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Reliability of volcano-sedimentary biotite ages across the Eocene–Oligocene boundary (Apennines, Italy)

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ABSTRACT

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This paper presents and discusses volcano-sedimentary biotite radioisotopic ages, obtained from the Paleogene sequence of the northeastern Apennines using Rb–Sr and K–Ar dating methods. In particular, we discuss criteria which enable us to select the most reliable ages. K contents of $<6.4\%$, or traces of vermiculite indicate dubious reliability. Ion microprobe analyses of individual biotite flakes from each dated sample allowed us to determine whether these volcano-sedimentary biotites are composed of one or more populations of minerals. Chemically heterogeneous samples suspected of yielding spurious radioisotopic ages were tested for geochronological homogeneity using ^{40}Ar–^{39}Ar laser fusion probe dating on several groups of grains. ^{40}Ar–^{39}Ar step-heating dating or biotite from two stratigraphic levels from one locality yielded age spectra with good plateaux. Two other samples representing the same stratigraphic levels in another locality yielded somewhat disturbed spectra. We selected K-rich biotites showing good geochemical homogeneity, and/or displaying a wide plateau, and/or giving reasonably consistent K–Ar and Rb–Sr ages from at least five stratigraphically distinct layers; they draw a picture consistent with the sequence. The selected radioisotopic ages permit accurate calibration of well-known bio-, magneto- and chemostratigraphic events from 36.4 to 28.1 Ma including a tightly interpolated age value of 33.7 ± 0.4 Ma (2σ) for the much debated Eocene–Oligocene boundary.

1. Interest of the dated sequence

The carbonate series of the northeastern Apennines provides a nearly continuous and complete record of the evolution of an epeiric deep sea of the western Tethyan realm, from the Early Jurassic passive margin phase, to the Miocene syn-orogenic flysch deposition (Alvarez and Montanari, 1988). The portion of the series between the Cenomanian–Turonian boundary and the Oligocene–Miocene boundary, known as the Scaglia sequence (Montanari et al., 1990), constitutes a remarkable record of planktonic foraminiferal and nannofossil biozones. The thinly bedded, pelagic limestones of the Scaglia sequence are extensively exposed throughout the Umbria and Marche regions (Fig. 1). The road and quarry exposures along the Bottaccione and Contessa valleys near Gubbio (Umbria) have been regarded as the best for continuity and completeness since the earliest biostratigraphic studies by Renz (1936). In later years, the exhaustive work by Baumann (1970) yielded a detailed planktonic foraminiferal and nannofossil biozonation of the Upper Eocene–Oligocene por-

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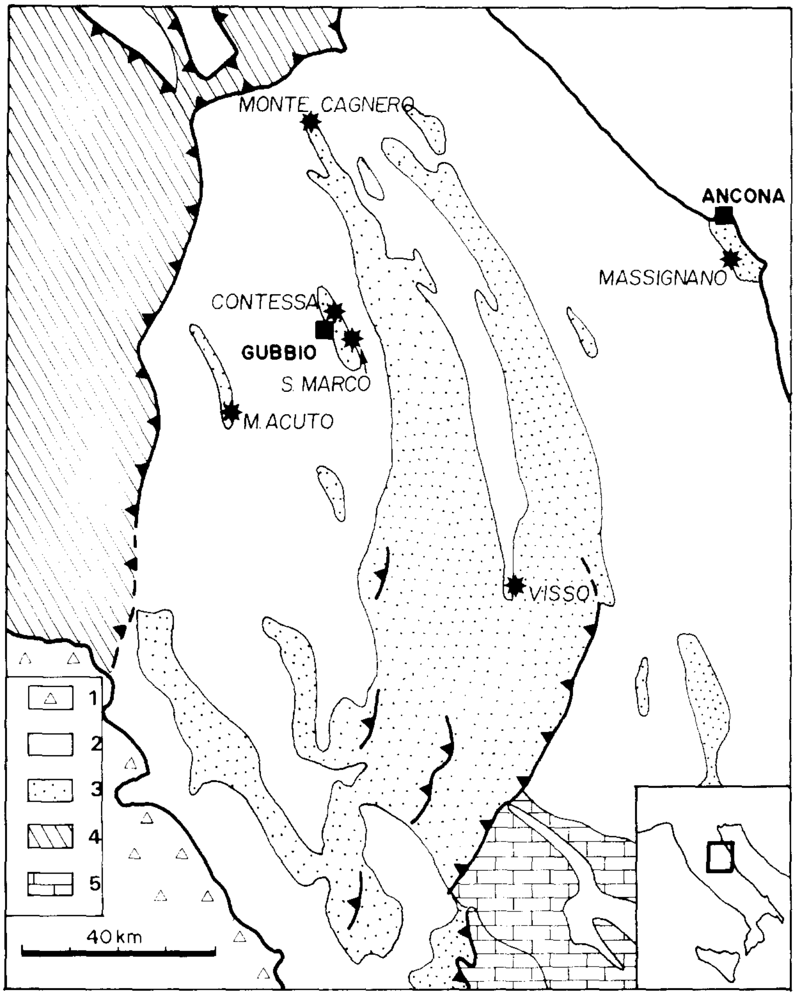

Fig. 1. Geological location of the sections studied from the Apennines (Italy). *1*=Latium volcanic province; *2*=Upper Tertiary siliciclastic rocks; *3*=Jurassic to Oligocene pelagic and folded sediments; *4*=Triassic to Oligocene platform; *5*=allochthonous.

tion of the sequence exposed in the whole region. The advent of paleomagnetic techniques promoted detailed interdisciplinary stratigraphic studies of the Gubbio sequence which produced direct biostratigraphic calibration points for the Cretaceous and Paleogene magnetic polarity sequence (e.g., Alvarez et al., 1977; Lowrie et al., 1982; Montanari and Bice, 1986; Nocchi et al., 1986; Napoleone, 1988). Geochemical characterization of the sequence using trace elements, rare elements, stable isotopes and Sr isotopic ratios has also been made available in recent years (Renard et al., 1986; Capo and DePaolo, 1988; Odin et al., 1988).

The discovery by W. Alvarez of thin, biotite-rich clayey layers (BRCL's), possibly of volcanic origin in the Upper Eocene portion of the Scaglia Cinerea (Lowrie et al., 1982), has led one of us (A.M.) to search for more such thin layers throughout the sequence. Other BRCL's were found in various sections (Fig. 1). The good preservation of the biotite in most of the outcrops promoted radioisotopic dating and direct calibration of the Eocene–Oligocene boundary (Montanari et al., 1983), and, eventually of the entire Upper Eocene–Oligocene magnetostratigraphic and biostratigraphic sequence exposed at Gubbio (Montanari et al., 1985). These geochronologic results showed some internal inconsistencies. For instance, a biotite sample from a biostratigraphically defined Upper Eocene layer in the Massignano section (80 km E from Gubbio, Fig. 1) yielded an age significantly younger than another biotite from the Lower Oligocene in the Contessa section. Moreover, some of the dates seemed to agree with an Eocene–Oligocene boundary age at ~37 Ma at that time popular (e.g., Pal-

