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APPENDIX 1 A. ^{40}Ar / ^{39}Ar dates with analytical data

Two ignimbrites which form the basement of the Misti in the canyon of Río Chili (Fig. 2B) were dated by laser step heating on single biotite grains. Biotites from sample Mi 214 were extracted from a pumice 3 cm across in a pumice-rich unit; biotites of sample Mi 215 are idiomorphic phenocrysts from a pumice-poor unit 50 m beneath the latter. The samples were gently crushed and sieved; 800-micron-sized biotites were concentrated and grains for laser were hand-picked under a binocular microscope. Lavas from Misti mainly andesitic (Fig 6) were dated on whole rock because suitable minerals cannot be separated. About 100 mg of sample were used for high-frequency furnace step heating experiment.

The samples were irradiated in the 5C position of the McMaster University nuclear reactor (Hamilton, Canada). The samples Mi 214 and Mi215 were irradiated for 5 hours, together with the Fish Canyon Tuff sanidine (28.02 Ma; Renne et al, 1998) as neutron flux monitor. The Misti lava samples (whole rock) were irradiated for 1.5 hour with cadmium shielding together with the DRA sanidine (Wijbrans et al, 1995) as neutron flux monitor. An intercalibration of this standard with the Fish Canyon Tuff sanidine (28.02 Ma) gave us an age of 25.58 Ma that is used in this study.

^{40}Ar-^{39}Ar age determinations were performed by M. Fornari (IRD and UMR 6525 Géosciences Azur) at the Université de Nice, Sophia-Antipolis. Experimental techniques are described in detail by Ruffet et al. (1991) for the laser heating and by Féraud et al. (1982) for the high-frequency furnace heating procedures. The whole-rock sample analysis is performed with a mass spectrometer composed of a 120° M.A.S.S.E. tube, a Baur-Signer GS 98 source and a Balzers electron multiplier. For laser heating experiments, the gas extraction was carried out by a Coherent Innova 70-4 continuous laser. The mass spectrometer is a VG 3600 working with a Daly detector system. The typical blank values of the extraction and purification laser system are ranging from 9-5 x 10^{-13} ccSTP for ^{40}Ar, 8-1 x 10^{-14} ccSTP for ^{39}Ar, 2-1Êx 10^{-13} ccSTP for ^{37}Ar, and 7-3 x 10^{-14} ccSTP for ^{36}Ar, measured every third step. The criteria for defining a plateau age were the following: (1) the plateau should contain at least 70Ê% of released ^{39}Ar, (2) there should be at least three successive steps in the plateau, and (3) the integrated age of the plateau should agree with each apparent age of the plateau within a 2 sigma (2σ) interval. All errors are quoted at the 1σ level of confidence and do not include the errors on the age of the monitor. The error on the $^{40}Ar^*/^{39}Ar_K$ ratio of the monitor is included in the plateau age error bar calculation (see Table1).

The Mi 214 biotite age spectrum displays a plateau age of 13.12 ± 0.05 (Fig. 1) corresponding to 77% of the ^{39}Ar released, and following a more disturbed section probably due to chloritization. The Mi 215 biotite does not give a plateau age following our criteria, but a weighted mean age of 13.8 ± 0.1 Ma calculated on 5 concordant temperature steps (corresponding to 65% of the total ^{39}Ar released) may represent the best estimate of the age of this rock. This is straigthforward due to the fact that this age is slightly higher than the plateau age displayed by the sample Mi 214 located above this formation. It is also possible that this biotite was affected by chloritization. These ages are much older than the fission track age of 2.42 ± 0.11 Ma obtained on the uppermost ignimbrite unit termed 'white sillar' (Vatin-Perignon et al., 1996).

The sample Mi 100, corresponding to a fine grained, microcrystaline lava flow with millimetric phenocrysts of amphibole, displays an age spectrum characterized by decreasing apparent ages versus temperature, characteristic of 39Ar recoil during irradiation. However, a plateau age of 833 ± 6 ka (Fig. xB1) accounting for 74% of the total ^{39}Ar released for the temperature steps 850° to 1040°C could be obtained from the most potassic phases (probably grounmass) of the rock, as shown by the 37ArCa/39ArK spectrum (Fig. 1) –^{36}Ar/^{40}Ar versus ^{39}Ar/^{40}Ar correlation plot (not given) on all data displays a similar age of 833 ± 7 ka with an initial ^{40}Ar/^{36}Ar ratio of 297.3 ± 1.2 of atmospheric composition, but corresponding to a low quality fitting (MSWD = 8.3).

