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ESR dating applied to optically bleached quartz - a comparison with $^{40}\text{Ar}/^{39}\text{Ar}$ chronologies on Italian Middle Pleistocene sequences

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Abstract

The geological sequences of numerous Lower and Middle Palaeolithic sites of central and southern Italy, found in fluvio-lacustrine contexts and rich both in archaeological and palaeontological remains, have recorded various volcanic events all along the Middle Pleistocene timescale. These sedimentary sequences made of detritic and volcanic materials are suitable to compare independent numerical geochronological methods and thus develop a multi-method approach relying especially ESR method applied to optically bleached fluvial quartz and the $^{40}\text{Ar}/^{39}\text{Ar}$ on single grain isotopic method applied to potassium feldspars. In this present paper, geochronological data obtained using these two methods were used on several Middle Pleistocene Italian sites including volcanic and fluvial but also archaeological levels: Isoletta and Lademagne in Lazio and Notarchirico in Basilicata. In this contribution, ESR age estimates were performed using a multi-centre approach from Al, Ti-Li and Ti-H centres. We demonstrate for these sites that ESR-based framework is overall consistent with the $^{40}\text{Ar}/^{39}\text{Ar}$ chronology that over the 700 and 350 ka time window. This comparison validates the multi-centre approach proposed and demonstrates that the use of Ti-H for samples with equivalent doses higher than 280-300 Gy leads to systematic age underestimates.

Keywords: ESR dating, optically bleached quartz, $^{40}\text{Ar}/^{39}\text{Ar}$ dating, Middle Pleistocene Italian sites

38 1. Introduction

39 Since the mid-1990s, Quaternary river deposits have been the subject of in-depth multidisciplinary
40 studies, including systematic dating. This kind of research, partly initiated by a team of researchers
41 from the Muséum National d'Histoire Naturelle (MNHN) in Paris, France, has led to the electron spin
42 resonance (ESR) dating of stepped and embedded terrace systems for a large number of valleys in
43 Europe and Asia (e.g., Laurent et al., 1994, 1998; Voinchet et al., 2004, 2010, 2013; Despriée et al.,
44 2011). These numerous works have contributed to establish a detailed chronostratigraphic framework
45 for these river sequences covering most of the Pleistocene. Associated with some of these fluvial
46 formations, tens of Palaeolithic localities with lithic assemblages have also been dated by the same
47 way. The results obtained for each valley are consistent with each other, producing a robust
48 geochronological framework, although there is often no independent age control available so far.
49 Indeed, due to the nature or the chronology of the studied sedimentary sequences, ESR dating of
50 quartz grains has been for a long time one of the very few numerical dating methods that could be
51 used. In some area, the absence of fossil faunal remains, linked to the extreme acidity of quartz sands,
52 precludes any biochronological estimation for the archaeological localities, as well as the use of the
53 ESR/U-series method applied to teeth. In addition, the fluvial sediments are often coarse and
54 unconsolidated and therefore not suitable for magnetostratigraphic analysis (Parés et al. 2013). Finally,
55 the application of luminescence dating of sediments using standard procedures (OSL, IRSL, TL) was
56 long limited to Middle and Upper Pleistocene deposits (Arnold et al., 2003). As a result, for a long-
57 time alternative dating estimates derived from independent methods has not been possible for the
58 oldest deposits and sites of these valleys. Although recent methodological developments have shown
59 that a multi-technique dating approach can now be confidently envisaged to date Early to Middle
60 Pleistocene fluvial deposits (e.g., Duval et al., this volume) this overall lack of independent age control
61 is considered by many as prejudicial. Its casts doubt on the relevance of the obtained chronology, for
62 example regarding the exact period of arrival of the first human migration in Western Europe (Muttoni
63 et al., 2013, Muttoni et al., 2018)

64 Fortunately, the particular case of central and southern Middle Pleistocene river sequences in central
65 and southern Italian peninsula, where fluvial deposits include K-rich volcanic material, allows the