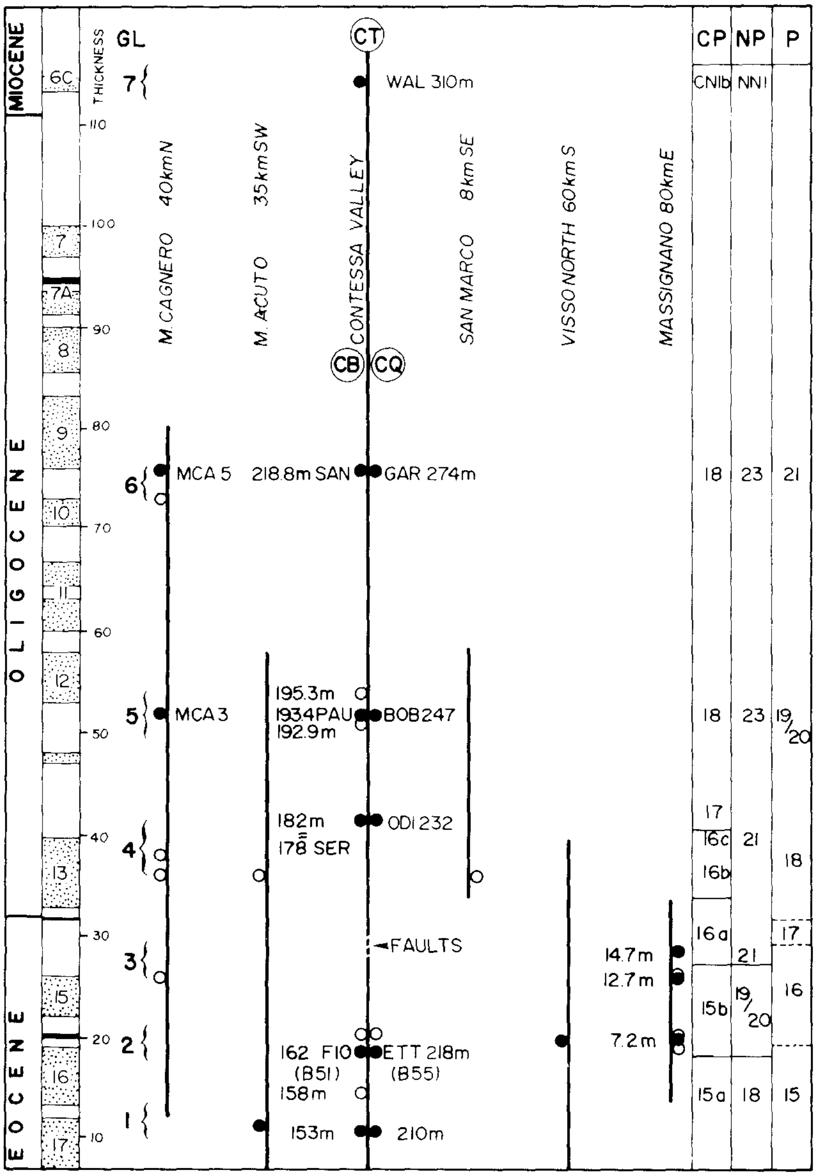

Fig. 2. Stratigraphic distribution of volcano-sedimentary layers in six sections from the Apennines. Seven "*Group Levels*" can be identified for purpose of easy designation although precise contemporaneity cannot be asserted. *Dots* are for biotite-bearing layers radioisotopically dated (*filled dots*), not dated (*empty dots*). Meter spacing, magnetic and biostratigraphic controls refer to the Contessa valley area: Contessa Quarry (*CQ*) and Contessa Barbieri (*CB*) composite section. Biostratigraphic zonation according to Okada and Bukry (1980; *CP* for calcareous nannoplankton), Martini (1971; *NP* for nannoplankton) and Blow (1969; *P* for planktonic *Foraminifera*).

mer, 1983), whereas other dates were more consistent with ages between 35 and 33 Ma supported by Odin (1975), Curry and Odin (1982), or Glass et al. (1986). This is the critical question that lead us to examine more closely the accuracy of radioisotopic age measurements on biotite.

2. Distribution of biotite-rich clay layers (BRCL's)

We have placed the BRCL's into seven Group levels as shown in Fig. 2. It is estimated, on the basis of the average accumulation rate of these pelagic limestones (6–8 m Ma^{-1}), that each group is <0.5 Ma in duration. Group *3*, which is represented at Massignano by several BRCL's, is not represented in the Contessa quarry sections. Similarly, Group *5* is represented by one very biotite rich level at Monte Cagnero, whereas, at Contessa, it consists of several layers with very scarce biotite. Once the relative stratigraphic position of the BRCL's had been established by detailed biostratigraphic and magnetostratigraphic studies on the sections in Fig. 2 (Coccioni et al., 1986; Nocchi et al., 1986; Montanari and Bice, 1986), our aim was to obtain, from the best preserved BRCL's, radioisotopic age determinations with the purpose of calibrating the Paleogene sequence.

3. Petrography and origin of the biotite-rich clayey layers (BRCL's)

Lowrie et al. (1982) and Montanari et al. (1985) have claimed that the freshness and euhedral shape of biotite flakes from these clayey layers imply a volcanic air-fall origin. Montanari et al. (1985) also pointed out the absence of sedimentary structures indicative of current transport, and the scarcity of equant sand-size grains associated with the relatively large biotite flakes; these observations suggest eolian transport and sorting. Further detailed chemo-petrographic analyses of these BRCL's were undertaken and show a bimodal size distribution (i.e. a very fine fraction made of clay and silt, and a coarser fraction made of sand).

The very fine fraction is 50–80% clay, and comprises $\gtrsim$95% of the bulk BRCL's. X-ray diffraction analyses of the clay-size fraction of BRCL samples from the Contessa section have shown a composition dominated by smectite, with less abundant illite and kaolinite (Mattias et al., 1987; Odin et al., 1988). The composition of the clay fraction in the marly limestones is also characterized predominantly by smectite (75–80%), illite (15–25%), and various other clay minerals: kaolinite, chlorite and mixed-layers (5–10%) (Deconinck and Chamley, 1987; Mattias et al., 1987). Further analyses (J.F. Deconinck, pers. commun., 1988) indicate that the biotite-rich clays are compositionally consistent with a mixture of volcanically derived clay, and inherited detrital clay common to the whole Tertiary sequence of the Northern Apennines; this suggests a vertical mixing caused by bioturbation, mostly represented by abundant *Zoophycos* and *Planolites*. Biotite flakes can be seen in the marly, pelagic limestones up to 60 cm above and below the BRCL's. The rest of the very fine fraction is made of siliciclastic silt, and authigenic and biogenic calcite.

The sand fraction of the BRCL's (usually <5%) is essentially composed of abundant (up to 30% of the bulk rock), mainly euhedral biotite flakes, benthonic and planktonic foraminiferal tests, and a finer fraction of angular to very angular volcanic grains, mostly clear quartz with rare dipyramidal terminations, and microcrystalline volcanic rock fragments often containing plagioclase phenocryst. The BRCL's also contain 5–350 ppm of pyroclastic apatite (estimated by weight) and 5–300 grains of zircon per kilogram of bulk rock. Other trace minerals such as jarosite, celestite, pyrite or marcasite, and chabasite have been found in some BRCL's and represent authigenic precipitates (Mattias et al., 1987). Authigenic fibrous calcite is common in BRCL where tectonization and flexural slip folding occurred. In summary, the BRCL's represent bentonites hybridized with the enclosing pelagic carbonate sediments through bioturbation and vertical mixing.

4. Geochronology of biotite

4.1. *Previous results and discussion*

The first account of K–Ar and Rb–Sr dating of biotites from the area is given by Montanari et al. (1985). The calculated ages from this early work are summarized in Table I. All levels except Group *3* are represented in the Contessa sections; Groups *2* and *3* are represented in the Massignano section; at Monte Cagnero only one age determination was originally made on one biotite separate belonging to Group *5*.

The analytical uncertainty of the K–Ar age of sample CQ-ETT is ±3.5%, and its calculated mean value is 1.5 Ma older than the more precise Rb–Sr age (Table I) although the difference is not analytically significant. The sample available for analysis was very small (~30 mg). This size of aliquot is not representative of the bulk sample; K and Ar measurements are not reproducible compared with analyses from normal sample weights (Odin et al., 1982, p. 126; 1986a). It follows that the K–Ar age of CQ-ETT must be weighted less heavily than other ages of Group *2* shown in Table I.

TABLE I

Calculated arithmetic mean ages of biotites from the Apennines from Montanari et al. (1985)

Sample	Group level	K–Ar age (Ma)		Rb–Sr age (Ma)
Contessa valley sections:				
CQ-GAR	6	28.1	(2)	27.8±0.2
CQ-BOB	5	32.0	(2)	
CQ-ODI + CB-178 m*	4	35.1–35.9	(4)	
CQ-ETT	2	36.9±1.3	(1)	35.4±0.2
CQ-210 m	1	36.4	(3)	
Massignano section:				
MAS-*2* (= 12.7 m)	3	33.8	(2)	34.4±0.2
MAS-*1* (= 7.2 m)	2	(33.2) 35.3	(4)	36.2
Monte Cagnero section:				
MCA-*3*	5	31.7	(1)	

Analytical error bars (2σ) usually ~0.5 Ma, except where shown. Number of Ar analyses in parentheses – one deviating analytical result in parentheses. Ages calculated in all figures and tables using conventional decay constants presently recommended by IUGS.
*CB-*178* actually corresponds to meter level 182 in the CB quarry face and, in a subsequent collection, to CB-SER (Table II).

Another analytical problem concerned the internal inconsistency of the four K–Ar ages calculated for two samples of BRCL MAS-*1* collected at 7.2 m in the Massignano section. Sample MAS/*83-1* yielded an age of 33.2±0.5 Ma, replicated at 36.1±1.0 Ma (2σ analytical error); the equivalent sample MAS/*84-1*, which was collected one year later, yielded an age of 35.1±0.8 Ma, and was replicated at 34.7±0.9 Ma (Fig. 3). These double replicated age measurements also indicate that the most "deviant" first measurement of 33.2 Ma (Fig. 3) was probably analytically incorrect. Therefore, we discarded it, and the calculated weighted mean K–Ar age for the biotite at the 7.2-m level in the Massignano section is 35.3±0.5 Ma. Replicated Rb–Sr ages on sample MAS/*83-1* are 36.0±0.5 and 36.5±0.4 Ma, thus slightly older than the calculated K–Ar age. The stratigraphic constraints available makes the age estimate of 35.3±0.5 Ma for Group *2* from the Massignano section consistent with the K–Ar age of 36.4±0.3 Ma of the underlying Group *1* (sample CQ-*210*).

