

K-Ar date and biostratigraphic position of a volcanic ash-layer in the marine Pliocene of Crete, Greece

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Abstract

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Four of five size fractions of two biotite samples from a volcanic ash bed in the marine Pliocene Prassas section on Crete yielded almost concordant K-Ar dates of 3.20 to 3.25 Ma. The youngest date of 3.20 ± 0.03 Ma is interpreted to be a close estimate of the age of the ash.

The tephra layer is situated in the lower part of the planktonic foraminiferal *Globorotalia crassaformis* Zone. In terms of calcareous nannofossil biostratigraphy, the ash bed can be assigned to the *Discoaster surculus* Zone (NN16). The ash bed was also recognized in the nearby sections of Aghios Vlassios and Finikia and on the island of Koufonisi, SE of Crete. A tentative correlation with an ash level in the Mediterranean D.S.D.P. site 378 is proposed. The biochronologic scheme of the Mediterranean Pliocene, based on four K-Ar dates from volcanic intercalations in marine sequences, differs by its greater age estimates from the one commonly constructed on the basis of age-extrapolation of geomagnetic or biostratigraphic horizons from other areas.

Introduction

Most numerical age estimates from the Mediterranean Pliocene have been inferred from extrapolation of the ages, assigned to biohorizons recognized in the Indian and Pacific Ocean (Hays et al. 1969, Gartner 1973), or have been based on the interpretation of geomagnetic reversal patterns (Ryan 1973, Cita & Ryan 1973, Tauxe et al. 1983). Numerical age determinations on volcanic intercalations in marine sedimentary sequences that allow detailed biostratigraphic analysis, are the direct means of estimating the age of biohorizons. Thus far, however, the number of ages by K-Ar and fission track methods reported from marine Plio-

cene sections in the Mediterranean area is low (Selli 1970, Ambrosetti et al. 1972, Arias et al. 1976, Selli et al. 1977, Benda et al. 1979, Obradovich et al. 1982). Only three localities provided numerical age data within a reasonably well established biostratigraphic scheme.

Müller et al. (1979) have given a date of 4.4 ± 0.2 Ma (K-Ar, single hornblende) from a tuff intercalation in the section Aghios Thomas on the island of Aegina (Greece). The planktonic foraminiferal associations (Benda et al. 1979) can be assigned to the *Globorotalia margaritae* – *G. puncticulata* Concurrent range zone. The calcareous nannofossils from the interval point to the *Ceratolithus rugosus* and *Discoaster asymmetricus* Zones (NN

13 and NN 14).

Two volcanic ash layers in the Late Pliocene sequence of Semaforo/Vrica (Calabria, Italy) have been dated by K-Ar and fission track methods (Selli 1970, Selli et al. 1977, Obradovich et al. 1982). According to the latter authors the age of the lower ash bed is 2.22 ± 0.03 Ma (K-Ar, single hornblende). This part of the section belongs to Interval 8 of Spaak (1983), which is in the upper part of the *Globorotalia crassaformis* Zone, and in the lower part of *Discoaster brouweri* Zone (NN 18) (Driever 1984). The upper ash layer (m-marker bed; see Selli et al. 1977) is situated in the interval proposed as the stratotype for the Neogene/Quaternary boundary. Obradovich et al. (1982) discussed the age of the m-marker bed and concluded it to be less than 1.99 ± 0.08 Ma (K-Ar, biotite). The planktonic foraminifera point to the *Globorotalia inflata* Zone while the calcareous nannofossils are indicative of the *Cyclococcolithus macintyreii* Subzone (Rio 1982).

In 1981, the first author discovered an ash level in the Cretan section of Prassas. Lateral dispersion of the tephra could be demonstrated with the aid of biostratigraphic and lithostratigraphic studies (Spaak 1983, Jonkers 1984). This tephra provides another opportunity for the calibration of biostratigraphy and geochronometry of the Mediterranean Pliocene.

Biotite was separated from the ash in Amsterdam and Karlsruhe; K-Ar analyses were performed at BGR, Hannover. The lithological and foraminiferal data on the section were compiled by Jonkers; the data on the calcareous nannofossils were obtained by Driever.