66 straightforward comparison between ESR and an independent reference radioisotopic method,
67 $^{40}\text{Ar}/^{39}\text{Ar}$. Indeed, in this area, the presence of numerous volcanoes, active during the Middle
68 Pleistocene and located mainly along the Tyrrhenian margin, has led to the emission of large and
69 widespread tephra. In consequence, volcanic materials are frequent into sedimentary sequences,
70 sometimes as primary tephra layers interspersed into the sequences or mixed with fluvial deposits. In
71 this case, the volcanic materials are not in primary position (i.e. within a volcanic deposit) but
72 reworked, sometimes by the river (secondary position). In this case, $^{40}\text{Ar}/^{39}\text{Ar}$ studies show the
73 presence of grain populations of various ages, the youngest being considered as the last volcanic event
74 locally recorded before the deposition of the analysed sediment. In other words, volcanic material
75 could be considered either as linked to a primary deposition or as a secondary one indicating the last
76 volcanic event recorded in the area. In central and southern Italy, such volcanic materials recovered in
77 primary or secondary position were dated by $^{40}\text{Ar}/^{39}\text{Ar}$ allowing the establishment of a robust and
78 precise chronostratigraphic framework (e.g., Pereira et al., 2018).

79 This framework offers the possibility to a comparison between palaeodosimetric and radio-isotopic
80 results. In the present contribution, we will compare ESR ages obtained on quartz using the multi-
81 centre method (ESR-MC) with $^{40}\text{Ar}/^{39}\text{Ar}$ dates on single feldspar grains in order to evaluate (i) the
82 accuracy of the ESR results and (ii) the reliability of the ESR-MC approach. Of course, it is worth
83 noticing that such comparison is only possible if stratigraphic knowledge of the sampling levels
84 confirms the sub-contemporaneity of the studied geological layers and of the evidenced volcanic
85 events. At the end, it should permit to improve the chronology of the studied sequences and, if the
86 data agree, to reinforce the robustness of the general chronological framework.

87

88 **2. ESR dating method**

89 Methodological developments in the ESR dating of optically bleached quartz grains over the two last
90 decades have made it a reference method for the dating of Quaternary fluvial deposits (Antoine et al.,
91 2007; Chauhan et al., 2017). Among these developments, one of the most important is the use of the
92 so-called multiple centre (MC) approach based on the study of several light-sensitive paramagnetic

93 centres in quartz (Toyoda et al; 2000, 2006; Tissoux et al., 2007; Duval and Guilarte, 2015; Duval et
94 al., 2015).

95 Concerning the ESR dating of sedimentary quartz grains found in alluvial terrace deposits, it is
96 essential that a "reset" of the geochronometers (here, the paramagnetic centres) occurred before
97 sediment deposition. Such reset is essential in order to date this deposition event and not the formation
98 of the quartz itself. This reset depends on the exposure to UV sunlight and is called optical bleaching.
99 It occurs during river transport before the deposition of the sediment (Yokoyama et al., 1985;
100 Voinchet et al., 2003; Voinchet et al., 2007). The main challenge for the ESR dating method lies in the
101 estimation of the bleaching rate of the analyzed quartz grains during the transport, which may
102 significantly varies among centres. The ESR-MC method is based on the systematic measurement of
103 both aluminum (Al) and titanium (Ti) centres (mainly, Titanium-Lithium (Ti-Li) and Titanium-
104 Hydrogen (Ti-H)) in a given quartz sample.

105 The Al centre has long been the most widely used in ESR dating of quartz (Voinchet et al., 2004)
106 because aluminum is particularly abundant in this mineral and the corresponding ESR signal is easily
107 measured and observed. In addition, this Al-centre has a long-life expectancy due to a thermal stability
108 (for temperatures below 100°C) that exceeding six million years (Toyoda et al, 1991). It can thus be
109 used to date samples as old as several million years (Laurent et al., 1998; Gouveia et al., 2020).
110 Nevertheless, the fact that this centre requires a long exposure to light to be bleached (about 1600
111 hours – Toyoda et al, 2000; Voinchet et al, 2003) and the fact that, even after such a long exposure, a
112 residual ESR signal is still observed, can sometimes be problematic. Indeed Al-centre is partially
113 optically bleached and its signal intensity decreases in relation to time exposure to solar light, until it
114 reaches a plateau value corresponding to a residual signal attributed to “Deep Aluminium Traps”
115 (DAT) (Tissoux et al 2013). These traps or centres cannot be reset by an exposure to sunlight. A
116 wrong estimation of the ratio between DAT and OBAT (Optically Bleachable Aluminium Traps) can
117 lead to a wrong estimation of the equivalent dose D_E and by extension of the age.