The sample Mi 50 displays a disturbed age spectrum probably due to 39Ar recoil, but displays a plateau age of 112 ± 6 ka that represents 84.5% of the total ^{39}Ar released (steps 700-1350°C) (Fig. 1) could be obtained on the K-rich phases (last steps excepted). The ^{36}Ar/^{40}Ar versus ^{39}Ar/^{40}Ar correlation plot (not given) on the plateau fraction does not fit very well, but gives a similar age of 109 ± 4 ka with an atmospheric initial ^{40}Ar/^{36}Ar ratio of 296.2 ± 1.7 (MSWD = 5.2).

References

Féraud, G., Gastaud, J., Auzende, J. M., Olivet, J.L., Cornen, G. 1982, ^{40}Ar/^{39}Ar ages for the alkaline volcanism and the basement of the Gorringe Bank, North Atlantic Ocean: Earth Planeteray Science Letters, 57, 211-226.

Hall, C. M., Walter, R. C., Westgate, J. A., York, D., 1984, Geochronology, stratigraphy and geochemistry of cinder tuffs in Pliocene hominid-bearing sediments of the Middle Awawsh Ethiopia: Nature, 308, 26-31.

Ruffet, G., Féraud, G., Amouric, M., 1991, Comparison of 40Ar-39Ar conventional and laser dating of biotites from the North Trégor Batolith: Geochimica Cosmochimica Acta, 55, 1675-1688.

Renne, P.R., Swisher, C.C., Deino, A.L., Karner, B.D., Owens, T, De Paolo D.J.,1988,

Intercalibration of standards, absolute ages and uncertainties in ^{40}Ar/^{39}Ar dating: Chemical Geology, 145, 117-152.

Wijbrans, J. R., Pringle M. S., Koppers A. A. P., & Scheveers R., 1995, Argon geochronology of small samples using the Vulkaan laser-probe: Proceedings Koniinkje Nederlandse Akademie Wetenschappen, v. 98, p.185-218.

APPENDIX 1 B. Thermoluminescence dating method (M. Frechen)

All measurements were carried out on the 4-11 µm grain-size fraction using the preparation technique described in Frechen et al. (1996) for all samples. All samples were irradiated in eight different dose steps (five discs per dose step) using a Cobalt-60 source. Alpha irradiation was undertaken by a 241Am source to determine the alpha effectiveness (a-value). As the 1-sigma standard deviation of the measured palaeodose equivalents of the a-values were large due to large scattering of the glow curves, an average value of 0.01 ± 0.002 was used for all samples. After irradiation all fine grain samples were preheated at 150°C for 16 hours in order to eliminate the unstable part of the glow curves. All discs were left at room temperature for at least 4 weeks after irradiation. Measurements were carried out using an automated Risö TL/OSL Reader. A filter combination of Schott BG-39 and Chance Pilkington HA-3 was placed between photomultiplier and aliquots. After the 25 seconds of IR shine down, carried out by an array of 32 diodes emitting a wavelength of 880 ± 80 nm, the same discs were measured immediately by TL. The aliquots were measured with a heating rate of 5°C/sec up to 450° C. Equivalent doses were obtained for the tephra samples by additive dose methods by integrating the 300-400°C range and the age plateau which is defined in an equivalent dose plot larger than 50°C yielding constant ED values (Berger 1991).

Luminescence Methods

Further information about principles of TL are found in Aitken (1985) and Wintle (1997). Thermoluminescence (TL) and Optical Stimulated Luminescence (OSL) is the light emitted from crystals like quartz, feldspar or zirconium when they are heated or stimulated with light after receiving a natural or artificial radiation dose. In nature the radiation results from the decay of radioactive isotopes like 235U, 238U, 235Th, 40K and some minor isotopes and cosmic rays. The luminescence clock (signal) is set to zero for volcanic material in respect to heating up of the minerals or growth and cooling of minerals and volcanic glass after eruption. With respect to volcanic glass the last cooling date of the minerals or glass or the eruption age will be determined.

The dating of volcanic material was attempted in the early 1970s when Wintle (1973) described anomalous fading by measuring feldspars from rhyolites near Naples and basalts from Iceland and France. Since that time it has been difficult to overcome the problem of anomalous fading which is understood as a rapid initial fading of the signal from feldspar after irradiation. This complicating property does not seem to conform a simple time dependent behaviour. A rapid initial fading is followed by a much slower TL loss with time. In the case of the Misti pumice samples, a delay of at least 4 weeks was applied between irradiation and TL measurements in order to minimise the effect of fading.

