$^{39}$Ar-$^{40}$Ar dating of an alkali-granite enclave from Pantelleria island

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ABSTRACT. — A peralkaline microgranitic enclave was found enclosed in the Green Tuff ignimbrite on Pantelleria island. This enclave represents the intrusive equivalent of pantelleritic lava flows. Its K-Na-feldspar has been dated by $^{39}$Ar-$^{40}$Ar and gave a plateau age of $517 \pm 19$ ka. This age is considerably older than all outcropping rocks dated so far ($< 324$ ka), and requires to shift the onset of magmatic activity on Pantelleria back in time.

RIASSUNTO. — Incluso nel Tufo Verde dell’Isola di Pantelleria è stato rinvenuto un microgranito peralcalino. A causa della somiglianza geochimica e mineralogica con le pantelleriti stesse. Una datazione con il metodo $^{39}$Ar-$^{40}$Ar sul K-Na feldspato, ha fornito un’età plateau di $517 \pm 19$ ka. Questo microgranito è considerevolmente più antico di tutte le vulcanite fin qui datate a Pantelleria ($< 324$ ka). Il suo rinvenimento sposta quindi indietro nel tempo di circa 200 ka l’inizio dell’attività magmatica nell’isola.

KEY WORDS: Pantelleria, peralkaline magmatism, $^{39}$Ar-$^{40}$Ar dating.

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INTRODUCTION

Pantelleria island is set on the NE-SW trending Pantelleria rift, which represents the westernmost portion of the Sicilian Channel rift zone. Pantelleria is characterized mostly by an acidic peralkaline magmatism, whose age has been estimated on the base of K-Ar dating to be in the range 300 – 5 ka, and subordinate mildly alkaline lavas, ranging from 120 to $< 10$ ka (Cornette et al., 1983; Civetta et al., 1984; Mahood and Hildreth, 1986). The geochemical and petrological aspects of the Pantelleria magmatism (e.g. Esperanca and Crisci, 1995) are outside the scope of the present short note.

The major volcano-tectonic features are two nested calderas located in the central part of the island (fig. 1): the older one has been dated at 114 ka (La Vecchia caldera, Mahood and Hildreth, 1986); the younger one, named Cinque Denti caldera by Mahood and Hildreth (1986) and Monastero caldera by Cornette et al. (1983), followed the eruption of the Green Tuff ignimbrite (GT). The GT is an important marker horizon and was dated at ca. 50 ka
Recently some attention has been paid to the intrusive enclaves enclosed in the silicic rocks: De Vivo et al. (1992) studying fluid inclusions in granitoid enclaves enclosed in pyroclastics or in lava flows (whose ages range from 79 to 5.5 ka), stated that the size of intrusive bodies beneath Pantelleria was relatively small and no convective geothermal system was associated to it. Fulignati et al. (1997) reported that microsyenitic enclaves from the deeper portions of drillholes bored south of M. Grande contain parageneses typical of high-temperature hydrothermal systems. It is of special relevance whether these enclaves are magmatic (Fulignati et al., 1997) or part of a metamorphic basement underlying Pantelleria.
**TABLE 1**
Mean mineral analyses and standard deviations. Analyses have been performed using a LEO™
440 scanning electron microscope coupled to an Oxford-Link EDS (University of Palermo).
Operating conditions were 20 kV accelerating voltage and 600 pA beam current. Natural mineral
standards were used to calibrate quantitative analyses.

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<th>OLIV</th>
<th>st. dev.</th>
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<th>st. dev.</th>
<th>AMPH</th>
<th>st. dev.</th>
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<td></td>
<td>(n=4)</td>
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<td>(n=8)</td>
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<td>0.05</td>
<td>18.84</td>
<td>0.49</td>
<td>0.79</td>
<td>0.4</td>
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<td></td>
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<td>MgO</td>
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<td>0.10</td>
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<td>0.01</td>
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<td>Total</td>
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<td>99.89</td>
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<td>97.00</td>
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<tr>
<td>Fo</td>
<td>1.3</td>
<td>An</td>
<td>0.1</td>
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<tr>
<td>Fa</td>
<td>84.7</td>
<td>Ab</td>
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<tr>
<td>Tefr</td>
<td>14.1</td>
<td>Or</td>
<td>69.9</td>
<td></td>
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</tbody>
</table>

**TABLE 2**
Whole rock chemical analysis of the alkali-granitic enclave. Major elements in wt%, minor
elements in ppm. Analyses have been performed by means of XRF, on a Philips PW 1400
spectrometer (University of Palermo), following analytical procedures of Franzini et al. (1975).

