equipped with photodiode-array detection. The fused silica capillaries used in the experiments were 53 cm in total length (45-cm effective length) with a 50-μm inner diameter and a 320-μm outer diameter. Running conditions were as follows: voltage, −20 kV; current, 17.6 μA; electrolytes, 5.5 mM 4-hydroxybenzoate and 0.5 mM tetradecyltrimethylammonium bromide, pH 11.6.
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$^{40}Ar/^{39}Ar$ Dating into the Historical Realm: Calibration Against Pliny the Younger

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Laser incremental heating of sanidine from the pumice deposited by the Plinian eruption of Vesuvius in 79 A.D. yielded a $^{40}Ar/^{39}Ar$ isochron age of 1925 ± 94 years ago. Close agreement with the Gregorian calendar–based age of 1918 years ago demonstrates that the $^{40}Ar/^{39}Ar$ method can be reliably extended into the temporal range of recorded history. Excess ^{40}Ar is present in the sanidine in concentrations that would cause significant errors if ignored in dating Holocene samples.

The ability to date geological events in the recent past is increasingly important in many areas of earth science. Applied to volcanogenic materials of high potassium content, the $^{40}Ar/^{40}K$ method of dating has been used to date samples into the Holocene, that is, less than 12,000 years old (*1*), although the precision is lower than is commonly reported for ^{14}C, uranium series, or other methods. The $^{40}Ar/^{39}Ar$ variant of this method, in which ^{40}K is measured by proxy through ^{39}Ar in irradiated samples (*2*), potentially allows recognition of xenocrystic contamination, nonatmospheric initial argon, and argon loss. For example, a young $^{40}Ar/^{39}Ar$ date of 5.3 ± 0.3 thousand years ago (Ka) has been reported (*3*) for sanidine from a tephra derived from the Mono Craters, California, whose age had been previously constrained by ^{14}C at 4.6 ± 0.1 Ka. Determination of this $^{40}Ar/^{39}Ar$ model age relied on the assumption that the significant scatter in apparent ages of single crystals was a result only of xenocrystic contamination.

Dating minerals in volcanic ejecta such as sanidine, which is potassium-rich and is thought to efficiently exclude initial argon at magmatic temperatures, is the most promising approach, although the possible effects of xenocrystic contamination (*4*) can be problematic. Analysis of single crystals, for example by laser fusion, can obviate xenocrystic contamination (*5*), but single crystals are seldom large enough to yield reliably measurable quantities of $^{40}Ar^*$ through radiogenic ingrowth in the Holocene. A relatively large spherical sanidine crystal 2 mm in diameter with 10 weight % K produces only about 2×10^{-18} moles of $^{40}Ar^*$ in 5000 years, and this quantity is one or two orders of magnitude smaller than the best attainable procedural background levels of ^{40}Ar.

We sought to investigate the limits of the $^{40}Ar/^{39}Ar$ method by application to ejecta from the infamous eruption of Vesuvius, which destroyed Pompeii and other Roman cities, as documented in the writings of Pliny the Younger (*6*). Vesuvius erupted pumice clasts up to 36 cm long beginning in the early afternoon of 24 August 79 A.D., 1918 calendar years ago. The white pumice that erupted initially is highly alkaline and contains up to 5% sanidine phenocrysts with 13.7 to 15.7 weight % K_2O (*7*), which are up to 8 mm in diameter. A sample of this pumice was collected at the Villa of Poppea, which was buried in the eruption and has only recently been excavated.

We divided irradiated sanidine from the pumice (*8*) into 12 samples totaling 0.430 g and analyzed them by incremental heating with a CO_2 laser (*9*). The samples yielded imprecise and dispersed apparent ages (*10*) of 24 to 521 Ka in the lower (1 to 2 W) laser power steps, which decreased and became more uniform (2 to 26 Ka) at 4 to 6 W, and became uniformly 2 to 3 Ka in the 7- to 20-W steps. The 1- to 2-W initial steps, each of which contained less than 0.1% of the total ^{39}Ar released, yielded $^{40}Ar/^{36}Ar$ values of 298 to 323, which are statistically indistinguishable at 95% confidence (critical value test) from the atmospheric ratio of 296 (*11*). A table of the argon isotopic data is available to *Science* Online subscribers at www.sciencemag.org.