References

Aitken, M.J., 1985, Themoluminescence Dating: Academic Press, pp. 1-365, London.
Berger, G.W., 1991, The use of glass for dating volcanic ash by thermoluminescence: Journal of Geophysical Research, 96, 19705-19720.
Frechen, M., Schweitzer, U., and Zander, A., 1996, Improvements in sample preparation for the fine grain technique: Ancient TL, 14, 15-17.
Wintle, A.G.,1973, Anomalous fading of thermoluminescence in mineral samples: Nature, 245, 143-144.
Wintle, A.G., 1997, Luminescence dating: laboratory procedures and protocols: Radiation Measurements, 27, 769-817.

App. 1A - Table 1 : Ar dating analytical data.

Single grain laser step heating ; irradiation MC23, 5h

interfering reactions: $^{40}Ar/^{39}K$ = 0.0297, $^{36}Ar/^{37}Ca$ = 0.000284, $^{39}Ar/^{37}Ca$ = 0.000706

Step nb. or T °C	Atmospheric contamination (%)	^{39}Ar (%)	$^{37}Ar_{Ca}/^{39}Ar_K$	$^{40}Ar^*/^{39}Ar_K$	Age (Ma)		
Sample Mi 214, Biotite ; J = 13.24 ; (v1363)							
1	97.24	0.37	0.065	2.987	6.43	±	3.80
2	94.70	0.68	0.045	2.039	4.39	±	1.60
3	88.13	0.63	0.048	3.531	7.60	±	1.15
4	76.90	0.71	0.025	5.120	11.01	±	1.08
5	60.30	1.44	0.016	6.025	12.95	±	0.65
6	52.99	1.80	0.017	6.031	12.96	±	0.38
7	39.92	4.28	0.014	6.295	13.52	±	0.22
8	31.09	5.29	0.017	6.311	13.56	±	0.15
9	28.18	6.92	0.025	6.279	13.49	±	0.13
10	22.52	10.19	0.033	6.142	13.20	±	0.07
11	17.82	17.13	0.047	6.131	13.17	±	0.06
12	18.56	11.46	0.063	6.117	13.14	±	0.06
13	17.74	9.20	0.062	6.084	13.07	±	0.08
14	17.63	9.36	0.065	6.105	13.12	±	0.09
15	17.70	8.15	0.144	6.096	13.10	±	0.08
16	17.10	11.79	0.136	6.062	13.03	±	0.07
Fuse	23.46	0.59	0.123	5.987	12.87	±	0.98
				integrated age	12.91	±	0.04
Sample Mi 215, Biotite ; J = 13.0 (v1362)							
1	98.40	1.33	0.023	2.952	6.45	±	2.88
2	89.11	0.27	0.000	4.689	10.24	±	3.06
3	82.66	2.58	0.021	4.734	10.34	±	0.60
4	74.52	3.88	0.014	5.567	12.15	±	0.29
5	54.62	3.04	0.016	6.054	13.21	±	0.29
6	61.13	5.94	0.017	5.923	12.92	±	0.29
7	48.23	9.11	0.021	6.328	13.80	±	0.14
8	42.75	9.85	0.034	6.369	13.89	±	0.14
9	38.42	10.39	0.035	6.331	13.81	±	0.11
10	33.02	25.58	0.026	6.320	13.79	±	0.08
11	27.15	10.14	0.062	6.317	13.78	±	0.11
12	24.06	15.09	0.159	6.149	13.46	±	0.09
13	32.92	2.14	0.166	6.026	13.19	±	0.49
fuse	39.34	0.67	0.249	6.153	13.46	±	1.08
				integrated age	13.31	±	0.06