The Prassas section: geological setting and biostratigraphy

In the marine Pliocene of the Iraklion province, central Crete, four facies types can be distinguished (Meulenkamp et al. 1979, Jonkers 1984). The base of the Pliocene sequence is formed by a marl breccia, which is in erosional contact with Upper Miocene deposits. The marl breccia is overlain by, successively, white marls (Kourtes facies), an

alternation of greyish marls and brown laminated sapropelic beds (Finikia facies), and yellowish silty marls in which the laminated intercalations are predominantly diatomites (Stavromenos facies).

The foraminiferal and calcareous nannofossil content of this succession has been studied by Thomas (1980), Driever (1981), Spaak (1983) and Jonkers (1984). Samples from the homogeneous marls usually contain rich and diversified faunas and floras. The non-homogeneous strata, however, contain either benthonic faunas dominated by *Bolivina*, *Bulimina* and *Uvigerina* species or are devoid of indigenous benthonic foraminifera. Generally, the planktonic foraminifera associations of the laminites are dominated by *Globigerina bulloides* and *Neogloboquadrina* spp. (Spaak 1983).

The facies sequence is exposed in four stratigraphically superimposed outcrops along the eastern approach to the Prassas village (fig. 1). These exposures should not be confused with the section Prassas along the main road from Aghios Nikolaos to Iraklion, which section was studied by Benda et al. (1974), Tsapralis (1976), Meulenkamp et al. (1978) and Georgiades-Dikeoulia (1979). From field evidence it is concluded that their

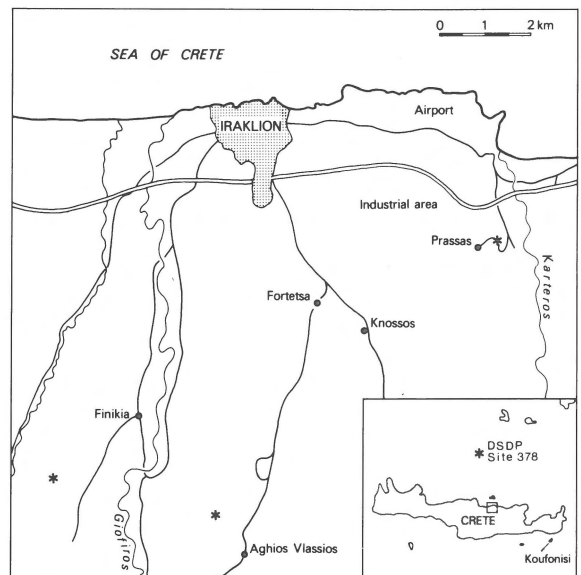


Fig. 1. Localities of the tephra-bearing Pliocene sections Prassas, Aghios Vlassios, Finikia, Kourtes and of D.S.D.P. site 378.

