Canadian Mineralogist
Vol. 29, pp. 587-598 (1991)

AUTHIGENIC SILICA POLYMORPHS AND THE GEOCHEMISTRY OF PLIOCENE SILICEOUS SWAMP SEDIMENTS OF THE ARIDEA VOLCANIC PROVINCE, GREECE

MICHAEL G. STAMATAKIS
Department of Geology, University of Athens, Panepistimiopolis, Ano Ilissia, 157 84, Athens, Greece

RAYMOND KANARIS-SOTIRIOU AND D. ALAN SPEARS
Earth Sciences, University of Sheffield, Beaumont Building, Brookhill, Sheffield S3 7HF, U.K.

ABSTRACT

The Pliocene Krop succession, deposited in a swamp environment, comprises limestone, porcellanite, and chert along with scant coal seams. It is sandwiched between tuffaceous rocks and lavas of the same age. Mineralogical analyses of these sediments show that carbonates, authigenic opal-C and chalcedony are the major constituents, accompanied by minor amounts of authigenic opal-CT and detrital quartz. Chemical analysis indicates that the silicic glass of associated volcanic rocks did not make any major contribution to the formation of authigenic silica minerals. We suggest that the silica polymorphs were formed from a biogenic silica (opal-A) precursor that was originally present in the form of diatom frustules. The diagenetic transformation of the original diatomaceous sediment is thought to result from elevated temperatures associated with the high heat-flow that existed in the Aridea volcanic terrane during the Early Pliocene.

Keywords: porcellanite, chert, diagenesis, heat flow, opal-C, opal-CT, chalcedony, Aridea, Greece.

SOMMAIRE

La séquence Krop, d'âge pliocène, déposée dans un milieu marécageux dans la province volcanique de Aridea, en Grèce, contient du calcaire, de la porcellanite et du chert, ainsi que de rares niveaux houillers. Elle est intercalée parmi des tufs et des coulées du même âge. Une analyse minéralogique de ces sédiments révèle que carbonates, opale-C authigène et calcédoine prédominent; ceux-ci sont accompagnés d'opale-CT authigène et de quartz détritique. Une analyse chimique montre que le verre des roches volcaniques associées n'a pas vraiment contribué à la formation des minéraux de silice authigènes. Nous croyons que les polymorphes de silice se sont formés à partir de la silice biogénique (opale-A), précurseur à l'origine sous forme de frustules de diatomées. La transformation diagénétique de ce sédiment riche en diatomées résulterait des températures élevées associées au flux de chaleur qui existait dans le champ volcanique de Aridea dans le Pliocène précoce.

(Traduit par la Rédaction)

Mots-clés: porcellanite, chert, diagenèse, flux de chaleur, opale-C, opale-CT, calcédoine, Aridea, Grèce.

INTRODUCTION

Authigenic silica occurs in siliceous limestone, chert, and tuffaceous rocks as a) disordered tridymite–cristobalite (opal-CT), b) low cristobalite (opal-C), c) chalcedony or microcrystalline quartz (or both), and d) tridymite (Hein *et al.* 1978, Kastner 1979, Siever 1983, Stamatakis 1989). These minerals have been variously interpreted as i) precipitates derived from silica-rich solutions formed by the dissolution of biogenic amorphous silica (opal-A), ii) products of the solid–solid inversion of an opal-A precursor, and iii) products of alteration of volcanic rocks, especially felsic volcanic glass (Henderson *et al.* 1971, Heath 1973, Iijima *et al.* 1980, Hein *et al.* 1978, 1983, Pevear *et al.* 1980, Hein & Yeh 1983, Stamatakis *et al.* 1988). Although the origins of authigenic silica minerals in diatomaceous rocks and volcanic tuffs have been documented, it is difficult to identify the precursor material of these minerals where biogenic silica and volcanic glass are intermixed (*cf.* Henderson *et al.* 1971, Mitsui & Taguchi 1977, Carver 1979, Pevear *et al.* 1980).

In this article, we describe the diagenetic transformation of interbedded porcellanite, limestone and chert in Pliocene swamp deposits, found in tuffaceous rocks of the same age in the Aridea volcanic province in northern Greece (Figs. 1, 2). We then infer which factors may have influenced the development of opal-C, chalcedony, and opal-CT.

GEOLOGICAL SETTING

The sedimentary rocks studied (referred to here as the Krop succession) occur in the volcanic sequence of Aridea (Almopia), about 20 km north

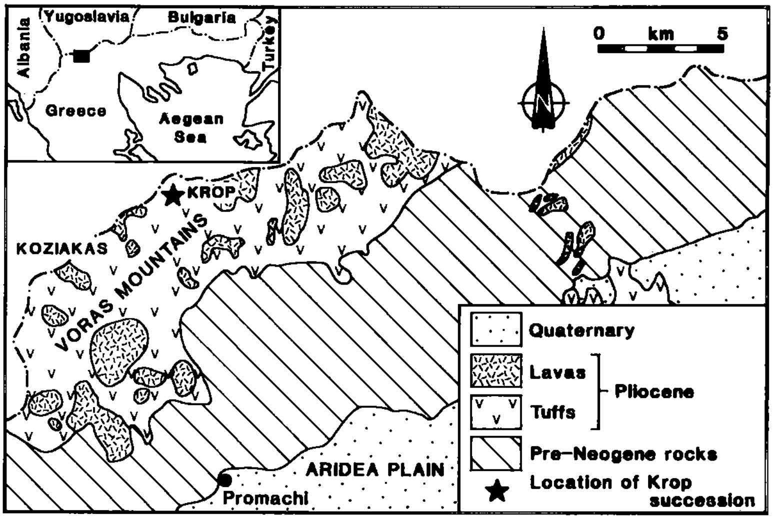

FIG. 1. Simplified geological map of the Aridea volcanic terrane after Kolios *et al.* (1980) and Chorianopoulou *et al.* (1984), showing the location of the Krop succession.

