieurs formes et un *tracht* variable. A la lumière des caractéristiques minéralogiques de la microcline et des propriétés sédimentologiques des shales, on propose une cristallisation lente et à basse température d'une microcline métastable dans le champ de stabilité de l'albite. La microcline persiste dans le sédiment en raison de sa solubilité inférieure à celle de l'albite. Le quartz, en cristaux idiomorphes et à faible indice de cristallinité, ainsi que l'opale-CT, seraient des sous-produits de la formation de la microcline. L'illite serait la phase détritique qui fournit le Ti et le Fe en plus de la silice et de l'alumine. Le Ti apparaît sous forme d'anatase idiomorphe authigène. Les minéraux de fer, les oxydes amorphes et les hydroxydes seraient les substrats sur lesquels ont précipité les minéraux silicatés à faible concentration de silice et d'alumine. On trouve la pyrite en monocristaux et en variétés framboïdale et microcristalline. La dissolution de l'illite a été facilitée par l'augmentation du pH de l'eau interstitielle lors de la décomposition des matières organiques. Les caractéristiques hydrophiles–hydrophobes de la matière organique affectent les processus de diffusion et influencent donc la croissance des minéraux authigènes.

(Traduit par la Rédaction)

Mots-clés: authigène, microcline, quartz, opale-CT, heulandite, anatase, déséquilibre, substrat, matière organique.

INTRODUCTION

Authigenic silicate minerals occur in a variety of sedimentary clastic and carbonate rocks deposited in marine and limnic environments. The chemical composition, optical and structural features and thermodynamic properties of the authigenic minerals and of possible reactant minerals have been discussed in connection with the paragenesis of authigenic feldspars (Kastner 1971, Kastner & Siever 1979). Experimental crystal growth of feldspars at low temperature (Flehmig 1977) has contributed to the understanding of the mechanisms of crystal growth and of several factors that may play a role in the formation of these minerals in sedimentary rocks. The main factors are the

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**dedicated to the memory of Simcha Zeira.

chemical composition of the solution, pH, temperature and properties of the substrate. Sedimentary organic matter plays a particular role in the dissolution and precipitation properties of carbonate minerals (*e.g.*, Chave & Suess 1967, Berner *et al.* 1978). The hydrophobic–hydrophylic properties of the organic matter seem to affect also the crystal growth of pyrite, as was observed in the bituminous calcareous shales investigated in the present study.

This study is based on assemblages of minerals that consist of authigenic silicate minerals including quartz, opal-CT, microcline and heulandite, along with anatase and pyrite. The major detrital clay mineral, kaolinite, is associated with minor amounts of montmorillonite and illite. These assemblages were investigated in calcareous shales, locally bituminous, of the Campanian–Maestrichtian Ghareb Formation, Israel. This formation is developed in synclines, three of which were investigated: Horon, Ef'e and Nebi–Musa. A general description of the mineralogical composition and organogeochemical characteristics of the bituminous Ghareb Formation is reported elsewhere (Spiro *et al.* 1978).

In this article we 1) compare the mineral assemblages, authigenic and detrital, that occur in the bituminous and nonbituminous rocks, 2) discuss the criteria for defining the minerals as authigenic, 3) clarify the effects of the physical and chemical properties of the organic matter on the weathering of detrital minerals and the formation of authigenic minerals, and 4) suggest a mechanism for the formation of authigenic silicate minerals with reference to their thermodynamic properties and those of possible reacting detrital minerals and the postulated environmental conditions.

EXPERIMENTAL

Eighteen samples were crushed and subsequently treated with diluted hydrochloric acid (1:6) to remove carbonate minerals. The clay minerals were separated by pipette.

X-ray powder-diffraction measurements for the mineralogical determinations were performed on a Philips PW 1730 X-ray generator using Cu$K\alpha$ radiation. The crystallinity index of quartz was measured following the method of Murata & Norman (1976). The nature of opal was determined from diffractograms obtained after heating to 1050°C for two days (Jones & Segnit 1971). The nature of the feldspar and zeolite minerals was determined from slow-scan diffractograms (4° 2θ per minute).

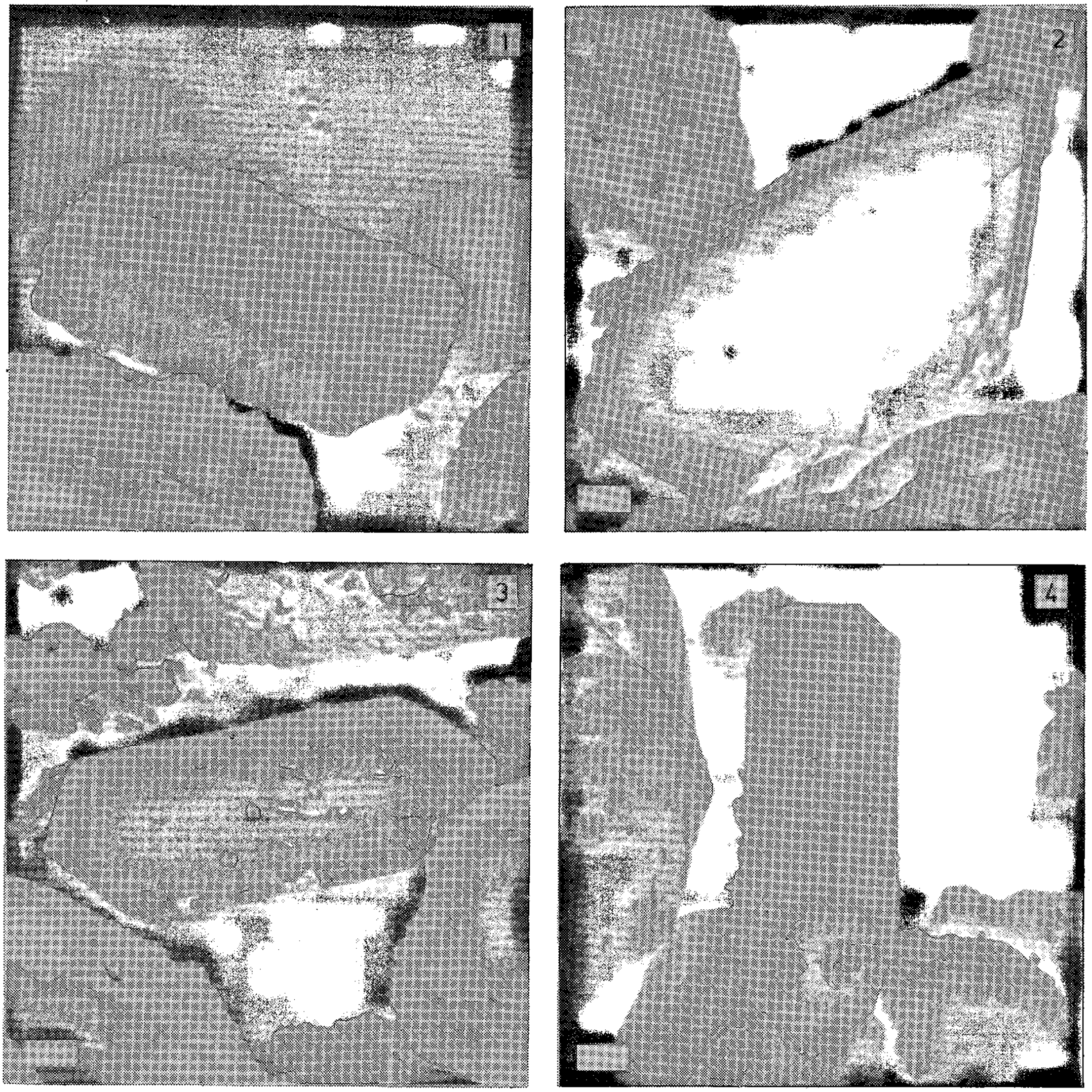
Optical microscopy and scanning-electron microscopy (Cambridge S4 instrument) were used for the investigation of textural and mineralogical features of the minerals. The chemical composition of 25 selected grains was determined by microprobe analysis (Jeol JAX5).