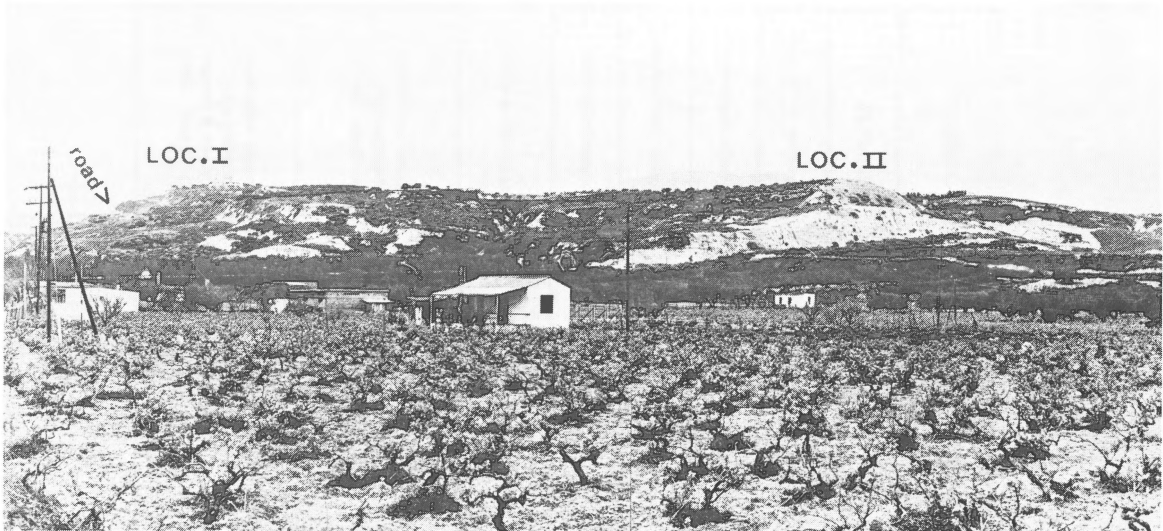


Fig. 2. Panoramic view of the Prassas area, seen from the northeast. The arrow marks the site where the ash was sampled. Localities indicated are related to the following articles: Loc. I: Section Prassas (see Thomas 1980, Spaak 1983, Jonkers 1984, this paper); Loc. II: Section Prassas and/or Prassa exposed along the main road from Iraklion to Aghios Nikolaos (see Benda et al. 1974, Tsapralis 1976, Meulenkamp et al. 1978, Georgiades-Dikeoulia 1979).

section has a higher stratigraphic position (fig. 2).

The ash level was found in the topmost outcrop of our Prassas succession. This exposure shows some 40 m of continually exposed sediments of the Finikia and Stavromenos facies (fig. 3). Here, the transition between the two facies types is very abrupt. Sedimentary features at the boundary suggest a major break in sedimentation. The white diatomaceous intervals of the Stavromenos facies may be over 8 m thick. On the partings of these laminites, perfectly fossilized fish and plant remains are found.

The tephra is situated at 1.30 m above the base of the third diatomite (figs. 3,4). The level with abundant volcanic material is approximately 5 cm thick. In this level one can distinguish a greyish ash layer of at least 1 cm thickness, overlain by reddish coloured diatomite which contains volcanic material as well. Red staining is sometimes observed on the lower surface of the grey ash bed. The mineral content of the entire ash interval consists mainly of olivine-green and reddish-brown biotites, feldspar, garnet, pyroxene, hornblende, quartz and ores. Pumiceous glass shards were observed in thin sections. Electron microprobe and neutron activation analyses, combined with petrographic descrip-

tions of thin sections and additional K-Ar analyses, are in progress (Bianchi, Klaver, Kreuzer & Meyer, in prep.).

The biostratigraphy of the topmost outcrop in the Prassas section is shown in fig. 3. Of the benthonic foraminifera, *Uvigerina rutila* ranges up to the facies boundary and indicates an Early Pliocene age for the lower part of the exposure. The joint occurrence of the planktonic foraminifera *Globorotalia margaritae* and *G. puncticulata* in this sedimentary interval points to the *G. margaritae* – *G. puncticulata* Concurrent range zone (MPL 3) of Cita (1975). The Stavromenos facies with the ash layer contains *G. bononiensis* and *G. crassaformis*, of which the latter is indicative of the *G. crassaformis* Zone of Bizon & Bizon (1972). *Sphaeroidinellopsis* spp. are sporadically present in the section. Biostratigraphic refinement is possible due to the presence of *G. crassaformis* associations which are predominantly dextral coiling. This places the marl-diatomite alternation in the lower part of Spaak's (1983) Interval 6.

From this faunal sequence it is evident that a major hiatus is present at the level of the facies change. The same observation can be deduced from the calcareous nannofossil record. Using the zonal scheme of Martini & Worsley (1970), the