Cast on an isotope correlation diagram (Fig. 1), the data define an isochron (*12*) that yields an intercept corresponding to $^{40}Ar^*/^{39}Ar_K = 0.07551 \pm 0.0037$, equivalent to an age of 1925 ± 94 years. The initial $^{40}Ar/^{36}Ar$ ratio defined by the isochron is 306.9 ± 1.3, significantly higher than the atmospheric value and indicative of a trapped component of extraneous ^{40}Ar. Excluding the 1- to 2-W steps, which are most likely to contain a significant proportion of adsorbed surficial argon (Fig. 1, inset), the remaining 33 steps yielded an isochron with indistinguishable age (1927 ± 102 years) and initial $^{40}Ar/^{36}Ar$ (306.9 ± 1.5) compared with results from the entire data set. The mean squared weighted deviation (MSWD) values of 0.51 ($N = 46$) and 0.55 ($N = 33$) indicate that observed scatter about the isochron is less than would be expected from the errors in the individual analyses; therefore, the errors on individual analyses are likely to have been slightly overestimated, or some error correlations are unaccounted for in the regression used. Because there is no objective basis for excluding the lowest temperature steps, we prefer the isochron obtained from all 46 analyses as the best estimate of the age of this sample.

The presence of extraneous ^{40}Ar is substantiated by the total gas results; the $^{40}Ar/^{39}Ar$ apparent age (*10*) calculated from the sum of all gas released is 3300 ± 500 years, clearly distinct within error from the known calendar age. With the known age, the con-

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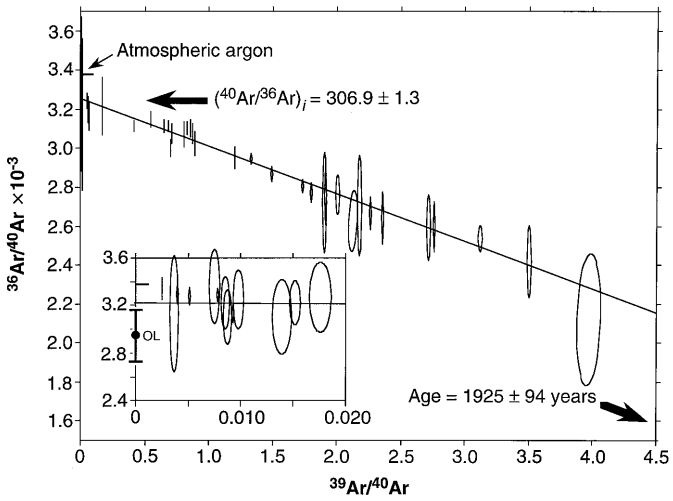

Fig. 1. Isotope correlation diagram showing isochron obtained by regression of 46 analyses. The inset shows detail of 13 analyses with the lowest $^{39}Ar/^{40}Ar$. The mean of five olivine analyses is shown on the $^{36}Ar/^{40}Ar$ axis of the inset with error bars, labeled OL. OL data are not included in the regression. Trapped component $[(^{40}Ar/^{36}Ar)_i]$ is shown by bold arrow.

centration of extraneous ^{40}Ar can be estimated from the weight of the sample (0.430 g), the total air-corrected ^{40}Ar released (2.9×10^{-14} mol), and the K content (12.5%) of the sanidine, yielding $(2.6 \pm 0.3) \times 10^{-14}$ mol/g. Uncertainties in mass spectrometer sensitivity calibration, sample weight, and K content limit the uncertainty to about ±10%. This concentration would translate, if unrecognized, to 1200 years of excess age during the Quaternary, and >10% error through the Holocene, a bias that is considerably larger than uncertainties for high-quality analyses.