118 In comparison, the Ti centres are less frequently observed in quartz samples and their ESR intensities
119 may be significantly smaller than those of the Al centre. For dating, two Ti centres can mostly be used,
120 the Ti-Li and Ti-H centres. These two centres have signals that are much more light-sensitive than the

121 Al and which therefore usually totally reset during sediment transport. Typically, Ti-H centre can be
122 zeroed or bleached within a day, while Ti-Li centre needs about 20 days for the complete zeroing
123 (Toyoda et al., 2000; Rink et al., 2007; Tissoux et al., 2007). However, Ti-H is also much more
124 radiosensitive than the Al and Ti-Li centre and saturates much faster (Duval and Guilarte, 2015).
125 Consequently, the Ti-H centre is usually considered as more suitable for small equivalent dose
126 estimates (few grays to tens of grays) and/or for recent samples (Miallier et al., 1994) between tens of
127 thousands of years (ka) and a few hundred of ka. The joint use of the Al and Ti centres, or MC
128 approach, is therefore intended to better estimate the quality of the sediment bleaching during
129 transport. This approach has been used several times in recent years, and several studies have shown
130 its potential in a variety of sedimentary contexts and for periods ranging from the Lower to the Upper
131 Pleistocene (Bartz et al. 2018, Duval et al. 2015, this volume; Gouveia et al. 2020; Kreutzer et al.
132 2018;).

133

134 3. Sampling

135 Three Italian archaeological sites were sampled in the frame of this work: Isoletta and Lademagne
136 sites in Lazio and Notarchirico in Basilicata (Fig.1). In order to limit the risks of bad bleaching, linked
137 to a transport of the quartz grains in opaque water, the fluvial sediments sampled for ESR dating are
138 made of fine sands without silt or clay in the matrix (Voinchet et al, 2015). These sediments have been
139 carried by clear water river, without any fine particles in suspension.

140 All of the analyzed geological levels correspond to fluvial deposits, containing fine quartz grains and
141 characterized by the occurrence of volcanic minerals, allowing the use of the $^{40}\text{Ar}/^{39}\text{Ar}$ single crystal
142 approach. The $^{40}\text{Ar}/^{39}\text{Ar}$ isotopic technique is one of the most accurate and precise dating methods
143 available for Middle Pleistocene time range (Pereira et al., 2015; 2018). In fact, the individual dating
144 of volcanic crystals allows the identification of the corpus of volcanic events reworked and drained in
145 sedimentary layers. In a geological layer, the juvenile crystals population highlighted by the related
146 probability diagram gives chronological information on the age of the youngest volcanic event
147 reworked (see Pereira et al., 2015, 2018 for further explanations). The uncertainties obtained on the
148 calculated ages are ranging between 1 to 5 % (2σ analytical uncertainty).

149 The volcanic materials found at Isoletta and Lademagne sites are originated from the nearby volcanic
150 complexes of Colli Albani or Ernici mounts (Pereira et al., 2018), whereas at Notarchirico they
151 derived from the mount Vulture stratovolcano activity (Lefèvre et al., 2010; Pereira et al., 2015).

152

153 3.1 Isoletta site

154
155 Isoletta is located in the Ceprano tectonic basin at the confluence of the Liri and Sacco Rivers, near the
156 town of Pofi in the Frosinone Basin, few kilometres south-east of the Campogrande/Ceprano *Homo*
157 *heidelbergensis* site location (Fig. 1). It displays a typical alluvial terrace stratigraphic sequence,
158 particularly thick (more than 30 m) (Fig.2. and 5). This sequence was punctually exposed thanks to the
159 high-speed train railways construction and was sampled in 2000. Three main units were then
160 individualized: gravels at the base, overlain by very fine sediments (silts and clays) rich in organic
161 matter and finally an alternation of medium to coarse sand beds over more than 10m (Fig.2). In this
162 sequence, two archaeological levels were identified (Fig.2): the first one in basal gravels, is
163 characterized by the presence of Mode 1 lithic (cores-and-flakes type) and bones industries while the
164 second one, in a sandy layer of the upper unit, has displayed Mode 2 (Acheulean) lithic artefacts and
165 “Galerian” faunal assemblage (corresponding to the first half of the Middle Pleistocene) (Biddittu,
166 1974, Sardella et al., 2006).