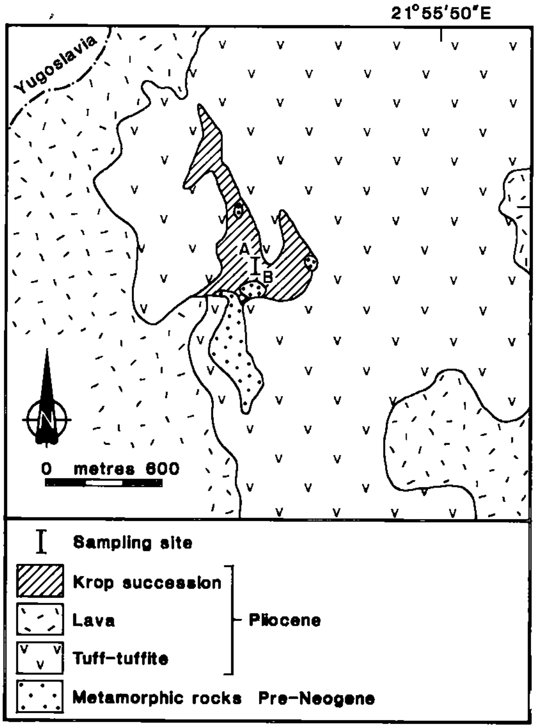

FIG. 2. Geological map showing the distribution and setting of the Krop succession (after Chorianopoulou *et al.* 1984).

of the village of Promachoi in northern Greece (Fig.1). They have a maximum thickness of 50 m and are sandwiched between tuffaceous rocks of Pliocene age. The maximum thickness of the overlying tuffaceous rocks does not exceed 30 m. The sediments locally lie on pre-Neogene metamorphic basement, this discordance resulting from Neogene tectonism, which also created a shallow swamp at an altitude of 1000 m surrounded by high mountains. The volcanic rocks of the area have a trachyandesitic composition (Marakis & Sideris 1973, Eleftheriadis 1977, Kolios *et al.* 1980).

The silica-carbonate rocks comprise a range of lithologies between pure limestone and pure chert (with abundant chalcedony) or porcellanite (with abundant opal-C), and also include a few thin lignitic horizons. The limestone tends to be more thickly bedded (up to 0.5 m thick), whereas most of the porcellanites are thinly laminated (up to 0.5 cm thick). The chert occurs as ellipsoidal to nearly spherical nodules, lenses and boudinaged layers at the base of the siliceous sediments. An Early Pliocene age for this sequence, and a swamp environment of deposition, were determined by pollen analysis (Chorianopoulou *et al.* 1984). The samples studied were taken from a representative section of the Krop succession (Figs. 2, 3).

ANALYTICAL TECHNIQUES

Mineralogical and textural analyses were carried out using X-ray diffraction (XRD), transmitted light microscopy, and scanning electron microscopy (SEM). In some samples, mineralogical analyses were performed after treatment with 1N HCl to remove the carbonates. XRD determinations of the

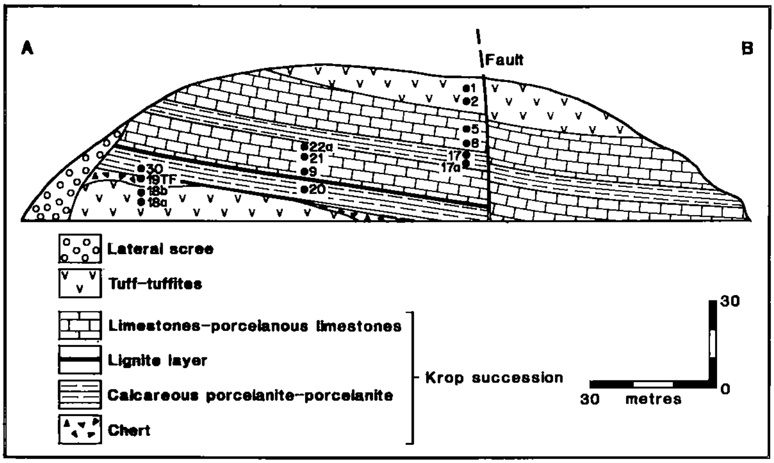

FIG. 3. Schematic section through the Krop succession along the sampling transect A–B (Fig. 2). The numbers indicate individual sampling sites. Samples 10 and 10a are located within the lignite horizon located between the samples 9 and 20.

nature of the silica phase and of the *d*(101) value were determined using the methods of Murata & Larson (1975) and Hein *et al.* (1978), which involved the use of quartz as an internal standard. Major- and trace-element analyses were carried out by X-ray-fluorescence spectrometry. Lithium tetraborate fusions with theoretical "alpha" matrix corrections were used for the major elements; pressed powder pellets prepared with a 'SX' binder (Van Zyl 1982), and Rh Compton scatter matrix corrections were used for trace elements. A rhodium anode tube was used for both techniques. Boron was determined using the colorimetric method of Stanton & McDonald (1966), slightly modified according to Stamatakis *et al.* (1989).

MINERALOGY AND PETROLOGY OF THE SILICA-CARBONATE ROCKS

The most common minerals in the Krop succession are calcite, opal-C, and quartz (Table 1). Subsidiary amounts of kaolinite, sulfates, sulfides, opal-CT, limonite, and elemental sulfur also occur. Trace amounts of dolomite, K-feldspar, plagioclase, and biotite were detected only by optical examination.

Carbonates

Calcite occurs as micritic to sparitic grains and also forms the shells of fossils such as gastropods. In places, rhombohedra of dolomite and calcite are dispersed in an opal-C groundmass. This relationship commonly occurs where authigenic silica is formed from a biogenic silica precursor in alkaline diagenetic environments (Dapples 1979, Stamatakis 1986, Stamatakis & Magganas 1988, Stamatakis *et al.* 1989).

Silica polymorphs

Opal-C is abundant in the thinly laminated (<0.5 cm) siliceous layers, which are intercalated with abundant thin, discontinuous laminae of

TABLE 1. MINERALOGY OF THE KROP SECTION, BASED ON X-RAY-DIFFRACTION ANALYSES

Sample	Lithology	Mineralogy
KR1	Tuff	Qtz, Kln, HSa, Sm
KR2	Tuff	Qtz, HSa, Sm, Klm, Ab
KR5	Porcellanous Limestone	Cal, Qtz, Crs
KR8	Limestone	Cal, Qtz
KR17	Calcareous Porcellanite	Qtz, Crs, oCT, Cal, Kln
KR17a	Calcareous Porcellanite	Crs, Qtz, Cal
KR22a	Porcellanous Limestone	Cal, Qtz, Crs
KR21	Limestone	Cal, Qtz
KR9	Fe-rich Limestone	Cal, Lm, Qtz
KR10	Sulphides	Py, Mar
KR10a	Sulphates	Roz, Me, Sf
KR20	Calcareous Porcellanite	Crs, Qtz, Cal, Kln
KR30	Porcellanite	Crs, Qtz, Kln, Cal
KR19Tf	Chert	Qtz, Crs, Cal, Kln
KR18b	Tuffite	HSa, Crs, Bt, Sm, Dol
KR18a	Tuff	HSa, Qtz, Bt, Sm, Kln, Ab

The sequence of samples is in stratigraphic order, youngest at the top. Symbols: Qtz quartz, Crs low cristobalite, oCT opal–CT, Ab albite, HSa high sanidine, Kln kaolinite, Sm smectite, Bt biotite, Cal calcite, Dol dolomite, Py pyrite, Mar marcasite, Roz rozenite, Me melanterite, Sf sulfur, Lm limonite.