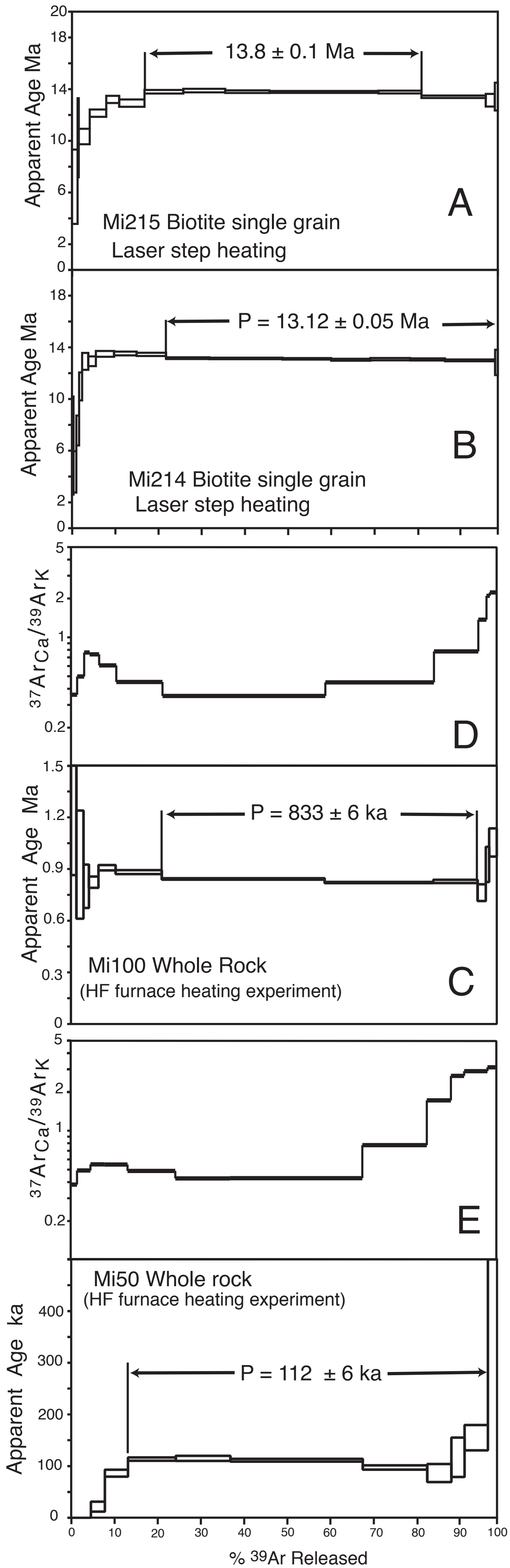
High frequency furnace step heating ; Irradiation (MC21) : 1.5 h with Cd shielding

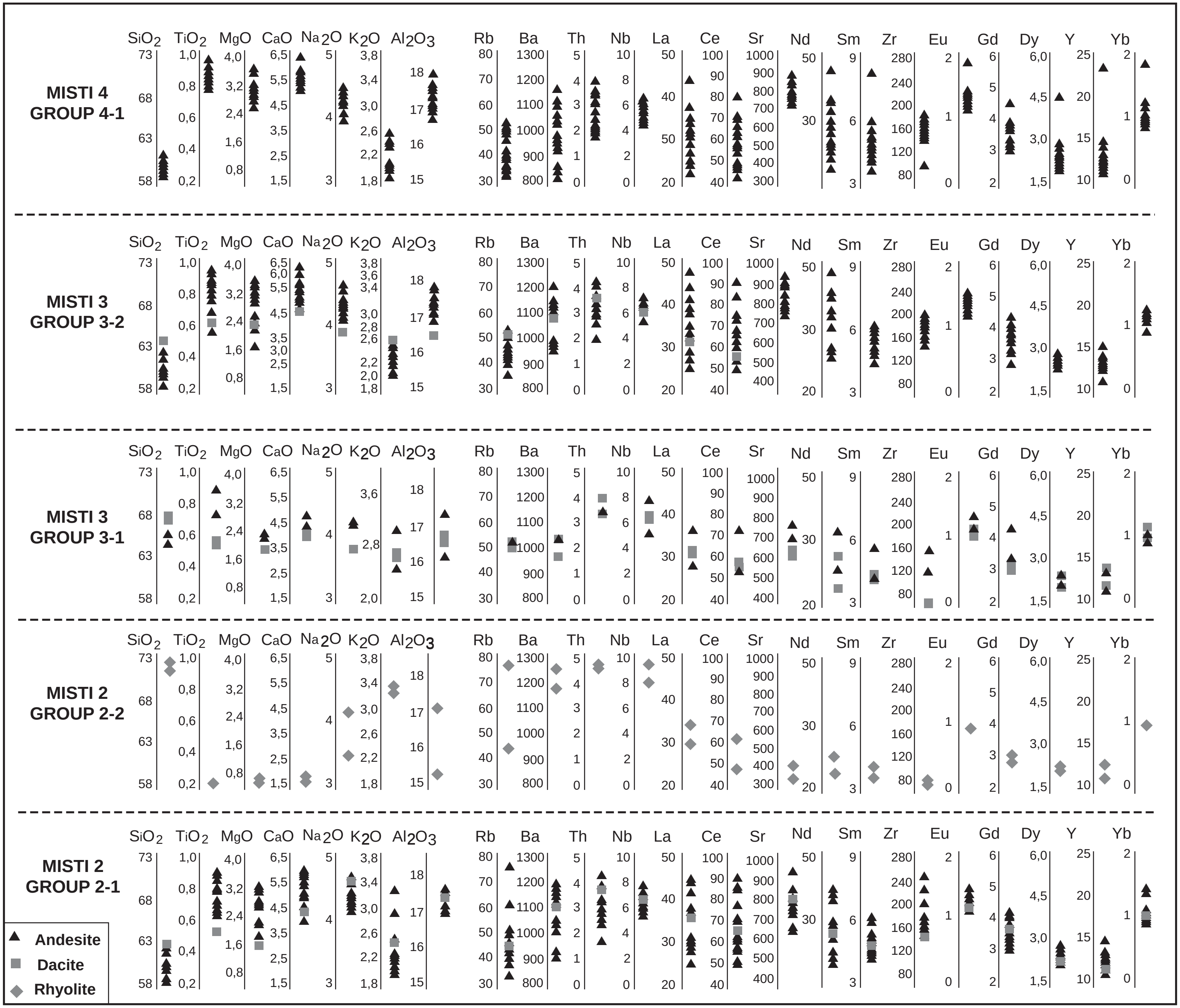
interfering reactions: $^{40}Ar/^{39}K$ = 0.001, $^{36}Ar/^{37}Ca$ = 0.000279, $^{39}Ar/^{37}Ca$ = 0.000706