Montanari et al. (1985) were faced with a more difficult problem, in that Group *3* sampled at Massignano (sample MAS-*2* in Table I) shows a Rb–Sr age, and a replicated and consistent K–Ar age ~1.5 Ma younger than four age values obtained from Group-*4* biotites in the Contessa valley sections (samples CQ-ODI and CB*178* in Table I); relative stratigraphy indicates that Group *3* should be at least 1 Ma older than Group *4*. New analyses were carried out and Table II gathers all pres-

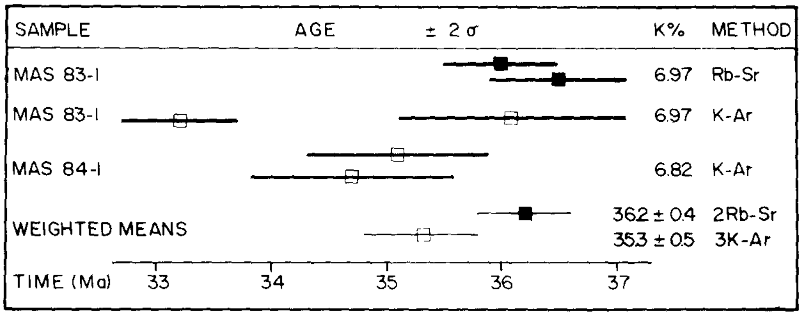

Fig. 3. Graphical comparison of the four K–Ar and two Rb–Sr calculated ages (±2σ) of biotite from the first BRCL in Massignano (MAS-7.2 m). The value at 33.2 Ma was rejected (data from Montanari et al., 1985). Ages calculated in all figures and tables using conventional decay constant presently recommended by IUGS.

TABLE II

K–Ar radioisotopic results obtained from biotites from volcano-sedimentary layers bracketing the Eocene–Oligocene boundary

Samples		K (%)	$^{40}Ar_{rad}$ (%)	Ar ($nl\,g^{-1}$)	Age ± 2σ (Ma)
CONTESSA SECTIONS (CQ and CB):					
Group level 4 (lowermost Oligocene):					
CQ-232 m		6.06	78.2	9.37	34.8±0.3
CQ-232 m		6.06	63.5	9.53	35.4±0.5
CQ-ODI	(=232 m)	7.24	77.5	10.1	35.7±0.7
CB-*178*		6.94	70.0	9.77	35.9±0.3
CB-SER	(=178 m)	2.08	59.5	3.83	46.7±0.9*
			Weighted mean		35.4±0.2
MASSIGNANO SECTION:					
Group level 3 (uppermost Eocene):					
B*50*	(=14.7 m)	7.15	97.7	9.68	34.6±0.3
	(=14.7 m)	7.10	98.2	9.66	
MAS-*2*	(=12.7 m)	7.13	87.0	9.42	33.7±0.4
MAS-2R	(=12.7 m)	7.13	67.4	9.51	34.0±0.8
			Weighted mean		34.2±0.2

Analytical calibration verified using reference "biotite LP-*6*" in Berkeley; and "glauconite GL-O" for sample B*50* in Hannover, cf. Odin et al., 1982).

*Not considered in the calculation of the mean.

ently available K–Ar results obtained for samples collected from both sides of the Eocene–Oligocene boundary. The discrepancy is clear; if the age of Group *4* from the Contessa section is correct, then the boundary must be older than 35.5 Ma, as suggested by Montanari et al. (1985). On the other hand, if the Rb–Sr and K–Ar ages from Group level *3* in the Massignano are correct, then the age of the boundary located above Group *3* must be younger than 34 Ma.

4.2. Possible reasons for discordancy of biotite ages

The reliability of radioisotopic ages used for time scale calibration depends on several groups of uncertainties (Odin, 1982); (1) accuracy of the relative stratigraphic correlation (*stratigraphic uncertainties*); (2) analytical factors, such as calibration of the dating methodology, sample representativity, analytical precision and reproducibility (*analytical uncertainties*); and (3) actual identity between the sand-box model and the geochronometer dated, which may deviate from the model due to alteration processes, detrital contamination, reworking, etc. (*geological uncertainties*).

Montanari et al. (1985) attributed the Group *3*/Group *4* discrepancy mentioned in Table II to the stratigraphic uncertainty of the Massignano section. However, further studies on the biostratigraphy (Coccioni et al., 1986), magnetostratigraphy (Montanari and Bice, 1986) and chemostratigraphy (Odin et al., 1986b) on the Massignano section demonstrated that the previous biostratigraphic location of the Eocene–Oligocene boundary by Baumann (1970) was essentially correct. The analytical precision of the K–Ar system of the

Berkeley Geochronology Center is also not the likely source of the 2-Ma discrepancy of the ages in the Massignano and Contessa sections because the reproducibility in this laboratory is routinely better than 0.6 Ma. Therefore, the age discrepancy between Group *3* and Group *4* was of geological origin.

4.3. Historical uncertainties: thermodynamic behaviour of biotites

During the geologic history of biotites, from the time of their formation in an igneous environment to the time when they are exposed on the face of an outcrop, pressure and temperature disturbances may result in preferential Ar loss. However, we are confident that thermal disturbances which would significantly invalidate radioisotopic age measurements of biotite, did not affect the carbonate sequence of the northeastern Apennines.

The tectonic deformation of the Contessa sections, expressed by faulting and shearing, is stronger than that visible at Massignano, and may have affected the biotite radioisotopic ages. The head of the Contessa valley is part of the NE limb of an anticline, perhaps representing the front of a NE verging blind thrust which was subsequently faulted in the rear by the eastern master fault of the Gubbio graben (Fig. 1). Massignano, instead, is located on the gently SW sloping limb of the Monte Cònero thrust-anticline (also verging toward the NE), and is structurally less disturbed than the Contessa area. One would expect preferential Ar loss from strained biotite imbedded in tectonized rocks. Thus, one would expect rejuvenation of biotite at Contessa compared to that at Massignano but the age discrepancy between the two sections indicates the exact opposite (Table II).

4.4. Geochronometric effects of weathering in biotite

Weathering is an important and common problem for volcano-sedimentary biotites. Vermiculite is the clay product of alteration of these Italian biotites and can be readily recognized in the field with a hand lens because altered biotite lacks its typical luster. Minor vermiculite can be detected with X-ray diffractometry (Fig. 4) and correlates with biotite separates that show an exceedingly low content of K (i.e. $< 6\%$). This alteration affects the apparent radioisotopic age of biotite in an unpredictable manner.

Case *A* in Fig. 4 shows that an objectively bad geochronometer may give a radioisotopic age consistent with existing time scales. Sample CT/*83*-WAL, recovered from an ash layer in the lower part of the Bisciaro in the Contessa section, contains only 2% K and the biotite is mostly replaced by vermiculite. Sample CT/*84*-WAL, collected one year later from the same layer but in another part of the outcrop, is entirely replaced by vermiculite and contains $\sim 0.2\%$ K. The K–Ar age of CT/*83*-WAL (23.7 ± 1.4 Ma), although consistent with the age of that particular stratigraphic level, should not be used to calibrate that stratigraphic level.

The unpredictability of the effect of mineral alteration on radioisotopic age measurements, as described by Obradovich and Cobban (1975), is clearly shown by case *B* in Fig. 4. The three samples of biotite belong to Group level *2* exposed in three distant outcrops. Sample MAS/*84-1* does not show any trace of alteration, and yielded a K–Ar age of 35.3 Ma. The other two samples show slightly different degrees of alteration but considerably different K–Ar ages. Sample VIS/*84-1* yielded an exceedingly young age and sample CB/*83*-FIO yielded a radioisotopic age consistent with that of MAS/*84*-1.

Other biotite separates with minor degrees of vermiculite alteration show significant radioisotopic age anomalies. Samples CQ/*83*-GAR and CB/*83*-SAN (Fig. 4C) are both from the same layer exposed on different outcrops in the Contessa quarry (Group level *5*), and the latter exibits some vermiculite alteration. Although altered, the K content in biotite CQ/