MINERAL DESCRIPTIONS

Microcline

The only feldspar mineral detected is microcline. Under the optical microscope it appears generally as single (rarely twinned) crystals 10–60 μm in size, and reveals no zoning features or cores that could be considered of detrital origin. The chemical composition obtained by microprobe analysis is essentially pure $KAlSi_3O_8$. The grains are homogeneous, with up to 0.8% Na. The $d_{\bar{2}01}$ of 4.26 Å is also indicative of pure microcline (Smith 1974). The structural types of feldspars and the degree of Si–Al order were estimated from the $2\theta_{060}$ and $2\theta_{\bar{2}04}$ reflections (Wright 1968), which occur at 41.79 and 50.65°, respectively, indicating a nearly maximum microcline. A quantitative determination of the degree of order based on 2θ of $(\bar{2}04)$–(060), as correlated with the actual Al and Si distribution in the T_1O site (Sosedko 1976), defines the microcline of the Ghareb Formation as moderately disordered: 0.45 as compared with that of maximum microcline (1.0).

The crystals are generally idiomorphic with smooth faces; rough faces, possibly formed by imperfections in crystal growth or by acid-soluble carbonate inclusions, also occur (Figs. 1–10). However, inclusions were not detected by optical microscopy nor by microprobe analysis. Idiomorphic crystal faces locally occur on xenomorphic grains (Figs. 8, 11). Some small crystal faces that constitute a minor part of the crystal surface bear step-like and rod-like features (Figs. 5, 8–10). These features may be indicative of S (steps) and K (kinks) faces as defined by Hartman & Perdok (1955). The higher growth rate of these faces relative to the F (flat) faces explains their subordinate morphological occurrence. The microcline crystals are generally euhedral and exhibit a variety of forms, but also differ considerably in *tracht, i.e.*, the different relative development of faces in crystals showing the same form (Smith 1974, p. 249). A choice of representative forms is shown in Figures 1-9, including crystals with only two faces developed, a variety of adularia, crystals composed of several forms and twinned crystals. The variation in *tracht* ranges from flat through equant to elongated prismatic.



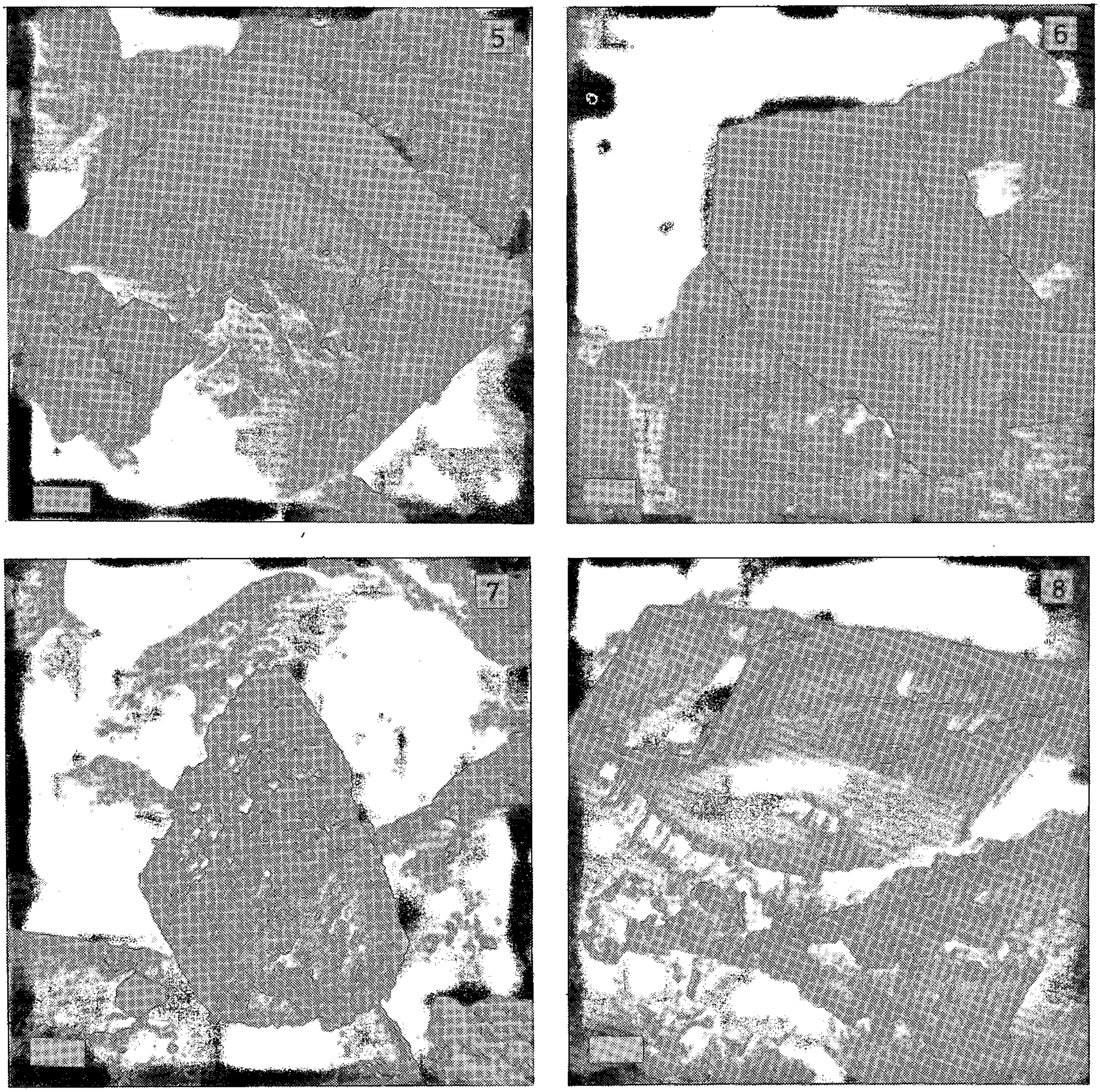
Figs. 1-4. Scanning electron micrographs of microcline crystals of various forms, *tracht* and surface features. 1. Platy crystal; only one form is developed (scale bar 5 μm). 2. Wedge-like crystal, 010, 001 $\bar{1}00$, 101 (scale bar 5 μm). 3. Tabular elongate crystal, 010, 001, (scale bar 5 μm). 4. Prismatic elongate crystal (scale bar 3 μm).

