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Direct comparison of astronomical and $^{40}Ar/^{39}Ar$ ages of ash beds: Potential implications for the age of mineral dating standards

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Abstract. We present first results of $^{40}Ar/^{39}Ar$ multiple single fusion datings on biotites and feldspars from two volcanic ash beds found on Crete, Gavdos and Koufonisi (Greece). Preferred $^{40}Ar/^{39}Ar$ ages - calculated against TCR sanidine with an age of 27.92 Ma, intercalibrated to an age of 28.09 ± 0.10 Ma (1σ) for FCT-3 biotite and an age of 24.99 ± 0.07 Ma for DRA sanidine - are slightly but consistently younger than astronomical ages obtained independently for the same ash beds. The best fit to the astronomical ages is obtained when the age of TCR sanidine is increased slightly to 27.98 ± 0.19 Ma, the age of FCT-3 biotite to 28.15 ± 0.19 Ma and the age of DRA sanidine to 25.05 ± 0.17 Ma. The ages for the standards arrive slightly younger if the $^{40}Ar/^{39}Ar$ age - of 6.936 ± 0.006 Ma (1σ) - for a single pure sanidine separate of the lower ash - dated astronomically at 6.941 Ma - is considered most reliable.

Introduction

The age uncertainty of neutron fluence monitors, or mineral dating standards, is the factor presently limiting the accuracy in $^{40}Ar/^{39}Ar$ dating. This uncertainty results in a 1 to 1.5 % error as compared with a 0.3 % precision of modern $^{40}Ar/^{39}Ar$ dating techniques. For instance, generally accepted ages for the Fish Canyon Tuff (FCT) sanidine, one of the main dating standards, range from 27.55 to 28.09 Ma (e.g. Izett et al., 1991; Renne et al., 1994) whereas reproducibility is much lower. One solution to reduce the uncertainty is to determine the absolute air calibration of the ^{38}Ar tracer for isotope dilution determination of ^{40}Ar more precisely (Kunk et al., 1994). Further careful comparison of different techniques applied to various minerals from ash horizons has been used with success in older parts of the timescale (Baadsgaard et al., 1992).

An alternative solution is to compare radiometric ($^{40}Ar/^{39}Ar$) ages with ages that have been obtained independently by astronomical dating. This dating method is based on the correlation or tuning of cyclic variations in the geological record to computed astronomical time series of orbital variations. Renne et al. (1994) recalculated published $^{40}Ar/^{39}Ar$ ages for seven polarity reversals younger than 3.5 million years to fit them to astronomical ages for the same reversals. The best fit was obtained when they adopted an age of 27.95 (or 28.03) ± 0.18 Ma (2σ) instead of 27.84 Ma for their FCT sanidine.

A disadvantage noted by Renne et al. (1994) of their approach is that the $^{40}Ar/^{39}Ar$ ages for 5 (out of 7) polarity reversals had to be calculated by linear interpolation of sediment accumulation rates between dated volcanic beds, thereby assuming a constant sedimentation rate in depositional settings where this may not be justified. But although linear interpolation is an imperfect means of calculation, this should produce non-systematic errors that will be cancelled out in a sufficiently large data set. Another potential disadvantage is that exact positions of reversal boundaries are not always known due post-depositional remagnetization and/or lack of sample density (Van Hoof et al., 1993; Lourens et al., 1996). Such short-comings are avoided by dating ash beds in sedimentary sequences that have been dated astronomically. This approach ensures $^{40}Ar/^{39}Ar$ ages to be compared directly with the astronomical ages. Clearly an accurate intercalibration of radioisotopic and astronomical time is important because standard timescales for the youngest part of the Earth's history are increasingly being based on astronomical rather than on radioisotopic dating (e.g., Cande and Kent, 1995).

Here, we present the first results of $^{40}Ar/^{39}Ar$ datings of volcanic ash beds intercalated in cyclically bedded marine successions of late Miocene age in the Mediterranean. The successions have been astronomically dated resulting in an astronomical time scale for the Mediterranean late Miocene (Hilgen et al., 1995).

Sections and stratigraphy

For our study we selected the Faneromeni, Kastelli and Agios Ioannis sections on Crete, the Metochia section on Gavdos and the Koufonisi section on Koufonisi. These open marine sections consist of cyclic alternations of white coloured homogeneous marls and brown coloured often well-laminated, organic-rich beds (termed sapropels) with minor intercalations of turbidites and volcanic ashbeds. All sections have been correlated in detail using a combination of cyclostratigraphy and planktonic foraminiferal biostratigraphy (Fig. 1). The resulting bed-to-bed correlations are confirmed by the position of the ashbeds.