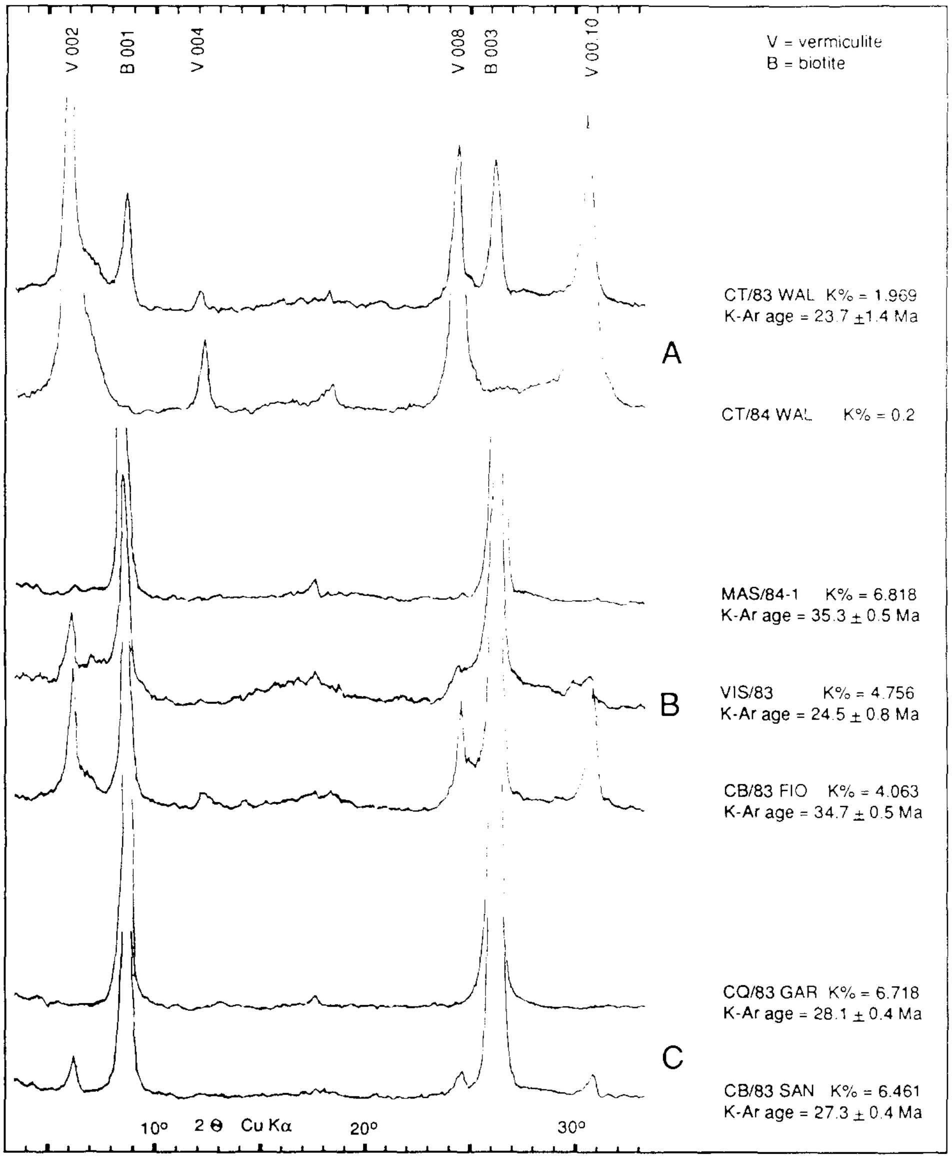

Fig. 4. X-ray diffraction patterns of biotites [oriented parallel to (001) samples] from the Upper Eocene to Miocene carbonate sequence of the Northern Apennines (*A* = Group level *7*; *B* = Group level *2*; *C* = Group level *6*).

83-SAN is fairly high (6.5%), and would tempt the geochronologist to overlook the alteration and consider this biotite separate as reliable material for geochronometry. On the other hand, sample CQ/*83*-GAR does not contain vermiculite and, despite the minor difference in K content, yields an age (slightly) older than that of the coeval CB/*83*/SAN. Because vermiculite denotes an open system, we rejected the age of sample CB/*83*-SAN for the calibration of the time scale. Table III gathers the radiometric results for biotites showing various K contents and notes the corresponding vermiculite contents. We only used separates of vermiculite-free biotite to calibrate the time scale.

TABLE III

Comparison between radioisotopic ages of variously weathered biotites from the Apennines

Sample		K^{*1} (%)	$^{40}Ar_{rad}$ (%)	Ar (nl g^{-1})	K–Ar age (±2σ) (Ma)	Vermiculite
Group level 7:						
CT/*83*-WAL	(Contessa)	1.97	27.0	1.83	23.7 ± 1.4^{*2}	very abundant
CT/*84*-WAL	(Contessa)	0.2				nearly total
Group level 6:						
CQ/*83*-GAR	(=274 m)	6.72	81.9	7.39	28.1 ± 0.3	absent
CQ/*83*-GAR(R)			66.0	7.41	28.2 ± 0.6	
CB/*83*-SAN	(=218.8 m)	6.46	71.1	6.92	27.3 ± 0.4^{*2}	traces
MCA-*5*	(M. Cagnero)	6.20	84.2	6.80	28.0 ± 0.7^{*2}	traces
Group level 4:						
(see Table II, Contessa CB)						
Group level 2:						
CQ/*83*-ETT	(=218 m)	6.46	39.0	9.36	36.9 ± 1.3^{*3}	absent
CQ/*82*-218 m		4.04	51.1	5.72	36.1 ± 1.2^{*2}	no data
CB/*82*-162 m		5.88	78.9	8.58	37.2 ± 0.9^{*2}	no data
CB/*83*-FIO	(=162 m)	4.06	75.3	5.54	34.7 ± 0.5^{*2}	abundant
VIS/*82-1*	(Visso)	4.76	39.6	4.56	24.5 ± 0.8^{*2}	abundant

Weathering is indicated by small K contents and presence of vermiculite; sample CT/*84* was not dated [data from Berkeley: Montanari et al. (1985), supplemented with later results gathered here].

^{*1}Potassium data are mean of two replicate flame photometry analyses.

^{*2}Ages not reliable due to the small K contents or presence of vermiculite.

^{*3}Age not reliable due to low quantity available resulting in large uncertainty in Ar measurement and bad representativity of the separate aliquots analysed for Ar and K.

4.5. Genetic uncertainties: biotite chemical heterogeneity

The successive Group levels *1*–*6* with their respective stratigraphic location and apparent ages obtained solely from reasonably K-rich, vermiculite-free biotites are shown in Table IV. These results show an acceptable age progression for all Group levels with the exception of Group *4* which shows ages similar to Group *2*. Our working hypothesis was that samples from Group *4* contain a proportion of "older" biotite. To test this hypothesis, the unaltered biotite separates which have been dated with K–Ar and Rb–Sr methods were analysed grain by grain with the electron microprobe (Montanari, 1988) for Fe and Mg. The geochemical Fe/Mg characterization of plutonic biotite, indic-

TABLE IV

Summarized analytically reliable radioisotopic ages obtained from vermiculite-free, K-rich biotites, from the Apennines

Group level	Sample	K (%)	K–Ar age (Ma)	Rb–Sr age (Ma)
GL *6*	CQ-GAR	6.7	28.1	27.8
GL *5*	MCA-*3*	7.4	31.7	
GL *5*	CQ-BOB	7.1	32.0	
GL *4*	CB-*178*	7.2	35.7	
GL *4*		6.9	35.9	
GL *3*	MAS-14.7 m	7.1	34.6	
GL *3*	MAS-12.7 m	7.1	33.8	34.4
GL *2*	CQ-ETT	6.5		35.4
GL *2*	MAS-*1* (=7.2 m)	6.9	35.3	36.2
GL *1*	CQ-210 m	6.7	36.4	

Data (arithmetic mean ages) shown in stratigraphical order.

ative of provenance (and possibly age), was described by Ague and Brimhall (1987).

The results of the analyses of fifteen biotites are summarized in Table V. There seems to be a consistent and similar chemistry amongst biotites considered to be nearly contemporaneous, even though collected in different and distant outcrops. For example, MAS-(12.7 m and MAS-(12.9 m), two distinct biotite-rich layers ~20 cm apart in the Massignano section, are compositionally undistinguishable, as are MAS/*86* (6.5 m) and MAS/*84-1* (7.2 m) which are only 70 cm apart in the same section. By comparison, MAS-(14.7 m) and MAS-*2* (12.7 m) give analytically different results, although their overall FeO and MgO composition is similar.

The chemical characterization of biotite indicates internal homogeneity of biotite separates from Group levels *1–3* and *5* (Fig. 5). However, three samples are found to be heterogeneous: samples CQ-GAR and MCA-*5* (Group *6*) and CQ-ODI (Group *4*). Microprobe analyses of single flakes of CQ-ODI show two K-rich populations, and a few flakes with a K content of <6.5%, perhaps representing slightly altered individuals (Fig. 6). The main population (*A*) is characterized by a MgO/FeO ratio of 0.77 significantly higher than that of older horizons in the stratigraphic sequence. In contrast, the less abundant population (*B*) is characterized by a MgO/FeO ratio of 0.56 which is comparable to the older samples such as those from Group level *2*. This might suggest that population *B* represents an older generation of volcanic material. Therefore, the chemical heterogeneity of sample CQ-ODI indicates that its K–Ar age determination is suspect (possibly older than the actual age of sedimentation of that particular BRCL. The same conclusion could be made for samples CQ-GAR and MCA-*5*. However, it should be pointed out that comagmatic chemical variability of minerals such as biotite is commonly found in explosive stratovolcanoes of intermediate composition (Hildreth, 1981; Christensen, 1987). In this case, the chemical heterogeneity per se cannot be taken as an absolute criterion to discriminate the reliability of a geochronometer. The ultimate test would be to physically separate the end-members of heterogeneous (or bimodal) populations and then date them. We have tried to accomplish such a separation using a magnetic separator, but the efficiency of this method was shown to be poor be electron microprobe analysis (Fig. 6).