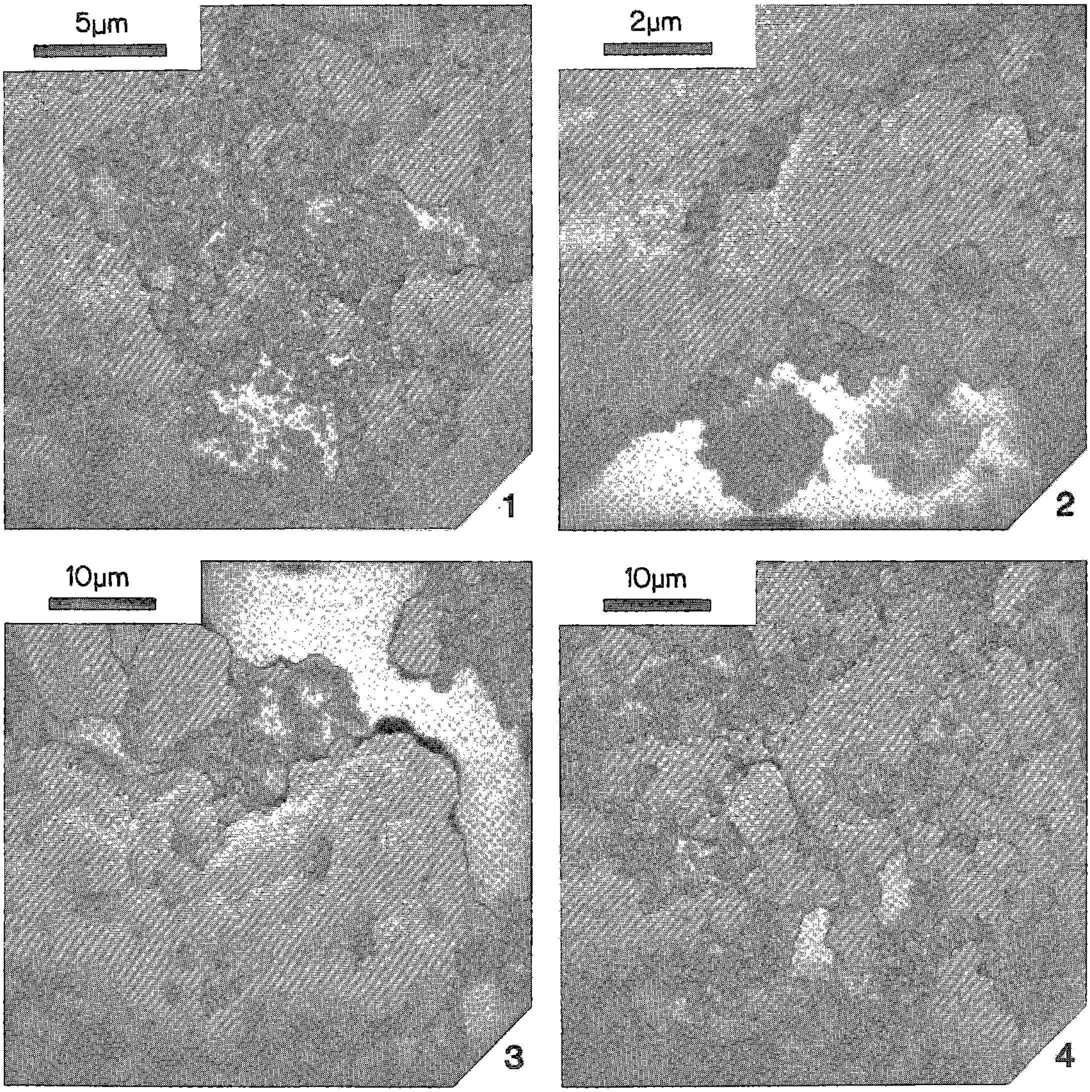

FIG. 4. Scanning electron micrographs of a finely laminated siliceous member (KR30) of the Krop succession. 1. Low cristobalite exhibiting a typical spongy texture. 2. Highly dissolved remains of a disc-shaped diatom frustule. 3 and 4. Low cristobalite forms resembling diatom morphologies.

carbonized plant remains. Opal-C also occurs as groundmass material containing carbonate rhombohedra, as pore-filling cement, as small concretions in a carbonate groundmass, and locally replacing micritic calcite or the shells of gastropods. SEM analyses of the thinly laminated horizons after treatment with 1N HCl show that the opal-C has a spongy texture and contains strongly etched relics of large frustules of diatoms (Fig. 4). This spongy texture is commonly observed in opal-CT and low cristobalite derived from a biogenic silica precursor (Henderson *et al.* 1971, Stamatakis & Magganas 1988). In the upper part of the succession, small amounts of opal-CT were detected along with abundant opal-C. Chalcedony occurs both as pore-fillings and as asymmetrical concretions in a calcareous matrix, that are especially abundant at the base of the Krop succession. Chalcedony also occurs in fissures and coating detrital quartz grains. Both chalcedony and opal-CT are associated with a fine-grained opal-C groundmass.

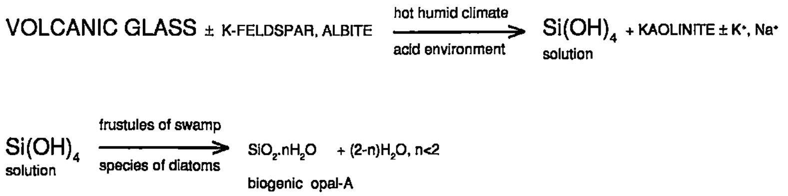

FIG. 5. Schematic representation of chemical processes involved in the formation of biogenic opal-A.

Other authigenic minerals

Fe-rich oxides-hydroxides accompanied by sulfide and sulfate minerals occur near the contact between silica-rich and organic-matter-rich layers (KR9; Fig. 3). In the black lignitic horizons (KR10, KR10a; Table 1), pyrite, marcasite, sulfur, rozenite, and melanterite have been found. A genetic association between these minerals and organic material has been suggested (Baltatzis *et al.* 1986). Kaolinite is the only clay mineral identified in the sedimentary rocks (Table 1), and we speculate that