Three prominent ash beds are present in the Kastelli and Agios Ioannis sections and have been labelled a1, a2 and a3. They generally contain feldspar, quartz and glass shards. The a1 and a3 ashes in addition contain abundant biotite, whereas the a2 contains no (or minor) biotite; this ash is rich in hornblende phenocrysts. The a1 - but not the a2 and a3 - is found in all sections studied. Additional thin volcanogenic beds are found in most of the sections. In these bedsm the crystals are badly preserved and rounded indicating substantial post-depositional transport.

Considerable effort was made to collect fresh unweathered material. However, even after considerable digging, the ash layers in the Kastelli, Agios Ioannis and Metochia sections maintained a red colouring due to weathering induced oxidation. Such a red colour is absent in the freshly exposed coastal cliff sections of Faneromeni and Koufonisi.

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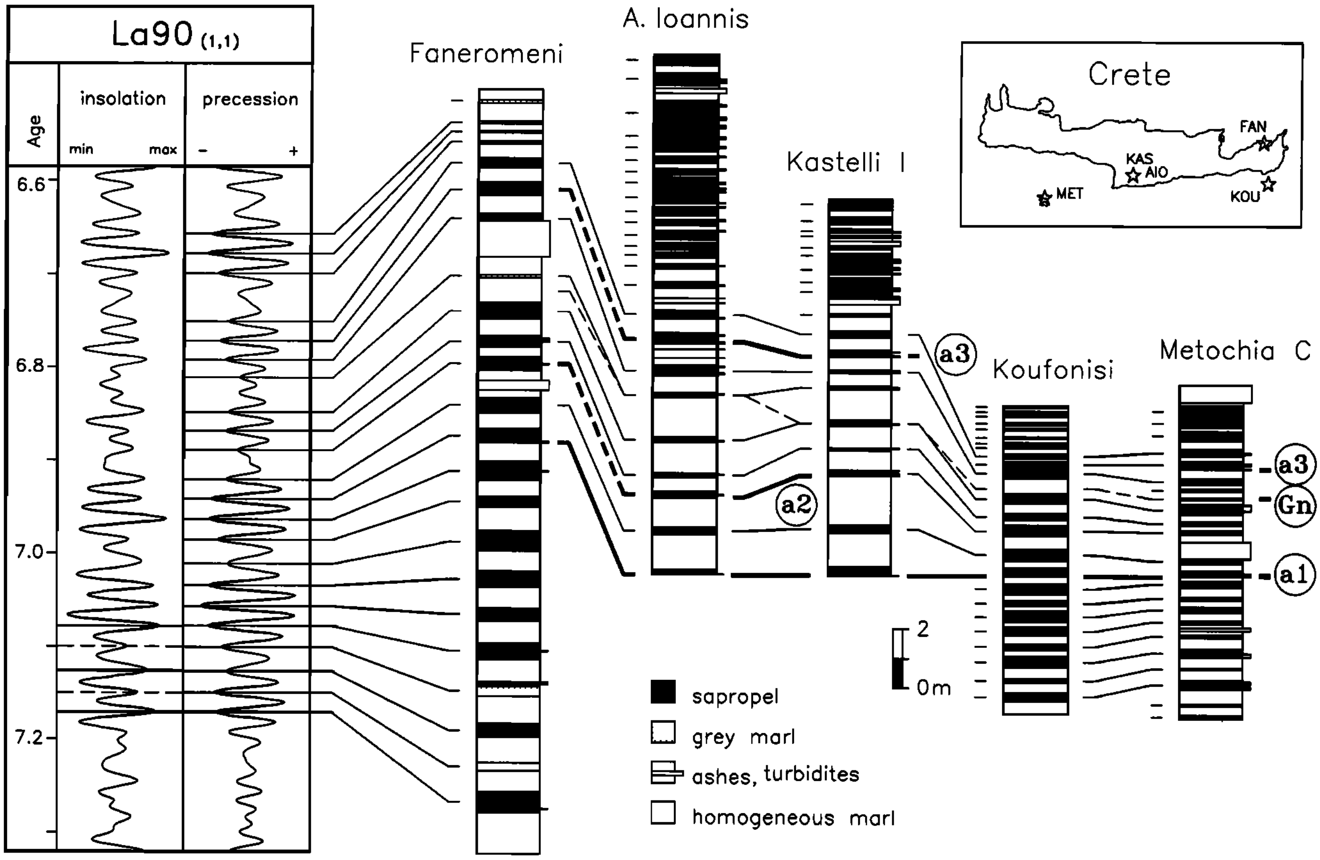

Figure 1. Cyclostratigraphic, tephrastratigraphic and biostratigraphic correlations between the studied sections and calibration of the sedimentary cycles to astronomical target curves (after Hilgen et al., 1995). A gross location map of the sections is included.