Step nb. or T °C	Atmospheric contamination (%)	^{39}Ar (%)	$^{37}Ar_{Ca}/^{39}Ar_K$	$^{40}Ar^*/^{39}Ar_K$	Age (Ma)		
Sample Mi 100, Whole Rock (99 mg) J = 38.0 (M1236)							
400	99.88	0.00	0.748	3.806	2.579	±	16.527
500	98.70	1.29	0.354	2.206	1.495	±	0.630
550	98.29	1.66	0.491	1.366	0.926	±	0.314
600	96.32	1.29	0.753	1.180	0.800	±	0.126
650	84.65	2.23	0.728	1.215	0.824	±	0.033
700	62.35	4.01	0.598	1.339	0.908	±	0.015
750	61.53	10.87	0.445	1.301	0.882	±	0.011
850	33.59	38.24	0.347	1.243	0.842	±	0.004
950	24.76	25.50	0.442	1.212	0.822	±	0.004
1040	56.69	10.42	0.767	1.222	0.828	±	0.009
1150	87.45	1.92	1.351	1.125	0.763	±	0.048
1300	94.09	0.80	2.065	1.368	0.927	±	0.102
1450	92.67	1.77	2.196	1.556	1.054	±	0.082
				integrated age	0.835	±	0.010
Sample Mi 50, Whole Rock (134 mg) J = 39.5 ; (M1233)							
400	100.	0.00	1.047	-	-		
500	100.	1.42	0.383	-	-		
550	100.	3.16	0.492	-	-		
600	97.90	3.29	0.549	0.033	0.022	±	0.010
650	84.18	5.42	0.547	0.128	0.087	±	0.007
700	68.88	11.22	0.489	0.168	0.114	±	0.003
750	82.45	12.84	0.427	0.170	0.115	±	0.005
850	71.17	31.06	0.429	0.165	0.112	±	0.003
950	78.97	15.16	0.774	0.144	0.098	±	0.004
1050	96.69	5.67	1.717	0.128	0.087	±	0.017
1200	98.12	3.08	2.656	0.173	0.118	±	0.038
1350	96.09	5.50	2.888	0.229	0.156	±	0.025
1450	92.25	2.18	3.097	0.848	0.575	±	0.057
				integrated age	0.108	±	0.003