<table>
<thead>
<tr>
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<th>PAN 2</th>
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<th>PAN 2</th>
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<td>SiO$_2$</td>
<td>71.88</td>
<td>V</td>
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<tr>
<td>TiO$_2$</td>
<td>0.30</td>
<td>Cr</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>11.00</td>
<td>Ni</td>
<td>18</td>
<td></td>
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<tr>
<td>FeO$_{tot}$</td>
<td>5.69</td>
<td>Rb</td>
<td>138</td>
<td></td>
</tr>
<tr>
<td>MnO</td>
<td>0.28</td>
<td>Sr</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>MgO</td>
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<td>Y</td>
<td>138</td>
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</tr>
<tr>
<td>CaO</td>
<td>0.23</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Na$_2$O</td>
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<td>Zr</td>
<td>1714</td>
<td></td>
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<tr>
<td>K$_2$O</td>
<td>4.02</td>
<td>Nb</td>
<td>371</td>
<td></td>
</tr>
<tr>
<td>P$_2$O$_5$</td>
<td>0.01</td>
<td>Ba</td>
<td>40</td>
<td></td>
</tr>
<tr>
<td>LOI</td>
<td>1.11</td>
<td>La</td>
<td>171</td>
<td></td>
</tr>
<tr>
<td>A.I.</td>
<td>1.18</td>
<td>Ce</td>
<td>379</td>
<td></td>
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</table>
In our opinion, the phase assemblage (Na-K-fsp + Na-px, see below) make a magmatic origin unquestionable.

Despite their scarce volumetric abundance, these enclaves are essential tracers of a heretofore unknown early evolution of Pantelleria, and their age is essential to constrain magmatogenetic models. So far, no age determination has been carried out on them; in this note we report the first $^{39}$Ar-$^{40}$Ar age determination.

**SAMPLE DESCRIPTION**

The sample ($22 \times 15 \times 10$ cm) has been taken at Cala Rossa, on the NNW side of the island at an altitude of 10 m a.s.l. It was enclosed in the GT together with several similar enclaves of smaller size.

Point counting (on 1400 points) gave the following results: $kfs = 55\%, \ aqtz = 27\%, \ Na-px = 6\%, \ ampl = 4\%, \ olivine < 1\%, \ ilm < 1\%, \ enigmatite < 1\%, \ voids = 8.0\%$. The texture is disequigranular medium-grained made up by:

- euhedral to subhedral anorthoclase, which is variably exsolved in albite-rich and sanidine-rich portions. Its size is up to 3-4 mm. Anorthoclase is almost unaltered, just slightly cloudy in some portions;
- anhedral to subhedral quartz grains (1-2 mm in size);
- euhedral zoned aegirine (1 mm in size), often enclosing euhedral Na-rich amphibole ($Na_2O$ up to 8.8 wt%, Table 1).

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**Fig. 2** BSE image of the relationships between fayalite, amphibole and Na-cps. $amp = $ amphibole; $cpx = Na-cpx$ (aegirine); $enigm = $ ebuglatute; $fay = $ fayalite; $ilm = $ ilmenite; $kfs = K$-feldspar; $mt = $ magnetite.
Fayalitic olivine is always in reaction relationships with Na-pyroxene and amphibole (fig. 2). Enigmatite and ilmenite are anhedral and mostly enclosed in amphibole. The petrochemical characters (Table 2) are indistinguishable from those of pantelleritic lava flows (e.g. Civetta et al., 1984), which crop out extensively and were produced during almost all the lifespan of volcanism in Pantelleria:

- high SiO₂ (71.9 wt%), low Al₂O₃ (11.0 wt%) and peralkaline agpaitic index (i.e. the (Na₂O+K₂O)/Al₂O₃ molar ratio) of 1.17
- very high Zr and Nb contents (1714 and 371 ppm, respectively)
- very low Sr and Ba (10 and 40 ppm, respectively).