Detailed descriptions of the morphological features, forms, *tracht* and types of faces are included in the captions of the figures.

Several of the crystals investigated by the nondispersive X-ray analyzer show signs of iron enrichment on their surfaces. This was observed on both well-developed and on less developed crystals. This iron content is probably related to the presence of amorphous iron oxides in the calcareous shales (Spiro & Rozenson 1980). Amorphous iron oxides were used as substrate in the experimental precipitation of feldspars (Flehmig 1977).

Quartz, opal-CT and heulandite

Quartz with low crystallinity index (CI: Murata & Norman 1976) is present in both bituminous and nonbituminous calcareous shales. The lowest values, 0.5–1.2, are from bituminous lenses, whereas the adjacent nonbituminous layers have CI values of 0.9–2.9. Quartz appears



FIGS. 5-8. Scanning electron micrographs of microcline crystals of various forms, *tracht* and surface features. 5. Adularia 110, $10\bar{1}$, 001, 010, stepped surface (S) on intersection of 010 and 110, kinks (K) on 110 (scale bar 1.5 μm). 6. Adularia 110, $1\bar{1}0$, $0\bar{1}0$, $0\bar{1}1$, twinned with 110, 001, 210 (scale bar 6 μm). 7. Wedge-like crystal showing imperfect faces (possibly due to dissolution of inclusions), 001, $\bar{1}00$, 010, 101 (scale bar 5 μm). 8. Faces of types F 100, $1\bar{1}0$ and S 001 of a crystal (upper) developed on one showing less well developed faces (lower; scale bar 2 μm).

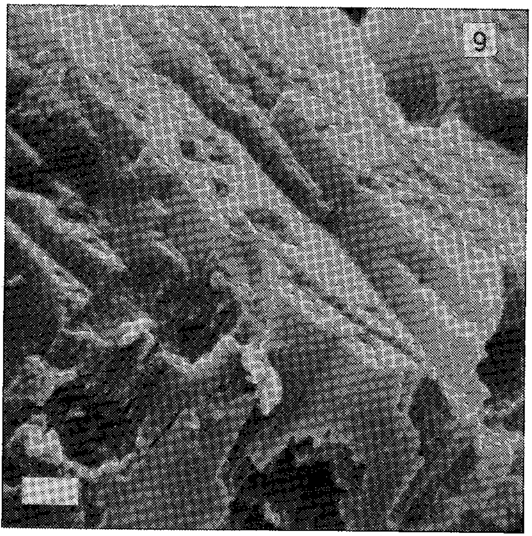
in thin section as small grains with diffuse boundaries. In the SEM, pseudohexagonal prismatic and pyramidal crystals were detected (Fig. 14). The low crystallinity index and idiomorphic morphology point to an authigenic origin, with a possible minor contribution of detrital quartz.

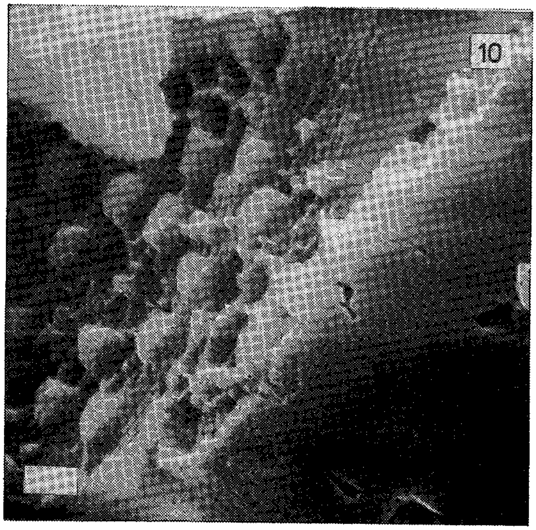
Opal-CT, a disordered interlayering of cristobalite and tridymite, was identified by the characteristic change in the X-ray powder-diffraction pattern upon heating at 1050°C for two days (Jones & Segnit 1971). No lepispheres (microspherical clusters of bladed crystals) characteristic of authigenic opal were detected. It seems, therefore, that the opal may be partly of biogenic origin.

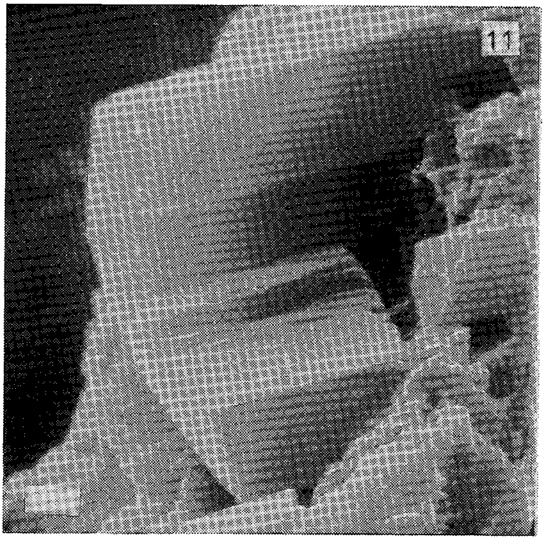
Heulandite occurs in a few bituminous samples, locally associated with microcline. It produces an unambiguous X-ray powder-diffraction pattern. The common mode of occurrence of heulandite is as infillings of foraminiferal tests (Figs. 12, 13), which leaves no doubt as to their authigenic origin.