Five unirradiated samples (20 to 75 mg each) of olivine from the pumice were degassed with a Nd–yttrium-aluminum-garnet (Nd-YAG) laser, yielding $^{40}Ar/^{36}Ar$ ratios (322 ± 10 to 385 ± 32) whose mean value (349 ± 24) is distinct at 95% confidence from the atmospheric ratio. The trapped component in the olivine is not distinguishable from that in the sanidine at 95% confidence, although it probably reflects an earlier stage in the isotopic evolution of excess argon in the magma.

The extraneous ^{40}Ar could be inherited (*13*), having been derived from incompletely degassed xenocrysts entrained from the magma conduit during eruption. The consistent results from 12 different samples, however, would require an improbably uniform admixture of such xenocrysts. More likely, the extraneous ^{40}Ar component is excess Ar entrapped in submicroscopic inclusions or defects within the sanidine during residence in the magma chamber (*14*). Whether the initial $^{40}Ar/^{36}Ar$ ratio of 307 determined by isochron regression reflects a magmatic argon isotopic composition or is biased by argon adsorbed after the eruption cannot be determined from our data.

Several aspects of laboratory procedure are most important in the ability to precisely resolve an $^{40}Ar/^{36}Ar$ date in Roman times: First, the broad-beam CO_2 laser system provides progressive, uniform heating with low backgrounds that appears to release nonradiogenic argon at lower temperatures than it releases $^{40}Ar^*$, which helps create spread on the isotope correlation diagram. Second, the mass discrimination and background corrections must be based on well-characterized and reproducible values. The short irradiation time (3 min) and use of cadmium shielding to reduce thermal neutron fluence (*15*) minimized the importance of the $(^{40}Ar/^{39}Ar)_K$ correction, which in this case would add only 20 years to the calculated age if ignored. Finally, the use of an appropriately aged (Quaternary) neutron fluence monitor reduced the dynamic range of isotopic ratios to be measured, which minimizes potential problems resulting from peak-tailing or detector nonlinearity.

Thus despite the presence of excess ^{40}Ar, a sample less than 2000 years old can be dated with better than 5% precision, validating $^{40}Ar/^{39}Ar$ dating as a reliable geochronometer into the late Holocene. These results also demonstrate that excess ^{40}Ar can be identified in volcanic sanidine, and that while perhaps negligible in pre-Holocene rocks, it has important consequences for samples at the limit of the method's applicability. Further improvement in precision of $^{40}Ar/^{39}Ar$ analysis of historically dated samples may lead to welcome refinements in the ages of neutron fluence monitors, currently a limitation on the accuracy of the $^{40}Ar/^{39}Ar$ method (*16*). Our results also substantiate validity of the $^{40}Ar/^{39}Ar$ method in establishing the eruptive histories of populated active volcanic regions, where such information is vital to volcanic hazard assessment (*17*).

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9. The samples weighed ~48 mg each and were loaded into 5-mm-diameter by 3-mm-deep wells in a copper disc. We degassed each sample in three to five steps up to fusion with a CO_2 laser using an integrator lens to provide uniform heating over the wells. The laser system is described by W. D. Sharp and A. L. Deino (*18*). The CO_2 laser allows controlled and progressive degassing of optically transmissive materials such as sanidine with minimal contribution to background levels of Ar [W. C. McIntosh and M. T. Heizler, *U.S. Geol. Surv. Circ.* **1107**, 212 (1994); (*18*)]. Background levels (blanks) of argon isotopes were measured between every one or two samples, and corrections were based on regression of the values over time. Mass discrimination was monitored by analysis of 45 samples of purified air interspersed with analysis of the unknowns, yielding a mean value of 1.0026 ± 0.0002 per atomic mass unit based on a power law relation.
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