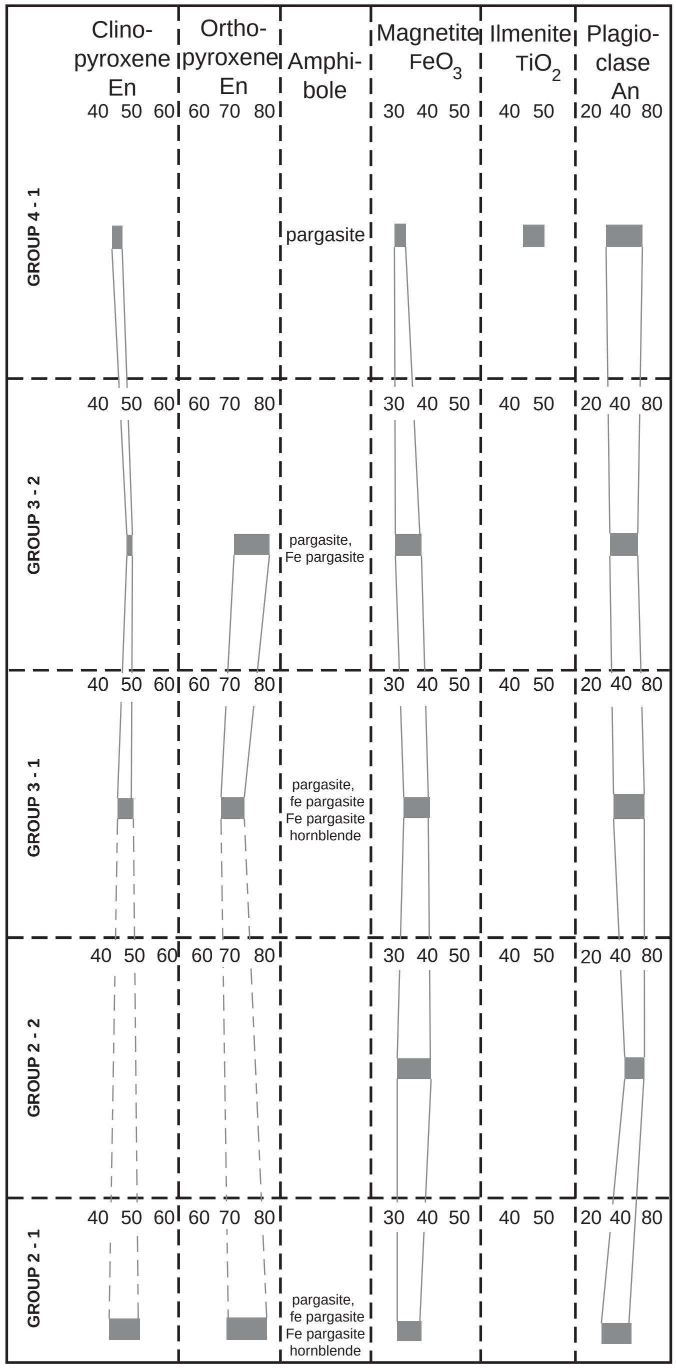
The whole rock sample analysis is performed with a mass spectrometer composed of a 120° M.A.S.S.E. tube, a Baur-Signer GS 98 source and a Balzers electron multiplier. For laser heating experiments, the gas extraction was carried out by a Coherent Innova 70-4 continuous laser. The mass spectrometer is a VG 3600 working with a Daly detector system. The typical blank values of the extraction and purification laser system are ranging from 9-5 x 10-13 ccSTP for 40Ar, 8-1 x 10-14 ccSTP for 39Ar, 2-1 x 10-13 ccSTP for 37Ar, and 7-3 x 10-14 ccSTP for 36Ar, measured every third step.

App. 1A - Fig. 1


13.8 ± 0.1 Ma
A
Mi215 Biotite single grain
Laser step heating
P = 13.12 ± 0.05 Ma
B
Mi214 Biotite single grain
Laser step heating
D
P = 833 ± 6 ka
Mi100 Whole Rock
(HF furnace heating experiment)
C
E
Mi50 Whole rock
(HF furnace heating experiment)
P = 112 ± 6 ka
Apparent Age Ma
Apparent Age ka
% 39Ar Released



MISTI 4
GROUP 4-1
MISTI 3
GROUP 3-2
MISTI 3
GROUP 3-1
MISTI 2
GROUP 2-2
MISTI 2
GROUP 2-1
SiO2 TiO2 MgO CaO Na2O K2O Al2O3
Rb Ba Th Nb La Ce Sr Nd Sm Zr Eu Gd Dy Y Yb
Andesite
Dacite
Rhyolite



App. 2B

(After Legendre, 1999)