^{40}Ar/^{39}Ar dating

Radiometric dating focussed on the biotite and feldspar populations of the a1, a2 and a3 ashbeds, because of the good preservation and (sub-)euhedral shape of individual crystals. These three ash beds are interpreted as primary fall-outs or to have undergone only limited post-depositional transport. The samples were washed and sieved to separate the >125 μ fraction. In addition, microprobe analyses were performed on a Geol-JXA 86000 superprobe, to investigate the composition and homogeneity of the biotites and feldspars.

Methods

Biotite fractions > 125 μm were mechanically separated using a Faul vibration table. This separation was followed by microscopic examination and hand-picking of individual crystals using euhedric shape and preservation as selection criteria. Feldspar crystals (>200 μm) were separated by sieving, Faul vibration table, magnetic separator and hand-picking under the microscope. Heavy liquid separation was applied to isolate sanidine crystals from sieved fractions of the Faneromeni a1-ash.

^{40}Ar/^{39}Ar geochronology was carried out using laser fusion of several replicate samples (usually n=5). A detailed description of techniques was published elsewhere (Wijbrans et al., 1995). In summary, approximately 20 mg aliquots of both feldspar and biotite were packaged in Al-foil, and loaded with the flux monitors (USGS standard 85G003 TCR sanidine, K/Ar age 27.92 Ma, ^{40}Ar/^{39}Ar reproducibility ≤ 0.3%) that were packaged in Cu-foil, in a 5 mm ID quartz tube. Standards were loaded between each set of 5 unknowns. Irradiation with fast neutrons was carried out in the B3 (Dummy fuel element) facility in the core of the Oregon State University TRIGA reactor. After irradiation, the samples were loaded in a Cu tray (60 mm diameter) with 2 mm diameter holes for each individual experiment. For both the standards and the unknowns, we applied a single fusion technique where for each sample 5 replicates were analysed. The biotites and feldspar samples were preheated to approximately 500 °C to remove some of the atmospheric argon that interferes with accurate analysis of the radiogenic argon component in young samples. Isotopic measurements of the pre-heat fraction shows that the amount of radiogenic argon released during the pre-heating step was minor (i.e. < 5%). The argon gas was measured isotopically using a double focussing noble gas mass spectrometer (MAP215-50) in static mode. Beam intensities were measured on a secondary electron multiplier detector (gain 10,000) by peak jumping at half mass intervals. System blanks were measured at least between every set of 5 unknowns.

Results

Results of microprobe analyses show that the biotites cluster in two groups which correspond to the a1 and a3 ash layers (a2 does not contain or contains only minor biotite). Only biotites of the a1 from Kastelli and Koufonisi diverge from the a1 cluster. The overall good clustering points to a homogeneity of the biotite populations, excludes the presence of detrital contaminants and confirms the cyclostratigraphic correlations between the sections. Results of the microprobe analysis in addition revealed major differences in the feldspar populations of the two dated ash layers

Table 1. ^{40}Ar/^{39}Ar ages and comparison with astronomical ages.

ash	Astr. age	mineral	Agios Ioannis	Kastelli	sections Faneromeni	Koufonisi	Metochia	preferred Ar/Ar age	apparent TCR age
a3	**6.771**	biotite	**6.747 ± 0.014**	6.668 ± 0.010			6.632 ± 0.021	**6.747 ± 0.014**	28.02 ± 0.08
		plagioclase	**6.776 ± 0.066**	**6.749 ± 0.044**				**6.757 ± 0.055**	27.98 ± 0.32
a1	**6.941**	biotite	**6.893 ± 0.013**	5.691 ± 0.055	**6.934 ± 0.016**	6.813 ± 0.012	6.768 ± 0.025	**6.909 ± 0.015**	28.05 ± 0.09
		feldspar	**6.923 ± 0.013**	6.844 ± 0.008	**6.936 ± 0.006**	7.164 ± 0.032	6.786 ± 0.027	**6.934 ± 0.009**	27.95 ± 0.05
									27.98 ± 0.19
a1	**6.941**	sanidine			**6.936 ± 0.006**			**6.936 ± 0.006**	**27.94 ± 0.03**

Astronomical ages of ash layers calculated as outlined in text. ^{40}Ar/^{39}Ar ages represent weighted mean of a limited number (usually 5) of individual total fusion experiments. Selected ^{40}Ar/^{39}Ar ages used to calculate preferred biotite and feldspar ages for the a1 and a3 are indicated in bold (see text for explanation). Preferred ages represent the inverse variance weighted mean of the selected ages. Apparent ages for the TCR standard were obtained by fitting the preferred ages to the astronomical ages using equations in Dalrymple et al. (1993) and Renne et al. (1994). The weighted mean of the apparent ages is the age of the standard after intercalibration with astronomical time. This age is compared with the age obtained if only the ^{40}Ar/^{39}Ar age of the Faneromeni a1-sanidine is used for intercalibration. Full data tables are available from the authors.