4.6. Geochronologic heterogeneity shown by ^{40}Ar–^{39}Ar laser fusion probe dating

We have used the ^{40}Ar–^{39}Ar laser fusion probe method of dating single crystals to check the intrinsic homogeneity of a bulk mineral separate. For this test, however, it was necessary to fuse small groups of 10–20 flakes of biotite at once in order to produce sufficient Ar for the analysis. The Italian biotites are generally fine grained (150–300 μm), and the flakes are very thin since the samples were cleaned using a ceramic ball mill. Therefore, ages obtained with this technique still represent mean ages of groups of crystals each of which represents an independent geochronometer. Both samples are vermiculite-free and high in K. Altered biotite may undergo recoiling during neutron activation which would create an artificial geochronologic heterogeneity (Hess and Lippolt, 1986; Hess et al., 1987). On the other hand, we suspect that very thin grains may also undergo recoiling which would cause partial loss of ^{39}Ar during irradiation and consequent yielding of artificially old radioisotopic ages. Deino et al. (1988) dated the more magnetic biotite population, and the less magnetic population physically sorted using the Franz® isomagnetic separator. The K_2O, MgO and FeO characterizations of the CQ-ODI and CQ-GAR are shown in Figs. 6 and 5, respectively.

Fig. 7 compares the ages of four biotite groups from the more magnetic fraction, and eleven groups from the less magnetic fraction,

TABLE V

Fe and Mg contents from biotites collected from the Apennines

Group level	Sample	FeO (%)	MgO (%)	MgO/FeO ($\pm 1\sigma$)	Homogeneity
GL *6* (28 Ma)	CQ-GAR (=274 m)	13.5–17	13–16	$A=1.06\pm0.04$, $B=0.83\pm0.06$	2 populations (*A*: 79%; *B*: 21%)
GL *6*	MCA-*5*	14 –18	13–16	$A=1.11\pm0.02$, $B=0.77\pm0.02$	heterogeneous (*A*: 67%; *B*: 33%)
GL *5* (32 Ma)	CQ-BOB (=247 m)	13.5–14.5	15–16	1.11 ± 0.04	homogeneous
GL *5*	MCA-*3*	14 –15	15–16	1.10 ± 0.05	homogeneous
GL *4* (33 Ma)	CQ-ODI (=232 m)	13 –20	9–14	$A=0.77\pm0.04$, $B=0.56\pm0.03$, C=altered	3 populations (*A*: 75%; *B*: 15%; *C*: 10%)
GL *3* (34 Ma)	MAS/*86*-14.7 m	19 –20	11	0.54 ± 0.02	homogeneous
GL *3*	MAS/*86*-12.9 m	20.5–21.5	10	0.48 ± 0.01	very homogeneous
GL *3*	MAS/*84*-12.7 m	20.5–21.5	10	0.47 ± 0.01	very homogeneous
GL *2* (35.5 Ma)	CQ-ETT (=218 m)	19.5–21	11–12	0.57 ± 0.03	homogeneous
GL *2*	MAS/*84*-7.2 m	18.5–21	10–12	0.56 ± 0.05	slightly heterogeneous
GL *2*	MAS/*86*-6.4 m	19 –21	11–12	0.59 ± 0.03	1 population
GL *1* (36.5 Ma)	CQ-CAT *A* (=210.5 m)	18 –20	12–13	0.66 ± 0.03	1 population
GL *1*	CQ-CAT *B* (=210.5 m)	18 –20	12–13	0.66 ± 0.04	1 population

Microprobe analyses on single flakes; 12–42 flakes analysed per sample. Proportions given for each "population" are approximate; note the very good reproducibility between samples in a given Group level (sometimes collected several 10 km apart), suggesting a common magma source (data obtained in Berkeley by A.M.).

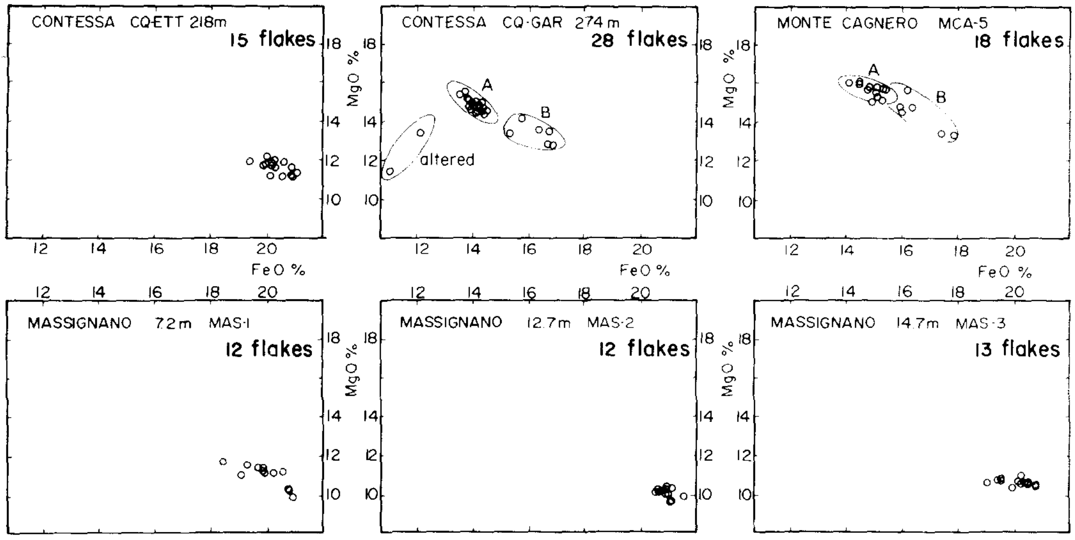

Fig. 5. Fe and Mg scanning electron microprobe analyses for 6 samples of biotite from the Apennines (each data point represents the average from ⩾5 measurements on a single grain). Samples CQ-ETT, MAS-12.7 m and MAS-14.7 m are homogeneous; this homogeneity validates to a certain extent, the reliability of radioisotopic age determinations; sample MAS-7.2 m is less homogeneous; sample MCA-*5* shows a wider heterogeneity, two indistinct populations are suggested; sample CQ-GAR may be subdivided into two distinct populations which, however, have a clear common chemical trend, the two analyses shown as "altered" correspond to K-poor flakes; although subdivided in different populations the chemical trend that populations *A* and *B* form in CQ-GAR or MCA-*5* corresponds to the overall composition of the phlogopite–annite series and is not inconsistent with comagmatic biotites (analyses by A.M., in Berkeley, number of biotite flakes analysed shown).

from the bulk CQ-GAR sample. Remarkably consistent ages with a mean of 29.31 ± 0.02 (2σ) Ma were obtained for the more magnetic biotite groups. The less magnetic biotites have shown nine dates clustering together around 28.87 ± 0.22 (2σ) Ma, and two deviant ages of ~35.3 Ma. The mean-age difference between the four more magnetic and the nine less magnetic biotite separates composing CQ-GAR is small. This would imply that sample CQ-GAR is geochronologically homogeneous.

Fig. 8 shows ^{40}Ar–^{39}Ar laser fusion probe dates obtained from the two magnetically separated fractions of biotite samples CQ-ODI. The more magnetic groups yielded radioisotopic ages scattered between 49 and 35 Ma. The ages obtained from the less magnetic groups are scattered between 38 and 33.5 Ma. These data demonstrate that the reproducible K–Ar apparent ages ranging between 35.9 and 34.8 Ma (see Table II) from reasonably K-rich Early Oligocene volcaniclastic biotite samples are derived from a mixture of biotites with different ^{40}Ar/K ratios.

4.7. ^{40}Ar–^{39}Ar step-heating technique for qualification of bulk biotite separates

Four samples were dated using the ^{40}Ar–^{39}Ar step-heating technique. Two new biotite separates were obtained from Group level *2* in the Contessa valley: B*55* corresponds exactly with sample CQ-ETT (218 m), whereas B*51* is the equivalent of CB-FIO (162 m). Sample B*51* collected in 1984 from a fresh quarry cut, shows a fairly high K content of 6.9% which is higher than the K content of 5.9% of the biotite from the corresponding sample CB-*162* collected in 1982, or 4.1% for CB-FIO collected in 1983. The K content of sample B*55* analysed in Leeds is comparable to the 6.4% measured at Berkeley in the corresponding CQ-ETT sample, and it also can be considered a priori suitable for radioisotopic dating. Two other biotite sam-

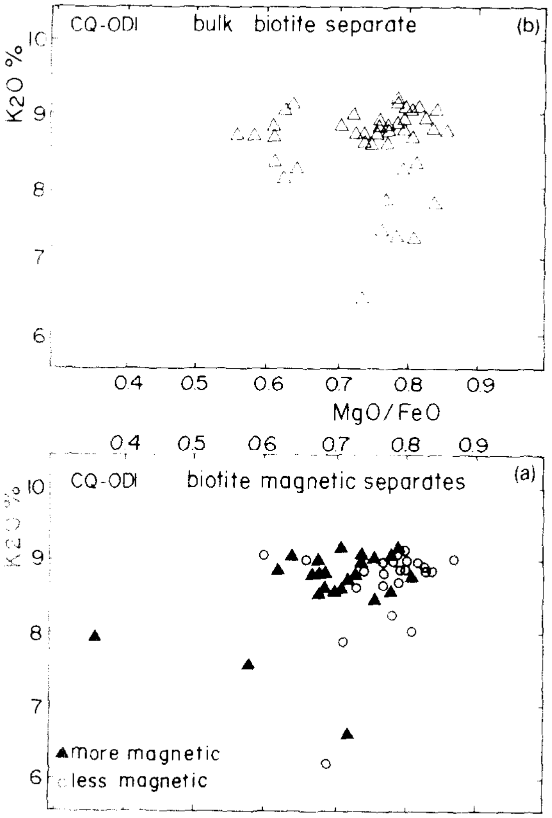

Fig. 6. Results of scanning electron microprobe analyses for earliest Oligocene biotite sample CQ-ODI: (b) bulk biotite separate; and (a) after magnetic separation in two fractions: less magnetic (*open circles*) and more magnetic (*filled triangles*). In (b), two populations with smaller (0.6) and higher (0.8) MgO/FeO ratios can be suggested: analyses corresponding to K_2O contents below 8% probably represent partly weathered biotite flakes. More magnetic biotite flakes have generally smaller MgO/FeO ratios (analyses by A.M., in Berkeley, note that the K contents are generally approximate using microprobe analysis).

ples were collected from the Massignano section at meter levels 12.7 (*B48*) and 14.7 (*B50*). The calibration of the analytical system has been precisely documented (neutron flux of the reactor known within < ± 1% at the time of measurement).