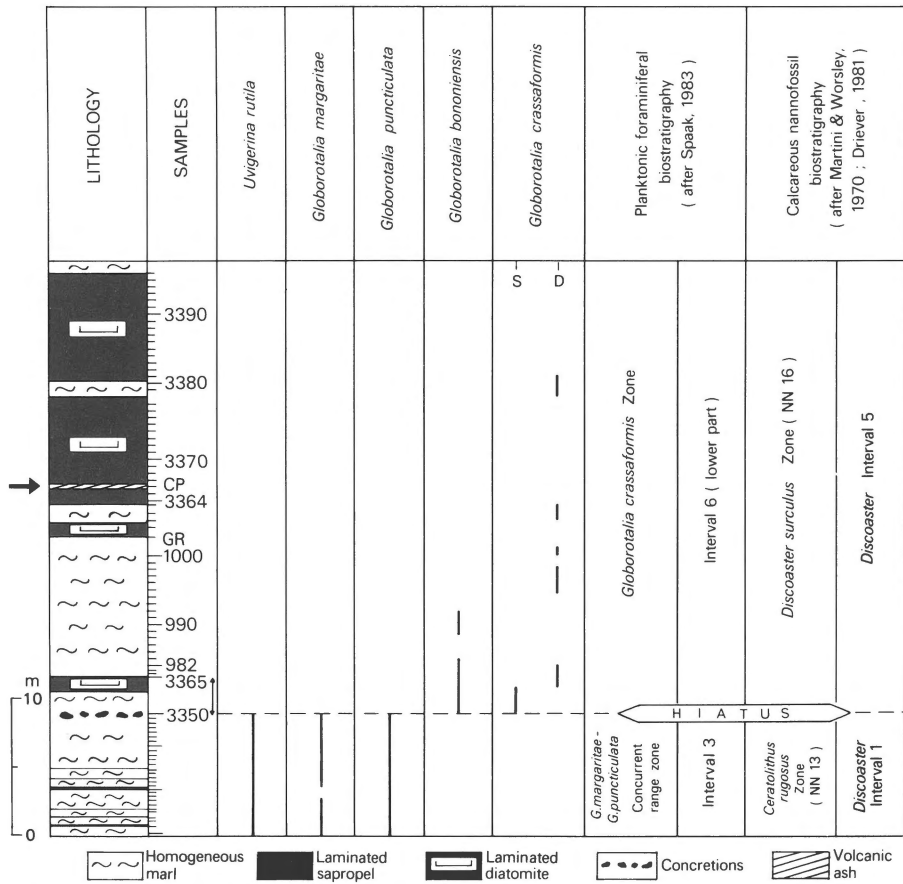


Fig. 3. Lithology and biostratigraphy of the topmost exposure of the Prassas section.

lower part of the exposure can be assigned to the *Ceratolithus rugosus* Zone (NN 13), as indicated by the presence of *Ceratolithus rugosus* and the absence of *Discoaster asymmetricus*. The higher part with the ash layer belongs to the *Discoaster surculus* Zone (NN 16), as inferred from the absence of *Reticulofenestra pseudoumbilica*. Following Driever's (1981) subdivision of the Mediterranean Pliocene, which is based on frequency patterns of *Discoaster* species, the lower part belongs to his *Discoaster* Interval 1; the upper part of the section belongs to Interval 5.

In terms of silicoflagellate biostratigraphy, the diatomites of Prassas can be placed in Bukry's (1977) *Dictyocha stapedia stapedia* Zone (K. Perch-Nielsen 1982, written comm.).

K-Ar dating: procedure and results

About 5 kg of material were collected from the entire ash interval (sample M5808.Bi81 Prassas 6), 3 kg of which were dried, crushed and dry-sieved,



Fig. 4. Lower part of the third Prassas diatomite with the ash bed. Photograph courtesy A.R. Fortuin.

using sieves with mesh-widths of 250 μm and 63 μm . Subsequent wet-sieving resulted in two fractions, one of 63 - 125 μm , and one of 125 - 250 μm . The olive-green biotite, which is most abundant, was concentrated from both fractions by means of a modified Frantz isodynamic magnetic separator and an overflow centrifuge, using a set of stabilized heavy liquids (Verschure & IJlst 1969; IJlst 1973a, b). The concentrates still contained red biotite, garnet, and some hornblende. In Karlsruhe the olive-green biotite was separated by repeatedly using a dry vibrating table, washing including ultrasonic treatment, and a Frantz isodynamic separator.