TABLE 2. CHEMICAL COMPOSITIONS OF SAMPLES FROM THE KROP SUCCESSION AND UNDERLYING TUFFS AND TUFFITES

Sample	KR5 KC1	KR8 KC2	KR17 KS3	KR17A KS4	KR22A KC5	KR21 KC6	KR9 KC7	KR20 KS8	KR30 KS9	KR19TF KS10	KR18B KT11	KR18A KT12
SiO_2	27.60	0.45	59.28	60.86	12.75	7.96	5.79	57.58	71.77	74.99	60.23	65.78
TiO_2	0.00	0.00	0.12	0.00	0.00	0.00	0.03	0.05	0.04	0.07	0.48	0.49
Al_2O_3	0.20	0.15	3.34	0.20	0.24	0.13	0.69	1.34	1.07	1.92	15.79	16.83
Fe_2O_3T	0.38	0.46	0.45	0.26	0.87	0.89	12.66	0.41	0.26	0.38	4.26	1.67
MnO	0.11	0.21	0.01	0.06	0.23	0.21	0.64	0.02	0.00	0.00	0.11	0.01
MgO	0.39	0.24	0.24	0.14	0.55	0.50	0.20	0.16	0.08	0.07	1.48	0.79
CaO	38.96	54.48	18.10	21.11	47.13	49.94	40.40	21.05	13.00	10.64	4.41	3.40
Na_2O	0.00	0.00	0.22	0.00	0.00	0.00	0.00	0.00	0.00	0.00	2.82	3.54
K_2O	0.03	0.00	0.48	0.02	0.04	0.01	0.06	0.23	0.18	0.35	3.98	4.34
P_2O_5	0.01	0.04	0.05	0.00	0.07	0.11	0.28	0.05	0.02	0.04	0.25	0.25
SO_3	0.05	0.04	0.08	0.07	0.14	1.04	0.37	0.09	0.12	0.13	0.00	0.16
LOI	32.80	43.80	18.30	17.70	38.10	39.50	38.30	18.60	12.70	10.90	5.80	1.90
Total	100.53	99.87	100.67	100.42	100.12	100.29	99.42	99.58	99.24	99.49	99.61	99.16
V	BDL	BDL	68	BDL	27	14	BDL	47	26	47	88	77
Cr	6	6	22	BDL	9	7	10	19	15	18	17	16
Mn	976	1864	148	619	2031	1873	4817	236	82	35	887	161
Ni	9	12	16	9	11	20	51	12	10	14	7	12
Cu	BDL	BDL	10	BDL	BDL	6	7	6	7	9	11	14
Zn	BDL	BDL	13	BDL	6	BDL	10	9	6	14	63	23
Rb	BDL	2	22	BDL	5	BDL	7	17	13	24	146	165
Sr	187	201	162	97	172	147	123	171	113	116	1023	1335
Y	1	BDL	5	BDL	5	7	2	8	3	7	20	14
Zr	17	15	44	16	29	21	24	36	26	37	164	145
Nb	2	1	4	2	BDL	2	2	3	2	3	8	12
Ba	61	65	116	89	53	46	72	82	84	82	1461	1977
Pb	7	5	13	BDL	5	8	BDL	7	7	10	82	74
Th	2	1	6	1	1	3	2	3	3	4	31	33
U	BDL	1	4	BDL	5	17	1	5	3	3	6	6
B	8	4	17	19	6	3	14	15	20	13	42	46

Symbols: KC calcareous sample, KS siliceous sample, KT tuffaceous sample. BDL: below detection limit (for V, Cr, Cu, Zn and Pb, 5 ppm; for Rb, Y, Nb and U, 1 ppm). Oxides and LOI are quoted in weight %, and trace elements, in ppm.

it may be an authigenic phase because the acid environment proposed in the marsh would have been appropriate for its neoformation (Fig. 5).

Detrital minerals

Common clastic grains of quartz, and rare clastic grains of high sanidine and biotite are present.

MINERALOGY OF THE TUFFACEOUS ROCKS

In the tuff layers above and below the Krop succession, both smectite and kaolinite have been found in addition to quartz, high sanidine, albite, and biotite. Dolomite and opal-C are confined to some tuffaceous horizons just below the Krop succession (Table 1).

GEOCHEMISTRY

Major elements

The major element concentrations in the Krop sedimentary rocks reflect the concentrations of calcite and silica polymorphs (Table 2, 3, Fig. 6). Al_2O_3, K_2O, and TiO_2 are all strongly positively correlated (Table 3, Fig. 7) and reflect the presence of minor amounts of kaolinite, feldspar, and biotite. These minerals all occur in much greater amounts in the tuffaceous material. Generally, the aluminum contents are higher in the silica-rich than carbonate-rich layers (Tables 1, 2), and particularly so in the highly siliceous samples KR17 and KR19TF, in which the high aluminum values are related to the presence of kaolinite (Table 1). Sample KR9, which is rich in organic matter, has high Fe_2O_3, MnO, P_2O_5, and SO_3 concentrations. The enrichment in both phosphorus and sulfur is to be expected in such organic-matter-rich material, and the high Fe and Mg contents are due to the presence of limonite. The calcareous sample KR21, which also contains organic matter, contains the highest SO_3 and uranium values in the succession, which suggests that the uranium may be organically bound. P_2O_5 is also higher than in other samples, with the exception of KR9. The two stratigraphically lowest samples of the Krop succession, KR19TF and KR30, are rich in chalcedony and opal-C, respectively. These samples have the highest SiO_2 contents and the lowest contents of calcium, magnesium, iron, manganese, and loss on ignition (LOI), but do not show any significant enrichment or depletion in the other major and trace elements, relative to volcanogenic materials. The small amounts of Mg in the siliceous sedimentary rocks could be due to the presence of authigenic dolomite in silica concretions, and some of the magnesium in tuffaceous samples is due to the presence of dispersed dolomite (Table 1).

TABLE 3. CORRELATION COEFFICIENTS FOR SAMPLES FROM THE KROP SUCCESSION*

Correlation Coefficient	Pairs of Oxides and Elements
1.00	Al_2O_3-TiO_2
0.98	TiO_2-K_2O, Al_2O_3-K_2O, Ni-P_2O_5
-0.98	SiO_2-CaO
0.97	Fe_2O_3-Ni, Zr-V
0.95	K_2O-Rb

* except tuffaceous material.

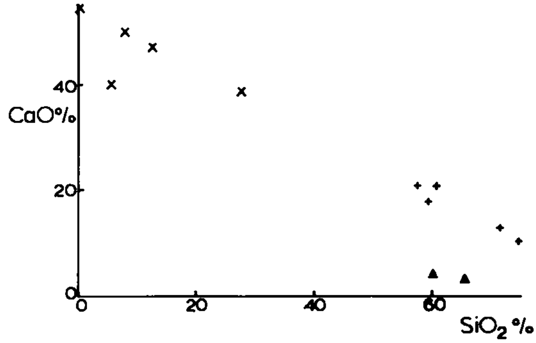

FIG. 6. Plot of SiO_2 *versus* CaO. Symbols: + siliceous samples, × calcareous samples, ▲ tuffaceous rocks.