The analytical results are summarized in Table VI and illustrated in Fig. 9. This figure shows that the two latest Eocene biotites from the Massignano section give undisturbed spectra, the flat portions of which are 95–100% wide and are called plateaux. The two Late Eocene biotites from Contessa valley show partly disturbed spectra. If a disturbed ^{40}Ar–^{39}Ar step-heating spectrum is taken as a criterion to estimate the unreliability of a geochronometer, then samples from Group level *2* from Contessa are less reliable than samples from Group *3* from Massignano.

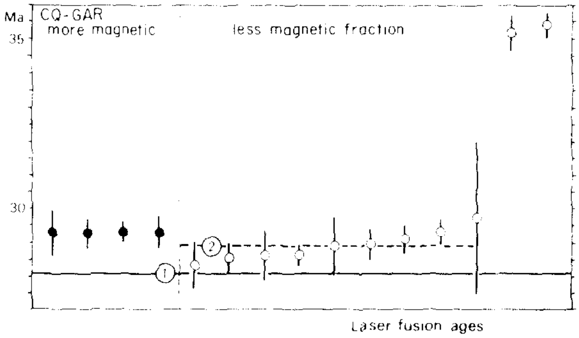

Fig. 7. Results of ^{40}Ar–^{39}Ar microanalyses (laser fusion technique) for sample CQ-GAR. Groups of 10–20 biotite grains were analysed, the results are arranged in order of increasing age (analytical precision $\pm 1\sigma$): (*1*) corresponding K–Ar measured age (isotope dilution technique); and (*2*) weighted mean age of the 9 groups of less magnetic biotite grains (analyses by A.D., in Berkeley; analytical calibration with hornblende MM Hb-*1*).

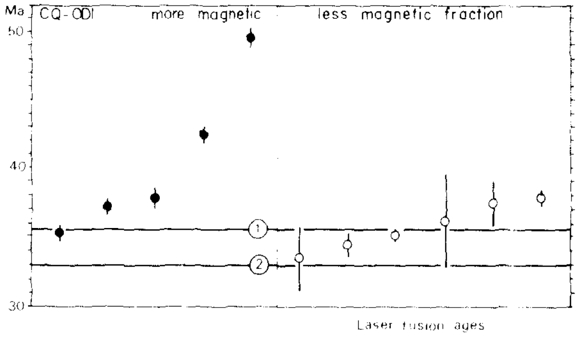

Fig. 8. Results of ^{40}Ar–^{39}Ar microanalyses for sample CQ-ODI: (*1*) K–Ar bulk biotite age (isotope dilution technique); and (*2*) probable stratigraphic ages as extrapolated from other dated samples. Conditions as for Fig. 7.

5. Discussion

The detailed stratigraphy available for the Italian sequence made it possible to eliminate inaccuracy in the stratigraphic location of the BRCL's. The analytical work reported in this

TABLE VI

^{40}Ar–^{39}Ar step-heating data for biotites from the Contessa valley and Massignano section

Sample	Sample weight (mg)	K (%)	Total fusion age (±2σ) (Ma)	Spectrum
Massignano section (GL *3*)^{*1}:				
B*50* (=MAS-14.7 m)	47.75	7.34	34.1±0.2	good plateau
B*48* (=MAS-12.7 m)	45.30	7.10	34.9±0.2	good plateau
Contessa sections (GL *2*)^{*2}:				
B*51* (=CB-162 m)	76.86	6.86	35.4±0.2	slightly disturbed
B*55* (=CQ-ETT-218 m)	71.77	6.40	36.4±0.2	disturbed

Data from D.C.R. and P.G.G. in Leeds, analytical calibration using LP-*6* and intralaboratory well known reference samples.
^{*1}Compare to ^{40}K–^{40}Ar ages of Group level *3* in Table II.
^{*2}Compare to ^{40}K–^{40}Ar ages of Group level *2* in Contessa valley in Table III.

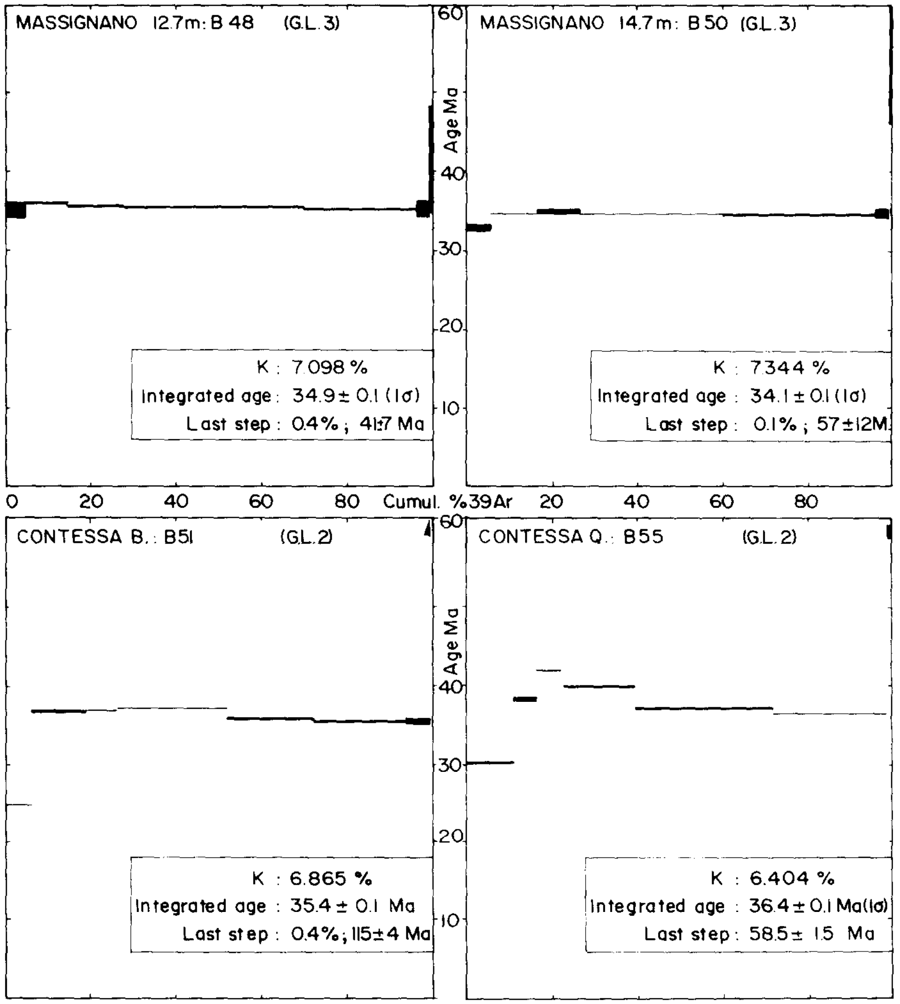

Fig. 9. ^{40}Ar–^{39}Ar step-heating spectra obtained from four Eocene biotite samples from the Apennines. The best (widest and up to 100% of the age spectrum) plateaux are obtained from biotites separated from BRCL's of Group level *3* in Massignano with comparatively larger K contents; spectra from samples B*51* and B*55* are suggestive of recoil loss (analyses by P.G.G. and D.C.R., in Leeds; analytical calibration with well-known intra-laboratory reference materials).

paper was carried out independently in different laboratories, allowing us to test the practical reliability of radioisotopic age measurements and their consistency between the different dating techniques used on equivalent samples.

5.1. *Analytical and intermethod inconsistency*

Out of a total of 29 traditional (isotope dilution) K–Ar dates, we found analytical problems only in sample MAS/*83-1* (K*4492*) which was discarded because of a suspected error during Ar extraction. Amongst unaltered and K-rich biotite samples, BRCL MAS-*1* (Fig. 3) has shown a mean K–Ar age (from three measurements = 35.3 ± 0.5 Ma) slightly different from a mean Rb–Sr date of 36.2 ± 0.4 Ma. The problem may reside in the fact that the initial Sr isotopic ratios used to calculate the Rb–Sr (very precise) ages are measured on insoluble residues possibly not compositionally similar to the original magma ratio.