(a1 and a3). The a1 contains a mixed sanidine-plagioclase population whereas the a3 contains only plagioclase. Again these results support the cyclostratigraphic correlations.

The results of the ^{40}Ar/^{39}Ar dating have been summarized in Table 1. The ^{40}Ar/^{39}Ar ages are in agreement with the stratigraphic succession because ages of the a1-ash are older than the ages of the a3-ash. The only exceptions are the discrepant young age of the Kastelli a1-biotite, and the Metochia a1-biotite which is slightly younger than the a3-plagioclase from Agios Ioannis. Biotites and feldspars in addition yield consistent ages - on the 2σ level - for the same sample except for the a1-ash in the Kastelli and Koufonisi sections. However, biotite ages are without exception younger than the feldspar ages for the same sample. Moreover, biotite and plagioclase ages are not always consistent for samples of the same ash bed but from different sections.

The discrepant young age of the Kastelli a1-biotite (and that of the Metochia a3-biotite) can best be explained by the influence of alteration due to weathering as indicated by a reduced K content. The lower number of K atoms per 22 O atoms suggests that these biotites have been altered partly to chlorite. This alteration is corroborated by the often non-glossy appearance of the biotites in the Kastelli a1 and Metochia a3 samples. Hence, older biotite ages for an ash bed may be considered more reliable than younger ages because of the potential influence of weathering. This approach would result in an age of 6.747 ± 0.014 Ma for the a3 (Agios Ioannis) and of 6.934 ± 0.016 Ma (1σ) for the a1 (Faneromeni) (Table 1). The Faneromeni a1-biotite comes from a freshly exposed coastal cliff section whereas the same ash shows a reddish colour typical of weathering induced oxidation in the inland sections of Kastelli, Agios Ioannis and Metochia. Using a 2σ overlap criterion, the Faneromeni a1-biotite age is consistent with the age of 6.893 ± 0.013 Ma for the Agios Ioannis a1-biotite. Combining these two ages results in a weighted (inverse variances) mean age of 6.909 ± 0.015 Ma for the a1-biotite (Table 1).

Our feldspar ages may be considered less reliable than the biotite ages because they have been obtained from plagioclase (a3) or from mixed plagioclase/sanidine (a1) populations. Only the Faneromeni-a1 feldspar age is derived from a pure sanidine separate. Plagioclase - present in the mixed feldspar populations - is less suitable because the lower K content makes precise measurements of radiogenic ^{40}Ar more difficult due to the combined effects of a larger proportion of atmospheric argon and possible problems with excess ^{40}Ar (see Krijgsman et al., 1997). Clearly such disturbing processes are responsible for the discrepantly old feldspar age of 7.164 Ma for the Koufonisi a1 as indicated by the much lower proportion of radiogenic argon (83 as compared with an average of 97% for other feldspar separates). Plagioclase in addition has a greater sensitivity to xenocrystic contamination.

Following this approach, the single sanidine age of 6.936 ± 0.006 Ma (1σ) for the Faneromeni a1-ash can be selected as the most reliable (feldspar) age for the a1. Using a 2σ overlap criterion, this sanidine age is consistent with the mixed feldspar age of 6.923 ± 0.013 Ma for the same ash in the Agios Ioannis section. This yields a weighted mean age of 6.934 ± 0.009 Ma for the a1-feldspar. The two plagioclase ages of the a3 are mutually indistinguishable and yield a weighted mean age - of 6.757 ± 0.054 Ma - that is in agreement with the selected biotite age (Table 1).

Comparison of ^{40}Ar/^{39}Ar and astronomical ages

The ^{40}Ar/^{39}Ar ages of the feldspars and biotites from the a1-ash and a3-ash are compared with the astronomical ages for these ashes in Table 1. The a1 and a3 are intercalated at the base of sapropels which have been dated astronomically at 6.938 and 6.768 Ma (Hilgen et al., 1995). The astronomical age of the a1 (a3) arrives at 6.941 (6.771) Ma because the age of 6.938 (6.768) Ma refers to the sapropel mid-point and the presently best estimate for the duration of a well-developed sapropel is in the order of 5-6 kyr. The age of the sapropel mid-point itself represents a 3 kyr lagged age of the correlative insolation maximum. This lag is based on the age difference between the calendar age of the youngest, Holocene sapropel and that of the correlative precession mimimum (see Hilgen et al., 1995). However, the constantness of this lag through time can be questioned, the alternative being a zero phase lag.