About 3 kg of the second sample of the ash (M5809.Bi81 Prassas 6) were processed. This sample material was taken from the ash layer proper and did not show any garnet; there was only a minor amount of red biotite with respect to the

olive-green/brown biotite. The sample was soaked and repeatedly treated in an ultrasonic bath and wet sieved before the same size fractions of the olive-green/brown biotite were separated as mentioned before by dry table, washing, and magnetic separation. Finally, the fine fraction of the separated biotite was split into the size fractions 63 - 90 μm and 90d - 125 μm by drysieving.

Potassium was determined by flame photometry, argon by standard total fusion isotope dilution analysis (Seidel et al. 1982). These analyses (Table 1) resulted in almost concordant K-Ar dates for four of the five analyzed fractions: 3.20 ± 0.03 , 3.23 ± 0.03 , and 3.25 ± 0.04 Ma. However, the date of the smallest size fraction of the second sample deviates significantly: 3.49 ± 0.04 Ma. This and the observation of garnet in the first sample suggest a contamination by older material. Also excess argon is to be taken into account (e.g.

Table 1. K-Ar data of middle Late Pliocene Prassas biotites and of the interlaboratory standard glauconite GL-O.

| Grain-size fraction (μm) | K (wt.%) | Argon | | ^{40}K | ^{40}Ar | K-Ar date (Ma) |
|---|-------------------|-------------------|--------------------|--|------------------|-------------------|
| | | atm. (pl/g)STP | rad. | ^{36}Ar ($\times 10^{-3}$) | ^{36}Ar | |
| Sample M5808.Bi81 | | | | | | |
| 125-250 | 7.323 ± 28 | 492 ± 29 | 911 ± 8 | 2954 | 845 | 3.20 ± 0.03 |
| 63-125 | 7.171 ± 38 | 384 ± 3 | 902 ± 5 | 3707 | 993 | 3.23 ± 0.03 |
| Sample M5809.Bi81 | | | | | | |
| 125-250 | 7.080 ± 29 | 2990 ± 60 | 895 ± 29 | 470 | 384.3 | 3.25 ± 0.11 |
| 90-125 | 7.018 ± 29 | 2352 ± 25 | 886 ± 9 | 592 | 407.3 | 3.25 ± 0.04 |
| 63-90 | 6.796 ± 35 | 2727 ± 28 | 924 ± 10 | 491 | 395.3 | 3.49 ± 0.04 |
| glauconite GL-O | 6.591 ± 35 | 920 ± 20 | 24740 ± 130 | | | 94.1 ± 0.7 |

(pl/g)STP = pico litre/gram at standard temperature and pressure, corrected for the mean values of blank analyses.

IUGS-recommended constants used (Steiger & Jäger 1977):

$$\lambda_c + \lambda'_c = 0.581 \times 10^{-10} \text{a}^{-1} \quad ^{40}\text{K}/\text{K} = 0.01167 \text{ atom } \%$$

$$\lambda_{\text{p}} = 4.962 \times 10^{-10} \text{a}^{-1} \quad ^{40}\text{Ar}/^{36}\text{Ar} = 295.5$$

The quoted limits of error refer to analytical uncertainty at a 95 % confidence level.

Obradovich et al. 1982: Table 1b, Müller et al. 1979: Table 4). Therefore, we interpret the youngest date as a maximum estimate of the age of the tephra layer. On the other hand, the two samples represent biotites of different origin as is demonstrated by grossly different concentrations of atmospheric argon. We argue that the same date for four size fractions of two different biotites within one ash interval points to a close approximation of the true age of the ashes by this date.

The ash bed in other localities

Subsequent field investigation revealed the ash to be also present in the nearby sections of Aghios Vlassios and Finikia (fig. 1). The Aghios Vlassios section lies about 1 km NW of the village of Aghios Vlassios, the Finikia section is situated 2 km SW of the village of Finikia. Both sections are less easily accessible compared to the outcrops along the road to Prassas. The sections are long and continuously exposed sequences with sediments of the Finikia and the Stavromenos facies. No stratigraphic discontinuity is apparent.

As in the Prassas section, the tephra layer was found in the lower part of the third white laminite of the Stavromenos facies. In sections Aghios Vlassios and Finikia, however, it is located only 9 cm above the base of this bed. Here, red staining of the grey ash bed or reddish coloration of the sediment directly above have not been observed. The biostratigraphic position of the tephra is identical, being in the lower part of Interval 6 in the *G. crassaformis* Zone, and in the *D. surculus* Zone or *Discoaster* Interval 5. Figure 5 shows the lithology and correlation of the three sections.