**GEOCHRONOLOGY**

Rock chips of the sample were carefully washed in distilled water before and after crushing. Anorthoclase was separated from the 0.125 – 0.250 mm size fraction by standard magnetic methods and heavy liquids. The anorthoclase separate, which was used for ⁴⁰Ar-³⁹Ar dating, was preliminarily checked by X-Ray diffractometry for the presence of alteration phases, and gave no effects in the 2θ region corresponding to interplanar spacing 7-14 Å.

³⁹Ar-⁴⁰Ar analyses followed Villa et al. (2000); results are shown in Table 3. K, Cl and Ca concentrations are calculated from the totals of the Ar isotopes and the interference and production factors given by Belluso et al. (2000)

The age spectrum is internally discordant (fig. 3), but still provides reliable chronological information. Step ages are always older than 415 ka, and there is no obvious age signature of the = 50 ka eruption age of the GT host.

The isochron diagram (fig. 4) shows the presence of a very high atmospheric contamination, resulting in high ³⁶Ar/⁴⁰Ar

**Table 3**

³⁹Ar/⁴⁰Ar stepwise heating results on anorthoclase separate. Irradiation, analysis and calculations followed Belluso et al. (2000). Uncertainties are indicated as 1 sigma.

All Ar concentrations are in picoliters per gram. The totals are calculated as follows:

Ar* (radiogenic ⁴⁰Ar) = Total ⁴⁰Ar - 295.5⁸ atmospheric ³⁶Ar; concentration of K (%), Cl (ppm) and Ca (ppm) were calculated from the total ³⁹Ar, ³⁸Ar and ³⁷Ar, respectively, which were produced during irradiation. The total age is by definition equivalent to the K/Ar age and therefore of dubious significance; the plateau age (tₚₚ) is calculated on the basis of weighted means of steps 4 to 6, which account for 50.5% of the total ³⁹Ar released.

<table>
<thead>
<tr>
<th>step</th>
<th>T(°C)</th>
<th>⁴⁰Ar_tot</th>
<th>³⁹Ar</th>
<th>³⁸Ar</th>
<th>³⁷Ar</th>
<th>³⁶Ar</th>
<th>Age (Ma) ±1σ</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>601</td>
<td>664.35 ± 0.3</td>
<td>33.03 ± 0.3</td>
<td>1.49 ± 0.004</td>
<td>0.23 ± 0.02</td>
<td>2.21 ± 0.008</td>
<td>0.46 ± 0.09</td>
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<tr>
<td>2</td>
<td>763</td>
<td>178.46 ± 0.01</td>
<td>44.04 ± 0.04</td>
<td>3.35 ± 0.006</td>
<td>0.005 ± 0.01</td>
<td>0.53 ± 0.004</td>
<td>0.64 ± 0.03</td>
</tr>
<tr>
<td>3</td>
<td>836</td>
<td>67.88 ± 0.01</td>
<td>17.66 ± 0.02</td>
<td>1.25 ± 0.003</td>
<td>0.000</td>
<td>0.21 ± 0.002</td>
<td>0.42 ± 0.04</td>
</tr>
<tr>
<td>4</td>
<td>918</td>
<td>76.26 ± 0.01</td>
<td>16.11 ± 0.01</td>
<td>1.20 ± 0.003</td>
<td>0.026 ± 0.02</td>
<td>0.24 ± 0.002</td>
<td>0.53 ± 0.06</td>
</tr>
<tr>
<td>5</td>
<td>995</td>
<td>174.26 ± 0.01</td>
<td>31.89 ± 0.03</td>
<td>3.79 ± 0.008</td>
<td>0.044 ± 0.04</td>
<td>0.54 ± 0.003</td>
<td>0.56 ± 0.04</td>
</tr>
<tr>
<td>6</td>
<td>1084</td>
<td>562.45 ± 0.03</td>
<td>99.55 ± 0.09</td>
<td>10.82 ± 0.020</td>
<td>0.124 ± 0.04</td>
<td>1.77 ± 0.007</td>
<td>0.49 ± 0.03</td>
</tr>
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<td>7</td>
<td>1224</td>
<td>276.27 ± 0.03</td>
<td>43.20 ± 0.04</td>
<td>3.93 ± 0.007</td>
<td>0.001 ± 0.04</td>
<td>0.82 ± 0.003</td>
<td>0.98 ± 0.03</td>
</tr>
<tr>
<td>8</td>
<td>1384</td>
<td>59.78 ± 0.01</td>
<td>6.70 ± 0.01</td>
<td>0.68 ± 0.002</td>
<td>0.001 ± 0.03</td>
<td>0.19 ± 0.002</td>
<td>0.75 ± 0.10</td>
</tr>
</tbody>
</table>