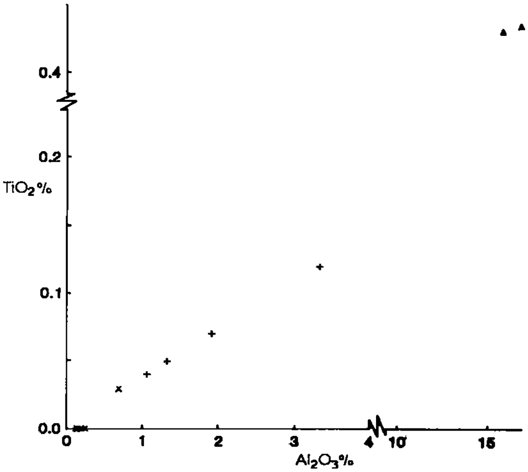

FIG. 7. Plot of Al_2O_3 *versus* TiO_2. Symbols as in Fig.6.

Trace elements

There are no significant differences in the concentration of Cr, Cu, Ni, Pb, Y, Th and Nb between the silica- and carbonate-rich samples

(Table 2). Slightly higher concentrations of V, Zn, Pb, Zr, B and Ba are found in the silica-rich layers, although the levels of these elements are still considerably lower than those in the volcanic rocks at the base of the succession. The higher Sr concentrations in the carbonate layers are to be expected, owing to the substitution of Sr for Ca in calcite. There are no systematic changes in major- and trace-element concentrations in either the carbonate- or silica-rich members, and changes related to the position of the samples within the stratigraphic sequence, as have been reported in other sequences showing silica transformations, are not seen (Mitsui & Taguchi 1977, Hein *et al.* 1981). Boron increases in concentration from the limestones through the cherts to the porcellanites (Tables 1, 2), the siliceous rocks having boron contents (14–20 ppm) similar to those reported in authigenic silica polymorphs derived from a biogenic silica precursor (Hein *et al.* 1981, 1983, Stamatakis 1986). Trace-element concentrations (Table 2) in the tuffaceous rocks are quite different from those in siliceous and calcareous sediments, with V, Rb, Sr, Zr, Ba, Pb, Nb, Y, Th, B and Cu all being much higher in the tuffaceous rocks.

DISCUSSION

Source of silica

The presence of opal-CT in saline-alkaline lake sediments, and of opal-CT – chalcedony as distinct horizons in stratigraphically thick marine successions, has been attributed to the conversion of biogenic silica, *via* an opal-CT intermediate, to stable microcrystalline quartz (chalcedony) (Murata & Larson 1975, Hein *et al.* 1981, Pisciotto 1981, Tada & Iijima 1983, Stamatakis *et al.* 1988). However, identification of the parentage and diagenetic reactions that produced low cristobalite (opal-C) in rock types involving mixed biogenic silica – volcanogenic precursors is still problematical. Using oxygen isotope data, Henderson *et al.* (1971) established that low cristobalite associated with smectite in a volcanic bentonite had a biogenic precursor. In this instance, opal-C was derived from the dissolution of diatom frustules, although no easily recognizable diatom relics were present.

In this study, opal-C occurs both in the siliceous and calcareous sedimentary rocks and in some of the tuffaceous rocks (Table 1). Low cristobalite is known not to occur as a primary constituent of volcanic glass (Henderson *et al.* 1971), and a primary volcanic origin for low cristobalite (opal-C) present in the Krop succession and adjacent tuffite is thus eliminated.

Several other possibilities exist, however, for the origin of the neoformed opal-C, chalcedony and opal-CT of the Krop area: (a) direct chemical precipitation, (b) alteration of volcanic material, and (c) transformation of biogenic silica. These possibilities are now evaluated in turn.

Direct precipitation of opal-C and chalcedony from hydrothermal fluids is unlikely to be the predominant mechanism of the silica authigenesis, since it is opal-CT which is synthesized hydrothermally in the laboratory from amorphous silica at low temperatures (150–200°C), rather than low cristobalite, which is formed at much higher temperatures (900–1100°C) (Flörke 1955, Mizutani 1966, 1977, Greenwood 1973). Precipitation of silica polymorphs rarely occurs in continental basins, but may take place in ephemeral or evaporitic continental basins, *via* a sodium silicate precursor (Hay 1968, Dapples 1979, Bjorlykke 1989). In this unusual case, biogenic silica (diatom frustules) supplied the soluble silica for the direct formation of α-cristobalite, *and* the sodium silicate precursor for the formation of quartz (Hay 1970).

The second possibility, that opal-C has been derived, along with the other silica phases, by the alteration of volcanic ash or volcanic glass, is supported by the abundance of low cristobalite in certain volcaniclastic sediments, tuffs, and lavas (Murata & Whitley 1973, Iijima *et al.* 1978, Iijima & Tada 1981). However, although volcanic glass was identified in both the underlying and overlying tuffs and tuffites, there is no evidence for the presence of either unaltered or altered volcanic glass in the siliceous sediments. Conversely, opal-C and chalcedony, which occur in abundance in the sedimentary rocks, have not been identified in the groundmass of the tuffs, although opal-C has been found in the tuffites (*e.g.*, KR18b), which are composed of both volcanic and biogenic or chemically precipitated material. It is, therefore, unlikely that volcanic glass is a precursor of the neoformed silica minerals in the Krop sedimentary rocks.

As shown in Table 2, the chemical compositions of the tuffs–tuffites do not resemble those of the siliceous rocks. Certain trace elements such as Zn, Cu, V, Rb, Sr, Y, Zr, Nb, Ba, Pb, Th, and Ti occur at much lower levels in the siliceous and calcareous rocks than in the tuffaceous ones. This weighs against the siliceous rocks having a large volcanogenic component, because even though leaching of the volcanic components into the swamp environment would occur, the immobile elements, including Zr, Ti, Y and Th, and possibly Ba, Pb, Cr, and V, are expected to be largely retained in the volcaniclastic rocks (Spears & Rice 1973, Spears & Kanaris-Sotiriou 1979). Furthermore, the trace-element concentrations in both the carbonate- and silica-rich members of the Krop succession are similar. This fact also suggests that the formation of the siliceous layers from ash-fall tephra introduced into the swamp basin is unlikely. The minor variations in the trace-element concentrations of the sedimentary rocks can be attributed to the presence of small amounts of kaolinite and clastic minerals in these rocks.

The third possibility is that silica neoformation occurred at the expense of biogenic silica (*cf.* Henderson *et al.* 1971, Hein *et al.* 1983, Kastner & Siever 1983). This mechanism for the formation of authigenic silica minerals seems to be the most plausible in view of the presence of diatom relics in the siliceous layers. Rare, highly corroded diatom frustules do occur in the Krop siliceous rocks, but clearly defined diatom morphology is lacking (Fig. 4). Similar intense dissolution of diatom frustules has been reported in association with the development of quartz in diagenetic zones from opal-A through opal-CT and low cristobalite to quartz (Tada & Iijima 1983, Stamatakis *et al.* 1988).