The ash was found also in Pliocene outcrops on the island of Koufonisi (J.M. Peters 1983, pers.comm.). Koufonisi is situated some 5 km off the southeastern coast of Crete (fig. 1). The tephra is intercalated in the upper part of the local marine Pliocene sequence in an alternation of homogeneous marls and laminites. The sediments below and above the ash-bed yield *G. crassaformis* and *G. bononiensis* (Peters, in preps.), and these faunal data are in accordance with Dermitzakis & Theo-

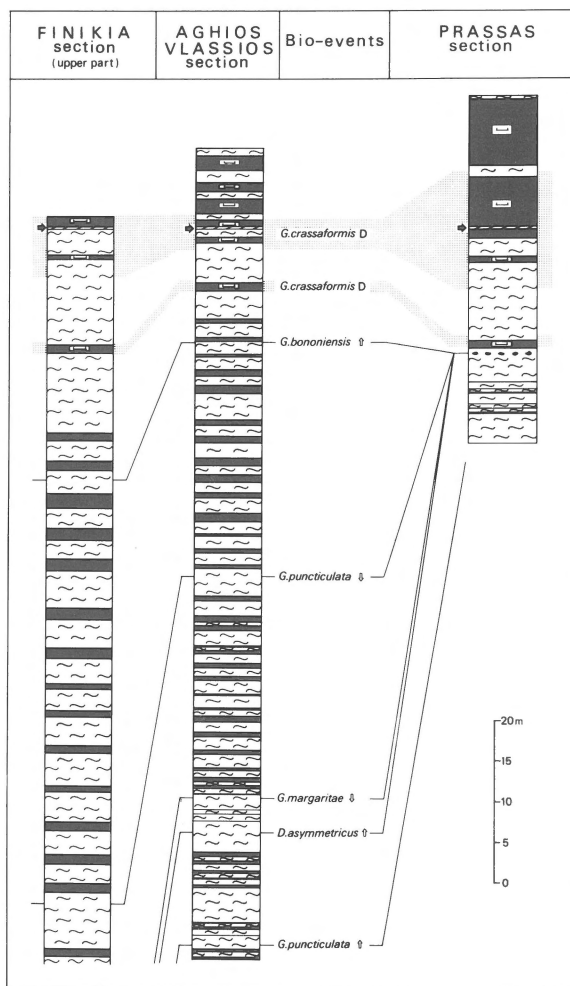


Fig. 5. Correlation of sections Finikia, Aghios Vlassios and Prassas. The tephra level is indicated by black arrows. For legend see fig. 3.

doridis (1978). Therefore these deposits belong to Interval 6 of the *G. crassaformis* Zone (Spaak 1983) and to *Discoaster* Interval 5 (Driever 1981). It seems that the NN 15 zonal assignment of Dermitzakis & Theodoridis (1978) for the upper part of the sequence is erroneous.

The tephra layer on Crete might correspond to one of the levels with volcanic material in core 8-2 of D.S.D.P. site 378 in the Sea of Crete (Emelyanov et al. 1978, Kidd et al. 1978) (fig. 1), for which levels no numerical ages are available. The joint presence of *G. bononiensis* and *G. crassaformis* in the core interval under consideration (Bizon et al. 1978) suggests an identical biostratigraphic pos-

ition for these tephra layers. The NN 16 zonal assignment by Müller (1978) further supports this assumption. This tentative correlation will be checked by means of neutron activation analyses on glass shards.

Discussion

In the literature on the Mediterranean Pliocene, numerical ages assigned to biohorizons are usually obtained through extrapolations. If one compares these ages with the radiometric age estimates from Mediterranean localities, discrepancies between the results are obvious.