Anatase

Idiomorphic plate-like Ti-bearing crystals were detected by the SEM coupled with the nondispersive X-ray analyzer (Fig. 15). Although no Ti-bearing mineral was detected in the X-ray diffractograms of the same material, these crystals are assumed to be anatase because of their morphology.







FIGS. 9-11. Scanning electron micrographs of microcline crystals of various forms, *tracht* and surface features. 9. Faces of types F, S and K, and features resembling screw dislocations (scale bar 1 μm). 10. Protrusions and grooves on face of type K (scale bar 2 μm). 11. Idiomorphic crystal developed on a rough surface of a xenomorphic crystal (scale bar 5 μm).

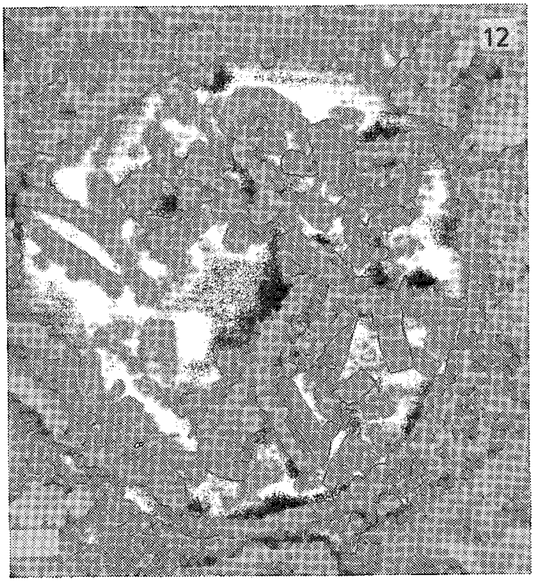
Pyrite

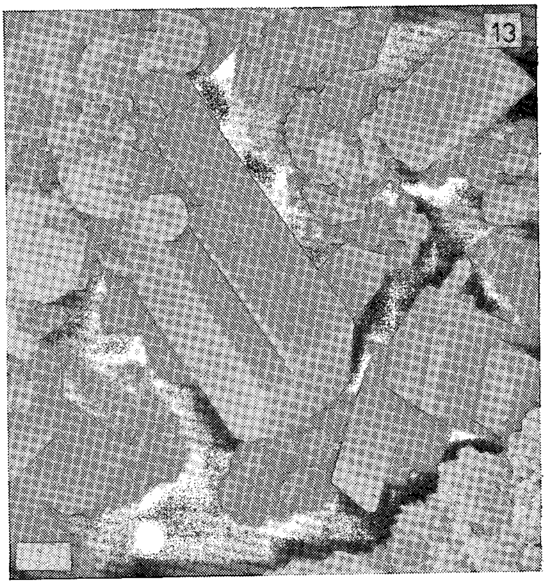
Pyrite is abundant in the bituminous beds and rare in the nonbituminous beds. It occurs as dispersed crystals, disordered clusters of crystals and framboids. A microcrystalline variety, undetected by X-ray diffraction or by infrared spectroscopy, was identified by Mössbauer spectroscopy (Spiro & Rozenson 1980).

Relation between organic matter and authigenic minerals

The authigenic minerals, silicates, anatase and pyrite differ in abundance, and their mineralogical properties are affected by the hydrophylic–hydrophobic properties of the organic matter in the calcareous shales. The authigenic silicates (microcline, quartz, heulandite and opal-CT), which are present in the lean calcareous shales, are abundant in the bituminous rocks with hydrophylic properties. On the other hand, microcline and heulandite were not detected in the bituminous rocks, with hydrophobic properties. Quartz has a lower crystallinity index, and pyrite occurs only in the microcrystalline variety in these hydrophobic rocks.

The characterization of organic matter as





FIGS. 12, 13. Heulandite crystals in a foraminifer (scale bar 20, 5 μm, respectively).

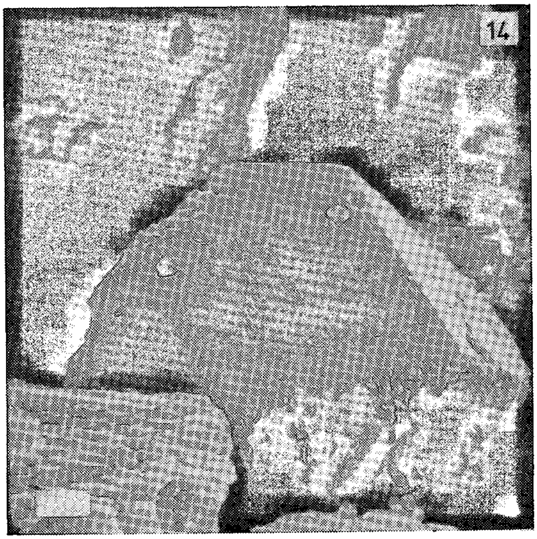


FIG. 14. Quartz, pseudohexagonal prismatic habit (scale bar 4 μm).

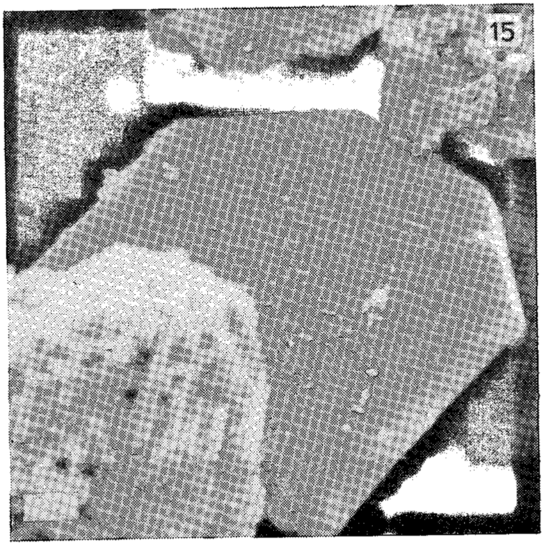


FIG. 15. Anatase, platy crystal (scale bar 6 μm).

hydrophylic or hydrophobic is based on striking differences in wettability. No further procedures were undertaken to quantify these properties; however, the distinctions described above suggest a substantial role by organic matter in monitoring the precipitation of minerals.