It is possible that the extensive development of biogenic silica in the Krop succession is due to the existence of ideal conditions for diatom growth, which may be related to high concentrations of silica resulting from the leaching of adjacent volcanic material in a humid and warm environment. This process is indicated schematically in Figure 5.

GENESIS OF THE SILICA POLYMORPHS

Controls on phase transformations

The factors that may affect the diagenetic transformation of biogenic silica to opal-CT, and then through opal-C to chalcedony or microcrystalline quartz are: burial depth, time, heat flow, host-rock lithology, pore-solution chemistry, morphology and size of particles of biogenic silica (Murata & Larson 1975, Keene 1975, Kastner *et al.* 1977, Carver 1979, Kastner 1979, Iijima & Tada 1981, Hein *et al.* 1981, Williams *et al.* 1985, Stamatakis & Magganas 1988, Stamatakis *et al.* 1989). The transformation of biogenic silica to both opal-C and chalcedony, with subsidiary amounts of opal-CT, in the Krop succession appears to have occurred under unusual diagenetic conditions, this conclusion being based on the following factors.

Time

The silica transformation has affected silica–carbonate deposits that are relatively young (5.3 Ma, *i.e.*, Early Pliocene: Chorianopoulou *et al.* 1984), when more than 10 Ma are required in the normal geothermal gradient of continental margins to produce chalcedony (Keene 1975, Hein *et al.* 1983).

Burial depth

The Krop deposits are stratigraphically thin (maximum 50 m) and are overlain by Pliocene tuffs of a comparable thickness. The burial depth in a normal geothermal gradient along which the conversion of opal-A to opal-C takes place is between 1000 and 1500 m (Mitsui & Taguchi 1977), and the formation of chalcedony requires even deeper burial. It is impossible for the Krop succession to have been buried to such a depth. This lack of burial depth control on the Krop sequence is also indicated by the intermixing of opal-C and chalcedony phases, *i.e.*, the lack of any distinct zonation of neoformed silica minerals with stratigraphic level. The exception to this occurs just above the contact between the volcanic and the sedimentary rocks, where chalcedony is the predominant authigenic silica polymorph. Intermixed silica polymorphs (opal-A–opal-CT) also have been reported in a shallow marine siliceous succession in the vicinity of volcanic rocks (Stamatakis & Magganas 1988). Burial depth, therefore, does not appear to have had an important influence on the formation of the authigenic silica minerals in this sequence.

Host-rock lithology

The neoformed silica minerals occur in highly siliceous layers, in layers containing clay (kaolinite), and also in carbonate-rich layers. Therefore, host-rock lithology does not seem to control the diagenetic transformations.

Effect of solution chemistry

The presence of kaolinite and the specific type of fossilized vegetation preserved in the succession (Chorianopoulou *et al.* 1984) suggest that the sediments were deposited in an acidic, humid swamp environment. The swamp became more alkaline and drier with time, as indicated both by the presence of authigenic dolomite rhombohedra in the diagenetic opal-C and chalcedony, and also by pollen analysis. Alkaline pore solutions are known to promote the transformation of biogenic silica to authigenic silica (Kastner *et al.* 1977). However, the presence of kaolinite and absence of evaporite minerals, zeolites, and authigenic K-feldspar in the Krop sequence suggest that alkalinity may not have been sufficiently high to be a critical factor.

Temperature

The only remaining factor that could have played a dominant role in controlling the formation of authigenic silica minerals is the high heat-flow in the volcanic terrane of the Aridea area. Diagenetic transformations related to time and burial depth affecting biogenic silica sediments have been reported from pre-Cenozoic to Late Miocene sediments (Lancelot 1973, Carver 1979, Iijima *et al.* 1978, 1980, Pisciotto 1981, Hein *et al.* 1983, Williams *et al.* 1985, Stamatakis *et al.* 1988). However, high heat-flow is the most important factor in creating such transformations in sediments younger than 10 Ma (Late Miocene) (Keene 1975, Hein *et al.* 1983, Kastner & Siever 1983, Stamatakis & Magganas 1988).

In the northern Aegean region, active volcanism and high heat-flow associated with extensional tectonism have existed since Pliocene times (Mercier 1976, Erickson *et al.* 1977, Angelier 1979, Kolios *et al.* 1980, Papadopoulos 1982). The estimated current heat-flow in the Aridea volcanic terrane is 80 to 100 mWm^{-2} (Fytikas & Kolios 1979), and is manifested today by the hot springs of Aridea (Stamatakis 1986).

Formation of opal-C or opal-CT (or both) in siliceous sediments older than Late Miocene may take place at temperatures lower than 50°C (Mitsui & Taguchi 1977, Hein *et al.* 1978). By contrast, temperatures of formation of silica polymorphs in young siliceous sediments sandwiched between igneous intrusions (sills) may have been as high as 300°C according to Kastner & Siever (1983). They also observed that at or near the contacts between the siliceous sediments and the intrusions, biogenic opal-A had been transformed directly to quartz, whereas metastable phases were formed in the sediments away from the contacts.

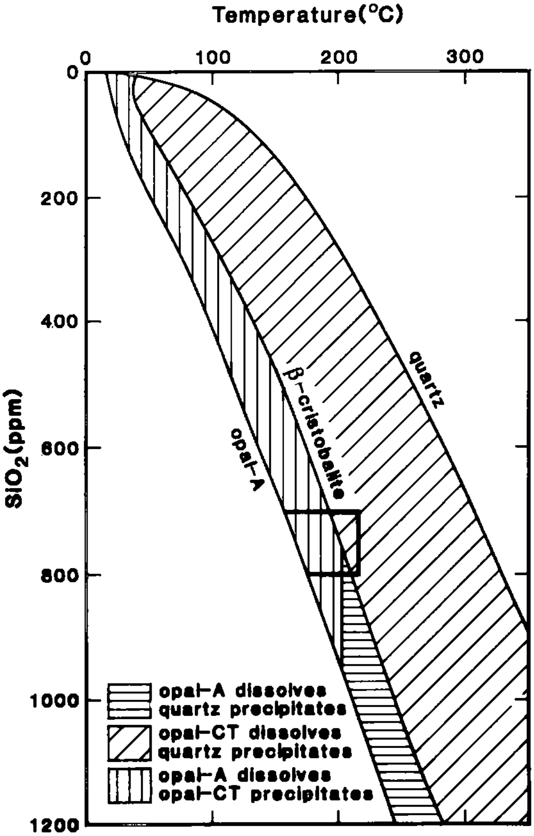

FIG. 8. Plot of stabilities of silica phases after Kastner & Siever (1983). In addition to their assumption that β-cristobalite has the same solubility as a "disordered" opal-CT, we also assume that β-cristobalite has a similar solubility to that of low cristobalite. The boxed-in area indicates the probable conditions of formation of the Krop silica polymorphs. The limits of this area are defined by the type and amount of each silica polymorph present in the study area.