167 The gravel level at the bottom and the sand levels of upper sequence are very rich in reworked
168 volcanic material (Fig.2.). Four samples were taken from different levels for ESR dating: the first in
169 the coarse level of the base (ESR 1) and the three others (ESR 2, 3 and 4) in three decimetre-thick
170 medium to fine sand beds showing fluvial sedimentation features. ESR 2 sample corresponds to the
171 higher archaeological level (“Acheulian level”, see GA6Z, Pereira et al., 2018). The basal part of the
172 sequence as well as the levels having provided ESR2 and ESR4 contain volcanic minerals (potassium
173 feldspars) that have been dated by $^{40}\text{Ar}/^{39}\text{Ar}$. The $^{40}\text{Ar}/^{39}\text{Ar}$ dated feldspars of this sequence are in
174 secondary position (it is not a tephra level but a fluvial deposit). This means that the age of this deposit
175 may be similar or younger than the $^{40}\text{Ar}/^{39}\text{Ar}$ estimate. Nevertheless, the $^{40}\text{Ar}/^{39}\text{Ar}$ age is constrained
176 by the higher levels in the stratigraphy which indicate that the river uptake of these volcanic minerals
177 occurred shortly after their primary deposit (Pereira et al, 2018).

178 3.2 Lademagne site

179 Lademagne site, located 5 km from Isoletta in the Ceprano tectonic basin was discovered in 1965 (Fig.
180 1). The stratigraphic sequence is mainly composed of sandy-gravelly deposits inter-bedded with
181 volcanic rich sediments (Fig.3) and is very similar to the upper part of Isoletta's sequence. Two
182 archaeological layers with both Mode 2 industries are mentioned in the literature (Biddittu et al., 2012)
183 and present palaeontological and archaeological assemblages close to those of Isoletta upper level
184 (Biddittu et al., 2012). One sample was taken for ESR dating at the top of the stratigraphy (named Lad
185 Sup) and can be compared with one sample taken in the same level for $^{40}\text{Ar}/^{39}\text{Ar}$ dating on single
186 crystal (named also Lad Sup in Pereira et al, 2018). As at Isoletta, the feldspars of this sequence are in
187 secondary position and provide therefore maximum ages to the sediment deposition.

188

189 3.3 Notarchirico

190 Discovered in 1979, Notarchirico site is an Early Middle Pleistocene site of the Venosa basin (Fig.1.)
191 (Piperno et al., 1999). The sequence is seven metres thick and is mainly composed of volcanoclastic
192 sediments deposited and reworked in a fluvial environment. Many stratigraphical levels are rich both
193 in volcanic materials coming from the close Monte Vulture stratovolcano and quartz transported by
194 the river (Fig.4. and 5).

195 The site is characterized by the record of repeated periods of human occupation, most part of them
196 linked to butchery activities. A total of eleven archaeological layers (Fig. 5. Piperno et al., 1990, 1999)
197 have been identified (Piperno and Tagliacozzo, 2001). One femur attributed chronologically to *Homo*
198 *heidelbergensis* has been discovered in the upper part of the sequence and some of the archaeological
199 levels (levels A, A₁, B, D and F) contain bifaces referred to Mode 2 technology (Piperno and
200 Tagliacozzo, 2001).

201 Three levels have been sampled at Notarchirico, one in the middle part of the sequence (level 2-6,
202 Notarchirico 2-6 sample) and two in the newly investigated lower part (level H1 and H1c,
203 Notarchirico H1 sample and Notarchirico H1c sample) (Fig.4. and 5). For now, only level 2-6 has
204 been dated by ESR applied on quartz (Al) and $^{40}\text{Ar}/^{39}\text{Ar}$ methods (Pereira et al., 2015) applied on

205 secondary deposit feldspars. It should be noticed that level 2.4 located between levels 2-6 and H1-H1c
206 corresponds to a tephra in primary position.