FORMATION OF AUTHIGENIC SILICATE MINERALS

The crystallographic and mineralogical features and the chemical composition of authigenic silicate minerals are indicative of the process of crystallization and the chemical composition of the each respective solution. The most interesting authigenic mineral in the assemblage is microcline.

The microcline crystals described above have a pure composition, display a diversity of forms and *tracht* and are disordered. The degree of ordering in general, and particularly in feldspars, is regarded as indicative of their origin; a high degree of ordering is related to low-temperature authigenesis and slow crystal growth (Fyfe 1964). Microcline of probable authigenic origin occurs, however, in a range of order–disorder levels (Kastner 1971, Kastner & Siever 1979). Based on thermodynamic considerations, low-temperature microclines are anticipated to be ordered. The observed disorder of the microcline in the calcareous shales of the Campanian–Maestrichtian Ghareb Formation seems to point to disequilibrium conditions affecting kinetic factors of crystal growth. The structural and morphological features, *i.e.*, the variety of forms and *tracht* and the crystal-growth features (probable S and K faces), are certainly related and stem from the crystal-growth mechanism. Since the distinction between S, K and F faces is considered in terms of differences in bond energy, the order–disorder property as such has no direct bearing on the assignment of the crystal faces as S, K or F or on their relative development. However, the relative importance of faces and the degree of ordering are related features, as is observed in olivines ('t Hart 1978). Therefore, S and K faces may have a particular morphological appearance in disordered crystals in contrast to ordered ones. Under equilibrium conditions a simple crystal form is expected; thus the diversity and complexity of the microcline crystals are indicative of a nonequilibrium crystal-growth process.

It seems, therefore, that the mineralogical features of the microcline are due to a high rate of growth; the numerous faces and low ordering indicate conditions of nonequilibrium, though the pure chemical composition of an end member is typical of equilibrium conditions at low temperature. The present case probably illustrates a general phenomenon described by Fyfe (1964): "Metastable arrangements are common when minerals are grown rapidly at low temperatures and may persist indefinitely in static conditions".

The compositions of the solutions, particularly the activities of SiO_2, Al_2O_3, K^+, Na^+ and the pH, are the major factors affecting the formation of the silicate minerals observed in the Ghareb Formation. The concentrations of silica and alumina have to be very low, as was demonstrated by the synthesis of kaolinite and smectite minerals by Harder (1976) and La Iglesia & van Oostervyck-Gastuche (1978). This synthesis is possible at low temperature, at SiO_2 and Al_2O_3 concentrations of only a few parts per million. At higher concentrations noncrystalline gels are produced. Similar conclusions can be drawn also from solubility diagrams of kaolinite (La Iglesia & van Oostervyck-Gastuche 1978). The stability diagram of K-feldspar, Na-feldspar and zeolite (Fig. 16) shows that this rule applies also to low-temperature feldspars. These diagrams may be regarded as precipitation diagrams if the supersaturation is very small, *i.e.* if the concentration of the reactants remains close to the equilibrium line of the diagram.

K- and Na-feldspars were synthesized at near room temperature on iron oxide gels from dilute solutions containing silica and alumina in concentrations of 3 and 0.01 ppm, respectively (Flehmig 1977). This precipitation mechanism may have taken place in the present case because amorphous iron oxides (with grain sizes smaller than 120 Å) were detected in these calcareous shales (Spiro & Rozenson 1980). Also, the hydrophylic properties of organic material may support crystallization.

This mechanism differs in principle from that in which saturation in silica is considered to be a limiting factor (Kastner 1971). Moreover, quartz was precipitated as a "by-product" in the formation of feldspars at a concentration far below that of saturation with respect to quartz or amorphous silica (Flehmig 1977). It seems that the presence of authigenic quartz and opal-CT, together with authigenic microcline, may be explained by a similar process at a concentration level of silica not much higher than that of normal interstitial water.

Authigenic K- or Na-feldspars (or both) may occur in carbonate rocks (Kastner 1971). If a critical ratio of $K/(K+Na)$ in the solution determines the nature of the feldspar(s), such a value might reveal important information about the composition of the solution in which the minerals precipitated. A limiting value of 0.035 for this ratio, above which microcline precipitates, was determined from experiments conducted at 100°C (Kastner 1971). It seems, therefore, that the ratio should be higher than the 0.035 limiting ratio in the interstitial waters that precipitated the microcline of the Ghareb Formation. However, it is difficult to regard the ratio of alkalis in the solution as the only factor that determines the occurrence of a certain feldspar. Microcline as the sole feldspar was formed in solutions with a much lower