total Ar*=136.4 K=5.57% Cl=959 ppm Ca=150 ppm

fₚₚ 0.517±0.019
ratios. The $^{36}$Ar concentrations are significantly higher than blank contributions (up to 200 times) and are thus a primary feature of the anorthoclase. Fits through the data-points always have high uncertainties on ages and atmospheric intercepts, and high dispersions (MSWD > 1). The least unacceptable isochron is obtained on steps 4-6: the age is 750±330 ka, with an MSWD of 2 and a trapped $^{40}$Ar/$^{36}$Ar ratio of 287±14. The uncertainty on the isochron age is about 10 times worse than the highest error on the individual steps; this is due to the conservative approach of error propagation routines which increase the estimated uncertainty whenever the dispersion parameter MSWD is too high. Because all isochrons define atmospheric trapped Ar, it is legitimate to calculate plateau ages (which are based on an atmospheric Ar correction). We will see below under what further assumptions a plateau age can be calculated.

The integrated age, which by definition corresponds to the K-Ar age, is 590 ± 40 ka. However, as discussed in more detail by Villa (1991), K-Ar ages have only a limited chronological value as they neither take into account the existence of excess Ar nor chemical or thermal overprinting.

The release pattern of Cl-derived $^{38}$Ar provides important information. The Cl/K ratio, calculated from the data in Table 3, is lowest in the first release step and fairly constant among all others. This means that the anorthoclase contains no saline fluid inclusions, and also that the contribution of sericite alteration (which would be revealed by high Cl/K ratios in steps below ca. 850°C: Villa, unpublished results) is negligible. The small variation range of the Cl/K ratio also means that the mineralogical composition of the analyzed separate is sufficiently uniform; only in this case is it meaningful to calculate a plateau.

From the weighted mean of steps having similar Cl/K ratios and defining the isochron with the smallest dispersion, steps 4-6 (accounting for 50.5% of the released $^{39}$Ar), we calculate a plateau age of 517±19 ka. This age is taken as the age of emplacement and chilling of the subvolcanic microgranite.

The oldest age previously reported for pantelleritic lavas is 324 ± 10 ka (Mahood and Hildreth, 1986). The present result is evidence for an even older stage of magmatic (subvolcanic) activity, whose effusive counterpart has so far not been identified.
CONCLUSION

A microgranitic enclave which was found enclosed in the Green Tuff has been dated by $^{39}$Ar-$^{40}$Ar. On the basis of its petrochemical and mineralogical affinities the enclave is considered as an intrusive equivalent of the pantelleritic lava flows which erupted extensively on Pantelleria island in the past 300 ka.

No evidence of alteration was found in this enclave, either by XRD or by Ar isotope systematics.

The anorthoclase which was separated from this enclave has yielded a reliable $^{39}$Ar-$^{40}$Ar age of 517 ± 19 ka, which is considerably higher than the previously reported ages on older effusive pantellerites (< 320 ka).

On the basis of this preliminary datum we may conclude that the magma chamber where pantelleritic liquids evolved was active at least $\approx$200 ka before the oldest dated rock on Pantelleria Island. This datum suggests to focus additional geochronological work on intrusive enclaves, in order to better constrain the beginning of volcanism on Pantelleria Island.

REFERENCES