Biotite separates from BRCL's CQ-ETT and CQ-GAR (Table I) yielded Rb–Sr ages consistent with their K–Ar ages. The HCl insoluble residues of these two samples have shown unusually high concentrations of Sr which Montanari et al. (1985) attributed to poor mixing of the tracer, they also pointed out that if the concentrations given are, in fact, incorrect, and if the initial concentrations were 10 or 20 times lower, it would yield an increase of the age of ~0.1–0.2 Ma. D. DePaolo (pers. commun., 1990) has recently suggested that the high Sr concentrations may be due to traces of authigenic celestite ($SrSO_4$). However, Mattias et al. (1987) have not detected any celestite in CQ-ETT and CQ-GAR.

Another example of intermethod and intertechnique comparison is represented by biotites from Group *3* in Massignano. MAS/*83-2* (i.e. 12.7-m level) yielded a Rb–Sr age of 34.4 ± 0.2 Ma (2σ) which is in agreement with the K–Ar ages of 34.0 ± 0.8 Ma and not very different from 33.7 ± 0.4 Ma (Table II). However, the ^{40}Ar–^{39}Ar, step-heating age calculation of 34.9 ± 0.2 Ma (2σ) done on another separate from the same BRCL (see integrated age of B*48*, Fig. 9) is ~0.5 Ma older. This allows us to identify interlaboratory differences and give real uncertainties placing BRCL MAS-*2* at 34–35 Ma with confidence.

Ages obtained by ^{40}Ar–^{39}Ar technique which are analytically too old are sometimes explained by advocating recoil effects; this seems relevant in the ages obtained with the ^{40}Ar–^{39}Ar laser fusion probe on the bimodal samples CQ-ODI and CQ-GAR which are consistently 3–6% older than apparent ages obtained from the same samples with the traditional K–Ar method (see Figs. 7 and 8). The effect of recoiling of ^{39}K that would cause loss of the activated ^{39}Ar, may be significant in very thin flakes; therefore, *in our study*, the ages obtained with this technique should not be considered reliable for the calibration of the time scale.

In Massignano, biotite sample B*50* [i.e. MAS-(14.7 m) which is possibly ~0.1 to 0.2 Ma younger than MAS-(12.7 m)] was dated at 34.6 ± 0.3 (2σ) Ma (isotope dilution technique in Hannover, Table II) and 34.1 ± 0.2 (2σ) Ma (^{40}Ar–^{39}Ar step-heating technique in Leeds, Fig. 9). Therefore, an age near 34 Ma for Group level *3* is geochronologically well documented.

In short, the consistency of radioisotopic age values obtained from K-rich biotites using different methods and techniques is generally good, and ensures geochronometric reliability.

5.2. *Surface weathering*

The geochronometric effects of surface weathering in biotite are widely documented in literature (Mitchell et al., 1988). Vermiculitization, which has affected biotite in several BRCL's described in Section 4.4, is the first stage of surface weathering in temperate and mediterranean climates (Penven et al., 1981). When strongly vermiculitized, biotite is easily recognizable with XRD. Minute quantities of vermiculite in biotite can be detected with detailed transmission electron microscopy (Hess et al., 1987). Alternatively, bulk K content has long been used as an indicator of weathering (e.g., Kulp and Engels, 1963; Marvin et al., 1965). Kulp and Engels (1963) have shown that removal or leaching of large amounts of K may not affect the K–Ar age of a given biotite but ...

> "the Rb–Sr age will be lowered relative to unchanged K–Ar age".

In our study we have realized that the K–Ar age in a given biotite separate may be unpredictably affected by alteration, either with preferential loss of K or with preferential loss of ^{40}Ar. For these reasons, biotite samples showing the presence of vermiculite, as well as those with $<6.4\%$ K have not been considered reliable geochronometers. The K content of 6.4% is an arbitrary limit; data gathered by Obradovich and Cobban (1975) indicate that biotite from bentonite with $\gtrsim 5.8\%$ K usually give acceptable ages; however, fresh biotites typically contain $>7\%$ K and if there is less K in the lattice, the charge balance is $>15\%$ from neutral and thus the system may become open; our limit of 6.4% is the median between the two.

5.3. *Biotite heterogeneity*

We have tried two approaches in order to find explanations for discrepancies; they are based on the presumption that an unreliable volcano-sedimentary K-rich biotite age results from some form of *heterogeneity* of the geochronometer. Single grain microprobe analysis of major elements for two Group levels shows the presence of compositional variations which indicate the presence of two (or more) distinct biotite populations.

How does compositional heterogeneity relate to age inconsistency?:

(1) the biotite flakes come from volcanic sources of different age and are co-deposited as a reworked mixture;

(2) the biotite flakes come from different volcanic sources erupted at nearly the same time;

(3) the biotite flakes come from the same volcanic source complex but were crystallized at geologically different times the oldest being extracted from the vent wall;

(4) the biotite flakes come from the same volcanic source and were crystallized together but from different compositional zones of the magma.

Hypotheses (1) and (3) may lead to increased ages. However, hypothesis, (1) is unlikely in the Apennines because sedimentological studies have shown that BRCL's result from a single depositional event. Hypothesis (3) is difficult to support because no pieces of the vent wall (i.e. composite grains of composition different from that of a typical cinerite) were observed. However, it is reasonable to consider that chemically heterogeneous biotites, although not necessarily unreliable (cf. CQ-GAR), should a priori be regarded as suspect as geochronometers and that, when available, chemically homogeneous biotites should be preferred to precisely date a BRCL.

Small populations laser fusion ^{40}Ar–^{39}Ar analyses from CQ-GAR indicate that this heterogeneous biotite sample is nearly homogeneous in age [hypothesis (2) or (4)]. However, there are complications with the isotopic systematics of this sample: (a) the two results at ~35 Ma significantly older than other analyses; and (b) the analytically significant different ages of 29.31 ± 0.02 and 28.9 ± 0.2 (2σ) Ma for the more magnetic and less magnetic fractions, respectively. We suggest that the isotope dilution K–Ar age should be regarded as more reliable mainly because the old ages found using ^{40}Ar–^{39}Ar technique may be due to recoil effect.

The compositional variation of biotite sample CQ-ODI is connected to age heterogeneity of laser fusion ^{40}Ar–^{39}Ar results. This leads us to discuss: either hypothesis (3) or technical problems with the old laser fusion apparent ages.

If hypothesis (3) is considered, then we should assume that the disintegrating volcanic edifice contained both biotite crystallized just before the explosion and one (or several) older generations. Previous generations of biotite would originate from earlier volcanic phases. The magma at the origin of Group level *2* is a good candidate as suggested by similar compositional properties ($MgO/FeO = 0.56$) for one of the two biotite populations (see Table V) recognized in Group level *4*. Another possibility would be that, prior to the explosion, the required high pressure could have caused the incorporation of magmatic ^{40}Ar locally in some of the crystallizing biotite. Contamination by older biotite can be ruled out as an explanation for the oldest analyses from CQ-ODI; the oldest analysis of nearly 50 Ma is ~16 Ma older than the youngest analyses. Assuming even as much as 50% contamination by older biotite, the age of the contaminant must be ~65 Ma. This hypothetical contaminant biotite would have been derived from an unrelated source rock with a geochemically unique signature and it is unlikely that it would show such a clear relationship as do the *A/B* populations of CQ-GAR and MCA-5 (Fig. 5).

The observed age inhomogeneity may be an analytical artifact of the ^{40}Ar–^{39}Ar process. Biotite may lose ^{39}Ar due to a recoil effect followed by diffusional loss during irradiation and bakeout. According to Hess and Lippolt (1986), direct recoil loss from biotite seems to be small compared to diffusion loss of recoil-implanted ^{39}Ar. Interlayer alteration products such as chlorite may receive recoiled ^{39}Ar, which is then easily lost from the chlorite during the low temperatures (100–200°C) encountered during irradiation and bakeout. This then leads to artificially old ages. Although the bulk K content of CQ-ODI is high (7.2%) microprobe analyses (Fig. 6) demonstrate that a third of the grains show a loss of K down to 5.9% and even 5.4% (K_2O of 7.1% to 6.5% in Fig. 6).

The principle of alteration of biotite during irradiation may be understood and illustrated by the study of the glauconitic mica, a more fragile, although structurally similar mineral. During irradiation, the latter loses 20% of neutron-induced Ar isotopes (^{39}Ar, ^{37}Ar) and radiogenic ^{40}Ar in smaller proportion. However, heating alone up to 220°C does not lead to ^{40}Ar loss (Odin and Bonhomme, 1982; Hess and Lippolt, 1986). Hess and Lippolt (1986) assume

> "that a combination of irradiation damage in the glauconitic minerals structure and heating during neutron activation produces argon loss".

The preferential loss of ^{39}Ar, during irradiation, has been documented in glauconitic minerals (Foland et al., 1984; Klay and Jessberger, 1984) and should be considered similarly for K-poor biotite which appears to have a comparable behaviour. The oldest ages shown in Figs. 7 and 8 could be explained by such a process. However, the recoil effect is generally *inversely proportional to the potassium content* (Hess and Lippolt, 1986) and bulk biotite sample CQ-ODI has a K content (7.2%) larger than the one for CQ-GAR with no very old apparent ages.