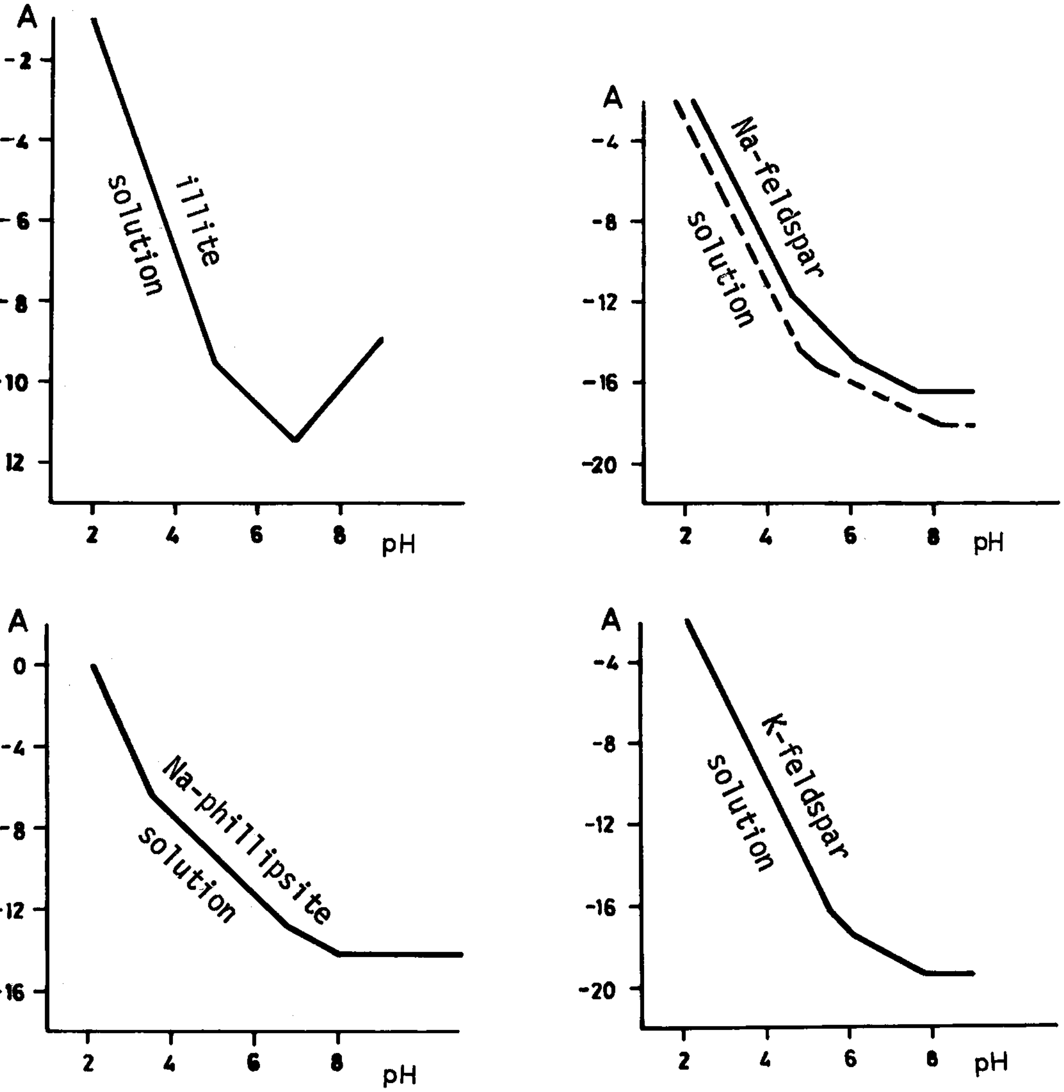


FIG. 16. Solubility diagram of illite, Na-feldspar, Na-phillipsite and K-feldspar. A is the logarithm of the solubility product of the aluminous and siliceous species soluble in the respective pH range. $A_{\text{illite}} = \log\text{Al} + \log\text{H}_4\text{SiO}_4$; $A_{\text{Na-feldspar}} = \log\text{Al} + \log\text{H}_4\text{SiO}_4$; $A_{\text{K-feldspar}} = \log\text{Al} + \log\text{H}_4\text{SiO}_4$; $A_{\text{phillipsite}} = \log\text{Al} + 2.33\log\text{H}_4\text{SiO}_4$. The diagrams for illite and K-feldspar were calculated for $[\text{K}^+] = 10^{-2.21}$; the diagram of Na-feldspar was calculated for $[\text{Na}^+] = 10^{-0.48}$ (dashed line) and $10^{-2.21}$ (full line); for phillipsite, $[\text{Na}^+]$ is $10^{-2.21}$. The curves were calculated according to the procedure of La Iglesia & van Oostervyck-Gastuche (1978) using thermodynamic data obtained from Tardy & Garrels (1974) and Glaccum & Boström (1976).

K/(K+Na) ratio (0.0046) between 0 and 80°C (Flehmig 1977). This may represent a nonequilibrium assemblage present for the duration of the experiment. The authors suggest that kinetic factors that control disequilibrium nucleation and crystal-growth processes are of major significance in determining the type and the morphological features of authigenic feldspars and other silicate minerals. Thus disequilibrium crystal-growth of microline within the stability field of albite and microcline affects both chemical and crystallographic characteristics of the mineral.

Albite is more soluble than microcline (Fig.

16), as was proven experimentally ($6 \cdot 10^{-7}$ versus $3 \cdot 10^{-7}$ mole per litre, respectively: Berner 1978). Nucleation seeds of both feldspars may form at the onset of the reaction, but even during the early stages of crystal growth, the more soluble phase disappears whereas the less soluble persists.

The synthesis of albite was conducted with a concentration of Na several orders of magnitude higher than that of the K needed for precipitation of microcline (Flehmig 1977). According to the stability diagram (Fig. 16), it does not seem likely that the Na concentration should have such an overriding importance. It is possible that there is a kinetic difference between the precipitation of microcline and albite. Although the order of reaction and its rate-limiting step are unknown, the increase in concentration of reactants relative to the equilibrium concentration may enhance the reaction rate. An increase in SiO_2 and Al_2O_3 reactant concentrations may result in the formation of gels, but an increase in Na concentration may favor the precipitation of albite.

Mineralogical features such as the variability of forms and a moderate level of disorder may be regarded as indicating disequilibrium and may possibly signify a metastable phase. These may also reflect rapid growth of microcline, possibly followed by recrystallization.

An important factor governing geochemical reactions is pH. In some stability diagrams relating to feldspars (Garrels & Christ 1965), the pH value is represented by $a\mathrm{K}/a\mathrm{H}$ which, together with $a\mathrm{H_4SiO_4}$, determines the stability field of K-feldspar and its relation to the stability fields of illite and kaolinite. These diagrams neglect the role of different chemical species of aluminum by regarding them as inert. Figure 16 takes into account these species as well. In the present case, the authigenic feldspars do not replace detrital feldspars but are possibly derived from illite or kaolinite. According to Figure 16, K-feldspar is more stable than illite at higher pH. K-feldspars were synthesized in a pH range of 8.5–9.0 by Flehmig (1977), although the term pH becomes meaningless when one describes reactions taking place on the surface of iron colloids. It may be possible to explain the precipitation of K-feldspars at a relatively high pH range by examining the stability of the species $Al(OH)_4^-$. This species dictates a fourfold co-ordination for aluminum already in the solution; thus the transfer of this moiety from solution to solid phase does not involve any change in co-ordination. At a lower pH, an aluminum species with co-ordination different from 4 is stable; therefore, illite, which contains aluminum in fourfold and sixfold co-ordination, is more stable. The presence of a titanium oxide mineral, possibly anatase, in the assemblage of the authigenic silicate minerals also points to illite as a source material. The pH range in the interstitial waters is wide but is generally lower than that of normal sea water. On the other hand, interstitial water in sediments rich in organic matter may attain pH values of 8.5 (Manheim & Schug 1978). Also, the authigenic feldspars of the Green River Formation were probably deposited under a high pH, as can be inferred from their association with nahcolite and dawsonite (Robb & Smith 1974). The rise in pH, which is related to the decomposition of organic matter and which is likely to have occurred in the interstitial water of the Ghareb Formation, could have led to the precipitation of K-feldspar while illite dissolved. The theoretical alternative of formation under acidic conditions (Fig. 16) is improbable, as such conditions are not likely to persist in the interstitial water of carbonate rocks.