All ^{40}Ar/^{39}Ar ages, apart from the Agios Ioannis a3-plagioclase and the discrepantly old Koufonisi a1-feldspar, are slightly younger than the corresponding astronomical age. More importantly, the same holds true for the preferred feldspar and biotite ages of the a1 and a3 (see Table 1). Our ^{40}Ar/^{39}Ar data were calculated against USGS standard TCR sanidine with an age of 27.92 Ma, intercalibrated to an age of 28.09 ± 0.10 Ma (1σ) for the FCT-3 biotite and of 24.99 ± 0.07 Ma for the DRA-1 sanidine (Wijbrans et al., 1995). Note that our intercalibration is not in agreement with previous attempts which suggest that the TCR sanidine is somewhat older than the FCT-3 biotite (e.g., Baksi et al., 1996).

The slightly younger ^{40}Ar/^{39}Ar ages of the a1 and a3 can be fitted to the astronomical age by a corresponding increase in the age of the dating standards (Table 1). The best fit is obtained when the age of the TCR sanidine is increased slightly to 27.98 ± 0.19 Ma, the age of the FCT-3 biotite to 28.15 ± 0.19 Ma and the age of the DRA sanidine to 25.05 ± 0.17 Ma. The respective ages for the standards arrive slightly younger at 27.94 ± 0.03, 28.11 ± 0.03 and 25.01 ± 0.03 Ma if the ^{40}Ar/^{39}Ar age - of 6.936 ± 0.006 Ma - for the single pure sanidine separate of the Faneromeni a1 is selected for the intercalibration with astronomical time (Table 1). In fact, this is the preferred option in case the Faneromeni a1-sanidine is considered the most reliable. This selection is validated because the alkali feldspar sanidine is generally considered the most suitable mineral for ^{40}Ar/^{39}Ar dating. In case of the Faneromeni a1-sanidine, this suitability is demonstrated by the excellent reproducibility of the individual (laser fusion) experiments and the excellent agreement with the oldest biotite age of this ash which comes from the same unweathered section. The reproducibility makes the Faneromeni a1-sanidine perfectly suitable for calculating the age of the mineral dating standards via intercalibration with astronomical time. The alternative option to calculate intercalibrated ages of the standards results in much larger standard deviations due to the incorporation of a3-plagioclase ages and, to a lesser extend, of biotite and mixed a1-feldspar ages. Finally, all intercalibrated ages of the monitor standards would increase with 0.011 or 0.012 Myr if we assume no phase lag between insolation maximum and sapropel mid-point.

Our results are consistent with the work of Renne et al. (1994) who reported a similar increase in the age of their dating standards via intercalibration with astronomical time. Recently, Lourens et al. (1996) evaluated the Pliocene astronomical time scale on which Renne et al. (1994) partly based their intercalibration. The increase in the age of the standards reported by Renne et al. (1994) is reduced from 110 (or 190) kyr to 40 kyr if the slightly modified astronomical ages of Pliocene reversal boundaries are taken into account. This is in excellent agreement with our results. Remarkably enough, all intercalibrated ages are indistinguishable from (at least some of the) currently accepted conventional ages of the dating standards despite an assumed error of 1 to 1.5% in the conventional ages. Finally, the inferred consistency with the results of Renne et al. (1994) supports the validity of the late Miocene astronomical time scale of Hilgen et al. (1995), indicating that, for this interval of time, the astronomical tuning of ODP Leg 138 sites (Shackleton et al., 1995) and the Geomagnetic Polarity Time Scales of Baksi (1995) and Cande and Kent (1995) are too young.

The ages we obtained here for the mineral dating standards should be considered preliminary because they are based on a limited number of single fusion experiments. Future research will especially focus on the a1-ash by dating sanidine separates from at least 4 different sections and using step-wise heating experiments in addition to multiple (>30) single fusion dating. That study aims to reduce the analytical error and to determine the age of the monitor dating standards more accurately. A direct intercalibration against other dating standards, such as the Fish Canyon sanidine, used by a number of US based laboratories is desirable (e.g. Renne et al., 1994; Baksi et al., 1996). Finally, the potential of the a1-ash for providing an astronomically dated mineral dating standard will be investigated.

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