In short, biotite sample CQ-ODI should be considered suspect in the light of its heterogeneous geochemical nature and of its ^{40}Ar–^{39}Ar heterogeneity despite its high K content. No definitive interpretation of the origin of these heterogeneities can yet be given.

5.4. Disturbed step-heating ^{40}Ar–^{39}Ar spectra

Hess et al. (1987) observed that biotites giving geologically acceptable ^{40}K–^{40}Ar ages gave disturbed ^{40}Ar–^{39}Ar spectra due to the analytical ^{39}Ar recoil effect itself connected to the K content. Hess et al. (1987) illustrate the point by comparison between disturbed spectra of biotite and undisturbed spectra of cogenetic or time-equivalent sanidine, muscovite and hornblende. Therefore, it is interesting to observe that the extent of the disturbances shown by our spectra obtained in Leeds (Fig. 9) is also correlated with K content. The disturbed spectra may actually be interpreted as showing an excess of ^{39}Ar released at low temperature (as ^{39}Ar produced from ^{39}K recoils to less stable crystallographic sites) followed by a lack of ^{39}Ar in material opened at intermediate temperature and then normal isotopic ratios at high temperature in the more stable sites where no recoil effect exists. In this interpretation, all four step-heating dated biotites are valid. If this interpretation is not accepted, at least two biotites from Massignano (Group level *3*) remain as undisturbed geochronometers in the classic interpretation of step-heating spectra (Lanphere and Dalrymple, 1971; Dallmeyer, 1979); they should be considered the best geochronometers.

6. Conclusions

The Paleogene pelagic sequence in the Apennines is well known stratigraphically. A major sedimentary feature is the presence of common biotite-rich clayey levels dateable by radioisotopic methods. The BRCL's have been reviewed in the best sections in order to give precise correlations; seven group levels, suggested to be approximately time equivalent, are defined. The probable air-fall process of deposition of the BRCL's is supported by the mineralogical study of all components in the horizons. A few years ago, Rb–Sr and K–Ar dating methods were applied with encouraging results. However, some inconsistencies occurred and a detailed study using new analytical methods and techniques has eliminated all but the best ages.

A few minor analytical problems have been identified by comparing results from different analytical methods resulting in elimination of anomalous age measurements. K-poor biotites or biotites showing vermiculitization caused by weathering yield unreliable results. Biotites with age and genetical differences at the time of deposition have been examined by MgO/FeO ratio determinations. The compositionally heterogeneous biotite may characterize a single eruptive event and are not necessarily unreliable but homogeneous character would be a good criterion for preliminary selection of a good geochronometer.

The laser fusion microprobe ^{40}Ar–^{39}Ar dating technique showed that the same biotite samples for which elementary composition was homogeneous result in homogeneous laser fusion ages. However, biotite samples with heterogeneous laser fusion ages are not necessarily unreliable; the irradiation process itself may have disturbed the dated material.

The ^{40}Ar–^{39}Ar step-heating technique was applied to four biotite samples. Two of them were known to be compositionally homogeneous and their spectra show well-shaped plateaux (flat portion of the age spectrum comprising $\geqslant 80\%$ vs. the whole Ar extraction); this is a good criterion of reliability of the corresponding ^{40}K–^{40}Ar and ^{40}Ar–^{39}Ar ages. The two biotite samples known to be compositionally less homogeneous have given disturbed spectra. The biotite with the lower K content gave the least convincing plateau (small or no flat portion on the age spectrum). A bad plateau is not necessarily a definitive criterion of unreliability since irradiation may have disturbed the isotopic equilibrium. Combining the different criteria considered in this paper, Table VII shows the reliable biotite dates (i.e. qualified ages) obtained from BRCL's of the Apennines in this and previous studies. The results can be considered very near ages of deposition for Group levels *1–3*, *5* and *6*.

Suggested calibration points are, from top to bottom:

GL *6*	bottom of anomaly *9*N; upper CP*18*, upper P*21* biozones = 28.1 ± 0.4 Ma
GL *5*	upper anomaly *12*R; near bottom CP*18*, near bottom P*20* = 31.9 ± 0.6 Ma

GL *3* lower anomaly *13*R; upper CP*15*b, upper P*16* = 34.2 ± 0.4 Ma
GL *2* top anomaly *16*N; mid-CP*15*b, mid-lower P*16* = 35.4 ± 0.5 Ma
GL *1* upper anomaly *17*N; mid-CP*15*a, mid-P*15* = 36.4 ± 0.3 Ma

These data are internally consistent and bracket the Eocene–Oligocene boundary. In Massignano and Contessa valleys, combination of BRCL dates with a mean sedimentation rate of 7–8 m Ma^{-1} gives a similar result locating the Eocene–Oligocene boundary within the interval of time 34.1 to 33.3 Ma.

The age of the boundary at 33.7 ± 0.4 Ma is in agreement with previous, although less precise, estimates based on radioisotopic data (Curry and Odin, 1982; Glass et al., 1986). The precision given for this age is based on the intercomparison of ages obtained in different laboratories using different dating methods and different reference materials and can be considered as the correct accuracy on the date. This age constitutes probably the best anchor for calibration of the Paleogene time scale; this is of special interest since one of the sections dated here is now accepted for definition of the

TABLE VII

Summary of selected K–Ar biotite dates from the Apennines, following discussion in this paper (Rb–Sr data after Montanari et al., 1985)

Group level	Sample	K (%)	% ^{40}Ar$_{rad}$	Ar (nl g^{-1})	Age (±2σ) (Ma)
GL *6*	CQ-GAR	6.72	81.9	7.41	28.1 ± 0.3*[1]
GL *6*	CQ-GAR		66.0	7.39	28.2 ± 0.6*[1]
GL *5*	MCA-*3*	7.41	84.2	9.21	31.7 ± 0.6
GL *5*	CQ-BOB	7.11	75.4	8.75	31.4 ± 0.6
GL *5*	CQ-BOB		67.5	9.09	32.6 ± 0.9
GL *3*	B*50* (= MAS-14.7 m)	7.15	97.7	9.68	34.6 ± 0.3
GL *3*	B*50* (= MAS-14.7 m)	7.10	98.2	9.66	
GL *3*	B*50* (= MAS-14.7 m)	7.34			34.1 ± 0.2*[2]
GL *3*	MAS-12.7 m (= B*48*)	7.13	87.0	9.42	33.7 ± 0.4
GL *3*	MAS-12.7 m (= B*48*)		67.4	9.51	34.0 ± 0.8
GL *3*	B*48* (= MAS-12.7 m)	7.10			34.9 ± 0.2*[2]
GL *2*	MAS-*1* (= 7.2 m)	6.82	53.4	9.30	35.1 ± 0.8
GL *2*	MAS-*1* (= 7.2 m)		75.8	9.28	34.7 ± 0.9
GL *2*	MAS-7.2 m)	6.97	80.0	9.86	36.1 ± 1.0
GL *1*	CQ-210 m *A*	6.84	76.2	9.69	36.1 ± 0.5
GL *1*	CQ-210 m *A*		68.8	9.83	36.6 ± 0.5
GL *1*	CQ-210 m *B*	6.62	76.8	9.47	36.5 ± 0.7

Group level	Sample	Sr (ppm)	^{87}Rb/^{86}Sr	^{87}Sr/^{86}Sr	Age ± 2σ
GL *6*	CQ-GAR (B)	33.30	29.390	0.717256 ± 0.000034	27.8 ± 0.2*[3]
	CQ-GAR (I)	11,200	0.0082	0.708029 ± 0.000031	
GL *3*	MAS-12.7 m (B)	16.96	65.39	0.741716 ± 0.000025	34.4 ± 0.2*[3]
	MAS-12.7 m (I)	127.8	2.685	0.711050 ± 0.000031	
GL *2*	CQ-ETT (B)	53.9	18.37	0.717358 ± 0.000028	35.4 ± 0.2*[3]
	CQ-ETT (I)	1,413	0.0371	0.708142 ± 0.000028	
GL *2*	MAS-7.2 m (B)	14.60	74.73	0.746447 ± 0.000044	36.0 ± 0.5
GL *2*	MAS-7.2 m (B)	14.39	74.76	0.746860 ± 0.000017	36.5 ± 0.6

*[1] To be weighted less heavily due to geochemical heterogeneity (CQ-GAR) or low K content (CQ-ETT).
*[2] ^{40}Ar–^{39}Ar dates on K-rich biotites displaying a large flat portion on their spectrum (plateau) when step heated.
*[3] Two-point isochron lines using biotite (B) and insoluble residue (I) separates.

Eocene–Oligocene boundary golden nail (Odin and Montanari, 1989).

From the methodological point of view, this study has shown that volcano-sedimentary biotites (even K-rich and well-preserved) should be considered carefully and their reliability established. In this context, a combination of various preliminary analyses followed by several dating methods and techniques is a fruitful approach for which we have presented here as an example.

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