The stability field of the zeolite mineral phillipsite, regarded as similar to that of heulandite, overlaps to a great extent that of the feldspars (Fig. 16). The predicted reaction induced by a change in pH is also similar. It is therefore difficult to determine the conditions under which either of these minerals would precipitate.

The association of anatase and kaolinite is very common (Dolcater *et al.* 1970, Weaver 1976). Titanium was found together with iron in the kaolinite structure (Rengasamy 1976). Anatase occurs as rounded subspherical grains in the Georgia kaolinite; the occasional tabular grains or aggregates are regarded as pseudomorphs after ilmenite (Weaver 1976). The source of anatase in the calcareous shales of the Ghareb Formation may be either detrital Ti oxide minerals or weathered illite. No detrital Ti oxide minerals were, however, detected. The formation of anatase in euhedral, relatively large crystals seems to be another slow crystallization process, occurring with the formation of the assemblage of silicate minerals at the expense of dissolved illite.

Organic matter affects the dissolution of biogenic and detrital minerals and the crystallization of authigenic minerals chemically, by changing the pH and Eh. These processes also seem to be affected by the physical properties of the organic matter, as was observed in carbonates by Chave & Suess (1967) and Berner *et al.* (1978). From the mineralogical features and distribution of the authigenic minerals in the Ghareb Formation, it is likely that, whereas hydrophylic organic matter provides a substrate for crystallization and promotes crystal growth, hydrophobic organic matter has inhibiting effects on crystal growth, probably by impeding diffusion. This phenomenon is manifested by the absence of authigenic microcline, heulandite and anatase in hydrophobic bituminous-rich beds, whereas these phases are present in adjacent bituminous-poor and hydrophyllic beds. This hindrance to crystal growth probably results in the low crystallinity of quartz and the development of pyrite only as a microcrystalline variety.

CONCLUSIONS

The chemical and structural characteristics of authigenic feldspars are (1) the pure composition of an end member, (2) a moderate level of ordering and (3) a variety of crystal forms and *tracht*. The growth mechanism can be explained by the model of Flehmig (1977), which suggests the crystallization of feldspars on colloidal iron oxide from an undersaturated solution. Crystallization under disequilibrium conditions, *i.e.*, the formation of microcline in the stability field of albite + microcline and the subsequent dissolution of the less stable albite, may explain the presence of microcline only in this assemblage.

Quartz and opal-CT may be by-products of the formation processes of feldspars from a solution undersaturated with respect to quartz or amorphous silica. Anatase is probably formed from titanium derived from the decomposition products of illite which is, according to the stability diagrams, the dissolving phase and source of silica and alumina. Illite is probably also the source of the iron that formed the ferruginous gel that acted as a substrate for the growth of the silicate minerals. Heulandite is formed under similar conditions and probably by a mechanism similar to that which formed the feldspar.

Organic matter affects the crystallization of the silicate minerals through an increase in pH. The hydrophobic properties of the organic matter have an inhibiting effect on crystal growth.

ACKNOWLEDGEMENTS

We thank Professor L. Heller-Kallai for helpful discussions and the anonymous reviewers for improving the manuscript. The support of this research by the Ministry of Energy and Infrastructure, Israel, is gratefully acknowledged.

REFERENCES

BERNER, R.A. (1978): Rate control of mineral dissolution under earth surface conditions. *Amer. J. Sci.* 278, 1235-1252.

———, WESTRICH, J.T., GRABER, R., SMITH, J. & MARTENS, C.S. (1978): Inhibition of aragonite precipitation from supersaturated sea-water: a laboratory and field study. *Amer. J. Sci.* 278, 816-837.

CHAVE, K.E. & SUESS, E. (1967): Suspended minerals in seawater. *New York Acad. Sci. Trans.* 29, 991-1000.

DOLCATER, D.L., SYRES, J.K. & JACKSON, M.L. (1970): Titanium as free oxide and substituted forms in kaolinite and other soil minerals. *Clays Clay Minerals* 18, 71-79.

FLEHMIG, W. (1977): The synthesis of feldspars at temperatures between 0–80°C, their ordering behaviour and twinning. *Contr. Mineral. Petrology* 65, 1-9.

FYFE, W.S. (1964): *Geochemistry of Solids*. McGraw-Hill, New York.

GARRELS, R.M. & CHRIST, C.L. (1965): *Solutions, Minerals and Equilibria*. Harper and Row, New York.

GLACCUM, R. & BOSTRÖM, K. (1976): (Na,K)-phillipsite: its stability conditions and geochemical role in deep sea. *Marine Geol.* 21, 47-58.

HARDER, H. (1976): Nontronite synthesis at low temperatures. *Chem. Geol.* 18, 169-180.

'T HART, J. (1978): The structural morphology of olivine. II. A quantitative derivation. *Can. Mineral.* 16, 547-560.

HARTMAN, P. (1973): Structure and morphology. *In* Crystal Growth. An Introduction (P. Hartman, ed.). North-Holland, Amsterdam.

——— & PERDOK, W.G. (1955): On relations between structure and morphology of crystals. I. *Acta Cryst.* 8, 49-52.

JONES, J.B. & SEGNIT, E.R. (1971): The nature of opal. 1. Nomenclature and constituent phases. *Geol. Soc. Aust. J.* 18, 57-68.

KASTNER, M. (1971): Authigenic feldspars in carbonate rocks. *Amer. Mineral.* 56, 1403-1442.

——— & SIEVER, R. (1979): Low temperature feldspars in sedimentary rocks. *Amer. J. Sci.* 279, 435-479.

LA IGLESIA, A. & VAN OOSTERVYCK-GASTUCHE, M.C. (1978): Kaolinite synthesis. 1. Crystallization conditions at low temperatures and calculation of thermodynamic equilibria. Application to laboratory and field observations. *Clays Clay Minerals* 26, 397-408.