207

208 **4. Material and method**

209 4.1 ESR dating

210 Sediment samples were prepared according to the procedure used in the Muséum National d'Histoire
211 Naturelle (MNHN) laboratory (Voinchet et al, 2004). Firstly, the 100-200 μm grain size fraction, the
212 most easily bleached during river transport (Voinchet et al. 2015), was collected by wet sieving. The
213 organic matter was removed by an attack with hydrogen peroxide (30%) and the carbonates were
214 destroyed using hydrochloric acid (36%). After ultrasonic use, in order to break the weakened minerals
215 with cleavage plane, the samples were then attacked with HF (40%) during 1h 40min to firstly destroy
216 the feldspar grains and then to remove the external part of the quartz grains. We observe that the
217 etching effect varies in thickness between 10 to 20 μm depending of the grain shape. Recent works
218 have demonstrated that the previously recommended 40min-long attack was sometimes not enough to
219 remove all the feldspar grains, especially in case of very feldspar rich sediments (Tissoux et al, 2017).
220 A new HCl attack eliminates then the fluorides formed during this etching. The heavy minerals and
221 the magnetic minerals are then removed with a sodium polytungstate heavy liquor at $d=2.72 \text{ g/ml}$ and
222 with magnets respectively.

223 The quartz grains thus separated were dated using the Multiple Aliquots Additive Dose (MAAD)
224 method. Each sample was divided into 11 aliquots (each one, around 100 mg, composed by several
225 thousand grains). Nine of them were irradiated using a ^{60}Co source (CEA, Saclay) with a dose rate of
226 $260 \pm 20 \text{ Gy/h}$. The following doses were applied to these aliquots: 264, 431, 653, 1048, 1663, 2640,
227 4460, 8010, 12500 Gy. In order to evaluate the residual non-bleachable ESR signals from the Al
228 centre, one aliquot was exposed to a SOL2 sunlight simulator (Dr Hönle) for about 1600h. The last
229 aliquot (natural aliquot) was neither irradiated nor exposed to sunlight.

230 All aliquots were then measured by ESR at the MNHN dating laboratory (Paris, France), using an
231 EMX Bruker X-band spectrometer with a high sensitivity spherical cavity. These measurements were
232 performed at low temperature ($\sim 100 \text{ K}$) by cooling the cavity with liquid nitrogen.

233 To apply the multi-centre method as defined by Toyoda et al (2000), the ESR signal intensities of the
234 Al and Ti centres (Ti-Li and Ti-H) were measured. The ESR intensities of these different centres were
235 measured on a single spectrum (fig.6) using the following acquisition parameters: a 5 mW microwave
236 power, 1024 points resolution, 20 mT sweep width, 100 kHz modulation frequency, 0.1 mT
237 modulation amplitude, 40 ms conversion time, 20 ms time constant. Two cumulative scans were
238 performed to reduce background noise on the Ti signals. The signal intensity of Al centre was
239 measured between the top of the first peak at $g=2.018$ and the bottom of the 16th peak at $g=1.993$
240 (fig.6) of the Aluminum hyperfine structure (Toyoda and Falguères, 2003). The ESR intensity of the
241 Ti-Li centre was determined by measuring the difference between the peak top ($g= 1.913$) and the
242 baseline (Toyoda et al, 2006, Tissoux et al, 2007, Duval et Guilarte, 2015), while the intensity of the
243 Ti-H centre was measured between the peak apex ($g= 1.917$) and the baseline (fig.6) (Toyoda et al,
244 2006, Tissoux et al, 2007, Duval et al, 2015).

245 Due to the angular dependence of the signal, linked to the heterogeneity of the grains orientations in
246 the ESR magnetic field, each aliquot of a given sample was measured 3 times after a tube rotation of
247 about 120° of its initial position in the cavity. In addition, the measurements were repeated three times
248 on different days to test the repeatability of the measured intensities and as a result of the equivalent
249 dose obtained. As a result, nine intensities were obtained for each measured signal (Ti-Li, Ti-H and
250 Al) in each aliquot of all quartz samples studied. ESR intensities are calculated using the average of
251 the nine measurements. The variation between the nine intensities of each aliquot measured on the
252 three days does not exceed 5%. If a measurement exceeds this percentage, it was removed from the
253 calculation, and a new measurement was made to determine if the previous value was due to a one-
254 time event.