The Krop succession represents sediments sandwiched between two tuffaceous bodies associated with contemporaneous lavas found in the vicinity of the sedimentary rocks to the southwest (Figs. 2, 3). The Krop succession may therefore be regarded as a closed system bounded by tuffs and lavas, analogous to the example described by Kastner & Siever (1983). The absence of notable opal-A in the Krop succession, the scarcity of opal-CT, and the abundance of chalcedony and opal-C all lead us to assume that elevated temperatures existed during the diagenetic transformations. Also, using Kastner's (1979) equations for opal-CT formation in these Early Pliocene rocks, a temperature of 50°C is expected. We can assume, from the scarcity of this mineral and the abundance of opal-C and chalcedony, that higher temperatures existed during the diagenesis of the Krop succession. The diagram of Kastner & Siever (1983) showing stability fields of silica polymorphs (Fig. 8) suggests that the temperature may have reached 200°C.

In the south Aegean area, the Aegina Island diatomites and porcellanites represent an example of partial transformation of opal-A to opal-CT (Stamatakis & Magganas 1988), produced in response to the high heat-flow of the south Aegean volcanic arc (estimated temperatures around 50°C). This contrasts with the diagenesis of opal-A to opal-C and chalcedony in Aridea volcanic terrane of northern Greece, which was controlled by the much higher temperatures developed in this area.

ACKNOWLEDGEMENTS

We are indebted to Prof. Robert F. Martin for his valuable comments and suggestions, and to Drs. James Hein, U.S. Geological Survey, Menlo Park, California, Ruiji Tada, University of Tokyo and Stephen Chryssoulis, University of Western Ontario, for their helpful reviews of the manuscript. We also thank Dr. Konstantinos Kyriakopoulos for his contribution to the field work for this study. We are grateful to Michael Cooper for drawing the diagrams, and Steve Ellins and Dr. Joe McQuaker for help with scanning electron microscopy.

REFERENCES

ANGELIER, J. (1979): Recent Quaternary tectonics in the Hellenic arc: examples of geological observation on land. *Tectonophysics* **52**, 267-275.

BALTATZIS, E.G., STAMATAKIS, M.G. & KYRIAKOPOULOS K.G. (1986): Rozenite and melanterite in lignitic layers from the Voras mountain, western Macedonia, Greece. *Mineral. Mag.* **50**, 737-739.

BJORLYKKE, K. (1989): *Sedimentology and Petroleum Geology*. Springer-Verlag, New York.

CARVER, R.E. (1979): Petrology of Paleocene–Eocene and Miocene opaline sediments, southeastern Atlantic coastal plain. *J. Sediment. Petrol.* **50**, 569-582.

CHORIANOPOULOU, P., GALEOS, A. & IOAKIM, C. (1984): Pliocene lacustrine sediments in the volcanic succession of Almopias, Macedonia, Greece. *In* The Geological Evolution of the Eastern Mediterranean (J.E. Dixon & A.H.F. Robertson, eds.). *Geol. Soc. London, Spec. Publ.* **17**, 795-806.

DAPPLES, E.C. (1979): Silica as an agent in diagenesis. *In* Diagenesis in Sediments and Sedimentary Rocks 25A (D. Larsen & G.V. Chillingar, eds.) Elsevier, Amsterdam (99-141).

ELEFTHERIADIS, G. (1977): *Contribution to the Study of the Volcanic Rocks of the Southern Almopia*. Ph.D. thesis, Aristotle University, Thessaloniki, Greece.

ERICKSON, A.J., SIMMONS, G. & RYAN, W.B.F. (1977): Review of heat flow data from the Mediterranean and Aegean seas. *In* Structural History of the Mediterranean Basins (B. Biju-Duval & L. Montadert, eds.). Editions Technip, Paris (263-280).

FLÖRKE, O.W. (1955): Zur Frage des "Hoch"-cristobalit in Opalen, Bentoniten und Gläsern. *Neues Jahrb. Mineral. Monatsh.*, 217-223.

FYTIKAS, M. & KOLIOS, N. (1979): Preliminary heat flow map of Greece. Edition of Inst. Geol. Mining Res., Athens, Greece.

GREENWOOD, R. (1973): Cristobalite; its relationship to chert formation in selected samples from the Deep-Sea Drilling Project. *J. Sediment. Petrol.* **43**, 700-708.

HAY, R.L. (1968): Chert and its sodium-silicate precursors in sodium-carbonate lakes of East Africa. *Contrib. Mineral. Petrol.* **17**, 255-274.

______ (1970): Silicate reactions in three lithofacies of a semi-arid basin, Olduvai gorge, Tanzania. *In* Mineralogy and Geochemistry of Non-Marine Evaporites (B.A. Morgan, ed.). *Mineral. Soc. Am., Spec. Pap.* **3**, 237-255.

HEATH, G.R. (1973): Cherts from the eastern Pacific, Leg 16, Deep Sea Drilling Project. *In* Initial Reports of the Deep Sea Drilling Project 7 (T.G. Van Andel, G.R. Heath *et al.*, eds.). U.S. Government Printing Office, Washington, D.C. (609-613).

HEIN, J.R., SANCETTA, C., & MORGENSON, L.A. (1983): Petrology and geochemistry of silicified upper Miocene chalk, Costa Rica Rift, DSDP Leg 69. *In* Initial Reports of the Deep Sea Drilling Project 69 (J.R. Cann, M.J. Langseth *et al.*, eds.). U.S. Government Printing Office, Washington, D.C. (395-422).

______, SCHOLL, D.W., BARRON, J.A., JONES, M.J. & MILLER, J. (1978): Diagenesis of Late Cenozoic diatomaceous deposits and formation of the bottom simulating reflector in the southern Bering Sea. *Sedimentology* **25**, 156-181.

______, VALLIER, T.L. & ALLAN, M.A. (1981): Chert petrology and geochemistry of Mid-Pacific Mountains and Hess Rise, Leg 62, DSDP. *In* Initial Reports of the Deep Sea Drilling Project 62 (J., Thiede, T.L. Vallier *et al.*, eds.). U.S. Government Printing Office, Washington, D.C. (711-768).

______ & YEH, H. (1983): Oxygen-isotope composition of secondary silica phases, Costa Rica Rift, DSDP Leg 69. *In* Initial Reports of the Deep Sea Drilling Project 69 (J.R. Cann, M.J. Langseth *et al.*, eds.). U.S. Government Printing Office, Washington, D.C. (423-442).

HENDERSON, J.H., JACKSON, M.L., SYERS, J.K., CLAYTON, R.N. & REX, R.W. (1971): Cristobalite authigenic origin in relation to montmorillonite and quartz origin in bentonites. *Clays Clay Miner.* **19**, 229-238.