MANHEIM, F.T. & SCHUG, D.M. (1978): Interstitial waters of Black Sea cores. *In* Initial Reports on Deep Sea Drilling Project (D. Ross, Y.P. Neptrochnov *et al.*, eds.), 42(2), 637-651.

MURATA, K.J. & NORMAN, N.B., II (1976): An index of crystallinity for quartz. *Amer. J. Sci.* **276**, 1120-1130.

RENGASAMY, P. (1976): Substitution of iron and titanium in kaolinites. *Clays Clay Minerals* **24**, 265-266.

ROBB, W.A. & SMITH, J.W. (1974): Mineral profile of oil shales in Colorado core hole No. 1, Piceance Creek Basin, Colorado. *In* Guidebook to the Energy Resources of the Piceance Creek Basin Colorado. *Rocky Mountain Assoc. Geol. 25th Field Conf.*, 91-100.

SMITH, J.V. (1974): *Feldspar Minerals. 2. Chemical and Textural Properties.* Springer-Verlag, New York.

SOSEDKO, T.A. (1976): Determination of ordering and distribution of aluminum in the structure of potassic feldspars by X-ray diffractometry. *Dokl. Acad. Sci. U.S.S.R., Earth Sci. Sect.* **228**, 133-135.

SPIRO, B., HELLER-KALLAI, L. & AIZENSHTAT, Z. (1978): Environment of deposition and diagenesis of some oil shales in Israel. *Tenth Int. Assoc. Sedimentologists Congr.* (*Jerusalem*), 632-633 (abstr.).

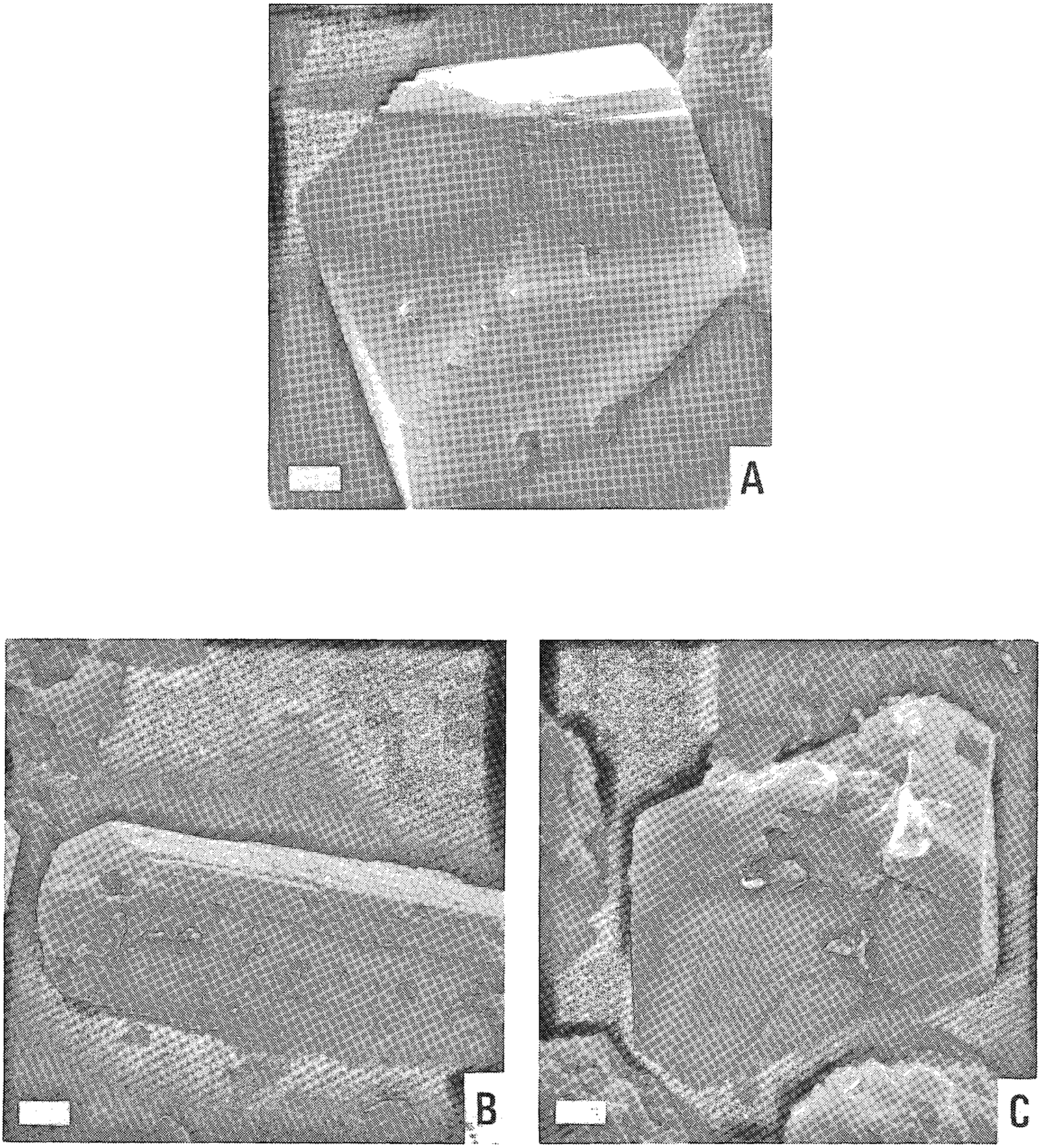
——— & ROZENSON, I, (1980): Distribution of iron species in some "oil shales" of the Judea desert, Israel. *Chem. Geol.* **28**, 41-54.

TARDY, Y. & GARRELS, R.M. (1974): A method of estimating the Gibbs energies of formation of layer silicates. *Geochim. Cosmochim. Acta* **38**, 1101-1116.

WEAVER, C.E. (1976): The nature of TiO_2 in kaolinite. *Clays Clay Minerals* **24**, 215-218.

WRIGHT, T.L. (1968): X-ray and optical study of alkali feldspar. II. An X-ray method for determining the composition and structural state from measurement of 2θ values for three reflections. *Amer. Mineral* **53**, 88-104.

Received December 1980, revised manuscript accepted November 1981.



Scanning electron micrographs of microcline crystals from bituminous calcareous shales, Ghareb Formation, Israel. A. Equant crystal (scale bar 5 μm). B. Prismatic elongate crystal showing numerous faces (scale bar 5 μm). C. Crystal of adularia showing faces 110, $\bar{1}10$, 001 and 010 (scale bar 4 μm).