For example, an age of 3.32 Ma is assigned to the exit-level of *Globorotalia margaritae* (Cita 1972), because it was observed to coincide with the Gilbert-Gauss boundary in cores from the Indian and Pacific Ocean (Hays et al. 1969). The age of this reversal was corrected to be 3.40 Ma by Mankinen & Dalrymple (1979). The K-Ar dates from Aegina (Benda et al. 1979) and Prassas (this

paper) would indicate that the exit-level of *G. margaritae* in the Mediterranean is considerably older and probably closer to 4.0 Ma. Since this biohorizon is used to define the boundary between the Early and Late Pliocene, i.e. between the Tabianian and Piacenzian Stages (Cita 1972), the duration of the Early Pliocene might be markedly restricted.

As was stated before, few Pliocene localities in the Mediterranean yielded radiometric dates and even fewer localities provided a setting suitable for a reliable biostratigraphic assignment. Hence, a scheme with first order data on biostratigraphy and radiometric dates can only be incomplete. In figure 6, all data considered appropriate are presented in combination with current planktonic foraminiferal zonal schemes. The scheme shows that certainly more isotope dates are needed to present a comprehensive scheme of Mediterranean Pliocene biochronology, especially, as single K-Ar dates do not allow a check for excess argon.

| EPOCHS | PLANKTONIC FORAMINIFERAL ZONATIONS | | | | BIOHORIZONS | | |
|------------------|---------------------------------------|---|---|---|--------------------------|---|--|
| | Bizon & Bizon (1972) | Cita (1975) | Speck (1983) | | | | |
| LATE PLEISTOCENE | <i>Globorotalia inflata</i> Zone | <i>Globorotalia inflata</i> Interval-zone MPL 6 | <i>Globorotalia inflata</i> Zone | | Interval 9 | ↔ ≤ 1.99 ± 0.08 Ma ① | |
| | <i>Globorotalia crassaformis</i> Zone | <i>Globigerinoides elongatus</i> Interval-zone MPL 5 | <i>Globorotalia crassaformis</i> Zone | | Interval 8 | ↑ <i>G. inflata</i> | |
| | | | | | Interval 7 | ↕ <i>G. bononiensis</i> ↕ <i>N. atlantica</i> ↕ <i>N. atlantica</i> | |
| | | | | | Interval 6 (upper/lower) | ↑ Reappearance <i>G. crassaformis</i> | |
| | <i>Globorotalia puncticulata</i> Zone | <i>Sphaeroidinellopsis subdehiscens</i> Interval-zone MPL 4 | <i>Globorotalia puncticulata</i> Zone | | Interval 5 | ↕ <i>G. puncticulata</i> | |
| | | | | | Interval 4 | ↕ <i>G. margaritae</i> | |
| | EARLY PLEISTOCENE | <i>Globorotalia margaritae</i> Zone | <i>G. margaritae</i> - <i>G. puncticulata</i> Concurrent range zone MPL 3 | <i>G. margaritae</i> - <i>G. puncticulata</i> Concurrent range zone | | Interval 3 | ↑ <i>G. puncticulata</i> |
| | | | | | | Interval 2 | ↑ <i>G. margaritae</i> |
| | | | | | | | <i>Sphaeroidinellopsis</i> Acme zone MPL 1 |

Fig. 6. K-Ar dates of four tephra layers in the Mediterranean Pliocene in relation with current planktonic foraminiferal zonal schemes. 1. Section Vrica, Southern Italy (Obradovich et al. 1982); m-marker bed of the Plio-Pleistocene boundary stratotype after Selli et al. (1977). 2. Section Stuni (Semaforo) (Obradovich et al. 1982). 3. Section Prassas, Crete (this paper). 4. Section Aghios Thomas, Aegina (Müller et al. 1979).

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Note edit in proof

Preliminary K-Ar results of a single size fraction of a biotite sample from the locality of the section of Aghios Vlassios reveal a date slightly younger than the dates of the section of Prassas. Reduced potassium concentration, demonstrated by K-Ar analyses under reservation and by microprobe analyses, could be the primary cause of the younger date (Bianchi et al., in prep.).

Local weathering influences not excluded, could have effected the quality of the Aghios Vlassios biotite with respect to those of Prassas.

It is clearly indicated (this article) that there be no doubt about the lithostratigraphic correlation of the tephra-horizon.

F.R. Bianchi, 25 April 1985