IIJIMA, A., KAKUWA, Y., YAMAZAKI, K. & YANAGIMOTO, Y. (1978): Shallow-sea organic origin of the

Triassic bedded chert in Japan. *J. Fac. Sci., Univ. Tokyo, Sec. ii,* **19**, 369-400.

______, Matsumoto, R. & Tada, R. (1980): Zeolitic and silica diagenesis and sandstone petrography at sites 438 and 439, DSDP/IPOD Leg 57. *In* Initial Reports of the Deep Sea Drilling Project 57 (M. Lee & L.N. Stout, eds.). U.S. Government Printing Office, Washington, D.C. (1143-1158).

______ & Tada, R. (1981): Silica diagenesis of Neogene diatomaceous and volcaniclastic sediments in northern Japan. *Sedimentology* **28**, 185-200.

Kastner, M. (1979): Silica polymorphs. *In* Marine Minerals (R.G. Burns, ed.). *Rev. Mineral.* **6**, 99-107.

______, Keene, J.B. & Gieskies, J.M. (1977): Diagenesis of siliceous oozes. I. Chemical controls on the rate of opal-A to opal-CT transformation - an experimental study. *Geochim. Cosmochim. Acta* **41**, 1041-1059.

______ & Siever, R. (1983): Siliceous sediments of the Guaymas basin: the effect of high thermal gradients on diagenesis. *J. Geol.* **91**, 629-641.

Keene, J.B. (1975): Cherts and porcellanites from the north Pacific DSDP, Leg 32. *In* Initial Reports of the Deep Sea Drilling Project 32 (R.L. Larson, R. Moberly *et al.*, eds.). U.S. Government Printing Office, Washington, D.C. (429-507).

Kolios, N., Innocenti, F., Manetti, P., Peccerillo, A. & Giuliani, O. (1980): The Pliocene volcanism of the Voras Mtns. (central Macedonia, Greece). *Bull. Volcanol.* **43**, 554-568.

Lancelot, Y. (1973): Chert and silica diagenesis in sediments from central Pacific. *In* Initial Reports of the Deep Sea Drilling Project 17 (E.L. Winterer, J.I. Erwing *et al.*, eds.). U.S. Government Printing Office, Washington, D.C. (377-405).

Marakis, G. & Sideris, C. (1973): Petrology of the Edessa area volcanic rocks, western Macedonia, Greece. *Bull. Volcanol.* **36**, 462-472.

Mercier, J. (1976): La néotectonique: ses méthodes et ses buts. Un exemple: l'arc Egéen (Méditerranée orientale). *Géograph. Phys. Dynam.* **18**, 323-346.

Mitsui, K. & Taguchi, K. (1977): Silica mineral diagenesis in Neogene Tertiary shales in the Tempoku district, Hokkaido, Japan. *J. Sediment. Petrol.* **47**, 158-167.

Mizutani, S. (1966): Transformation of silica under hydrothermal conditions. *J. Earth Sci., Nagoya Univ., Japan* **14**, 56-88.

______ (1977): Progressive ordering of cristobalitic silica in the early stage of diagenesis. *Contrib. Mineral. Petrol.* **61**, 129-140.

Murata, K.J. & Larson, R.R. (1975): Diagenesis of Miocene siliceous shale, Temblor Range, California. *J. Res. U.S. Geol. Surv.* **3**, 553-556.

______ & Whitley, K.R. (1973): Zeolites in the Miocene Briones Sandstone and related formations of the Central Coast Ranges, California. *J. Res. U.S. Geol. Surv.* **1**, 255-265.

Papadopoulos, G. (1982): *Active Deep Tectonics of the Aegean and Surrounding Area.* Ph.D. thesis, Aristotle University, Thessaloniki, Greece.

Pevear, D.R., Williams, V.E. & Mustoe, G.E. (1980): Kaolinite, smectite, and K-rectorite in bentonites: relation to coal rank at Tulameen, British Columbia. *Clays Clay Miner.* **28**, 241-254.

Pisciotto, K.A. (1981): Diagenetic trends in a siliceous facies of the Monterey Shale in the Santa Maria region, California. *Sedimentology* **28**, 547-571.

Siever, R. (1983): Evolution of chert at active and passive continental margins. *In* Siliceous Deposits in the Pacific Region (A. Iijima, J.R. Hein & R. Siever, eds.). Elsevier, New York (7-24).

Spears, D.A. & Rice, C.M. (1973): An Upper Carboniferous tonstein of volcanic origin. *Sedimentology* **20**, 281-294.

______ & Kanaris-Sotiriou, R. (1979): A geochemical and mineralogical investigation of some British and other European tonsteins. *Sedimentology* **26**, 407-425.

Stamatakis, M.G. (1986): *Boron Distribution in Hot Springs, Volcanic Emanations, Marine Evaporites and in Volcanic and Sedimentary Rocks of Cenozoic Age in Greece.* Ph.D. thesis, National Univ. of Athens, Athens, Greece.

______ (1989): Authigenic silicates and silica polymorphs in the Miocene saline–alkaline deposits of Karlovassi basin, Samos, Greece. *Econ. Geol.* **84**, 788-798.

______, Dermitzakis, M., Economou-Amilli, A. & Magganas, A. (1988): Petrology and diagenetic changes in Miocene marine diatomaceous deposits from Zakynthos Island, Greece. *In* Siliceous Deposits of the Pacific and Tethys Regions (J.R. Hein & J. Obradovic, eds). Springer–Verlag, New York (129-139).

______, Hein J.R. & Magganas, A.C. (1989): Geochemistry and diagenesis of Miocene lacustrine siliceous sedimentary and pyroclastic rocks, Mytilinii basin, Samos Island, Greece. *Sediment. Geol.* **64**, 65-78.

______ & Magganas, A.C. (1988): Thermally induced silica transformation on Pliocene diatomaceous layers from Aegina Island, Greece. *In* Siliceous Deposits of the Pacific and Tethys Regions (J.R. Hein & J. Obradovic, eds.). Springer-Verlag, New York (141-150).

Stanton, R.E. & McDonald, A.J. (1966): The colorimetric determination of boron in soils, sediments and rocks with methylene blue. *Analyst* **91**, 775-778.

Tada, R. & Iijima, A. (1983): Petrology and diagenetic changes of Neogene siliceous rocks in northern Japan. *J. Sediment. Petrol.* **53**, 911-930.

Van Zyl, C. (1982): Rapid preparation of robust powder briquettes containing a styrene and wax mixture as a binder. *X-Ray Spectrom.* **11**, 29-32.

Williams, L.A., Parks, G.A. & Crerar, D.A. (1985): Silica diagenesis. I. Solubility controls. *J. Sediment. Petrol.* **55**, 301-311.

Received March 9, 1990, revised manuscript accepted February 5, 1991.