255 For Al signals, the value of the ESR intensity of the bleached aliquot was systematically subtracted
256 from the ESR intensities of the other aliquots to account the centres that cannot be bleached by light
257 (DAT, Tissoux et al., 2012). The bleaching rate δ_{bl} (%) is then determined by comparison of the ESR
258 intensities of the natural and bleached aliquots ($\delta_{bl} = ((I_{nat} - I_{bl}) / I_{nat}) \times 100$).

259 After normalization of ESR intensities by aliquot mass and receiver gain, the equivalent doses (D_E)
260 were then determined from the averaged ESR intensities using a coupled exponential and linear fitting

261 function (E+L) for Al and Ti-Li (Duval et al, 2009, Duval, 2012; Voinchet et al., 2013). By limiting
262 the curve to the first six points (from natural to the 1663 Gy point) it is also possible to use a single
263 saturating exponential function for the Ti-Li D_E determination. For Ti-H centre, due to the shape of
264 growth curve (fig.7), we tested two functions (fig 7.), Ti-2 function by considering all the data points,
265 and single saturating exponential (SSE) one by considering only the points of the curve corresponding
266 to its increasing part (from natural to the 1663 Gy point).

267 Dose response curve fitting and D_E evaluation was performed using with Microcal OriginPro 8
268 software with $1/I^2$ weighting

269 The dose rate (D_a) determined from the sum of the alpha, beta, gamma and cosmic-ray contributions.
270 Gamma dose rate was determined by *in situ* measurements directly at the sampling point using an
271 Inspector 1000 gamma spectrometer (Canberra[®]), except for the Isoletta section sampled in 2000, i.e.
272 before the systematic use by our team of gamma spectrometer on the field, and now not yet accessible.

273 These *in situ* gamma doses were estimated using the threshold approach (Mercier and Falguères 2007).

274 External alpha and beta contributions were calculated from the sediment radioelement contents (U, Th
275 and K) as determined in the laboratory by high resolution and low background gamma-spectrometry.

276 The internal dose rate was considered as negligible because of the low contents of radionuclides
277 usually found in quartz grains (e.g., Murray and Roberts 1997; Vandenberghe et al. 2008). Age
278 calculations were performed using the dose-rate conversions factors from Guérin et al (2011) and a k-
279 value of 0.15 ± 0.1 (Yokoyama et al., 1985). Alpha and beta attenuations estimated for the selected
280 grain sizes (100-200 μ m) from the tables of Brennan et al., (1991) and Brennan (2003) respectively.

281 Alpha contribution takes account of an etching of 10 to 20 μ m of the grains. This difference of 10 μ m in
282 the thickness removed by the acid attack induces an age variation of 1 to 2% depending on the samples
283 and on its radioactive environment. Water contents (W%) were estimated by the difference in mass
284 between the natural sample and the same sample dried for a week in an oven at 50°C and water
285 attenuation were then determined using formula from Grün (1994). The cosmic dose rates were
286 calculated from the equations of Prescott and Hutton (1994). ESR age estimates are given with one
287 sigma error range. The doses rate and ages were calculated using a specific Microsoft[®] Excel template
288 including data mentioned previously.

289 When Al and Ti results agree with 1σ , weighted average ages combining the different ESR centres,
290 were calculated using IsoPlot3.0 (Ludwig, 2003). Mean Square of Weighted Deviates (MSWD) and
291 Probability (P) are then given for each result.

292

293 4.2 $^{40}\text{Ar}/^{39}\text{Ar}$ analyses

294 The single crystal dating using $^{40}\text{Ar}/^{39}\text{Ar}$ isotopic method is actually one of the most accurate methods
295 available for Middle Pleistocene time range (Pereira et al., 2015; 2018) and gave us the possibility to
296 date and identify the volcanic events recorded in sedimentary layers. In central Italy, the studied
297 deposits could contain minerals such as sanidines or feldspathoids leucites that have up to 11 to 18 %
298 of K. We therefore use mainly these minerals to establish our $^{40}\text{Ar}/^{39}\text{Ar}$ chronology (see Pereira et al.,
299 2015, 2018). The analytical protocols followed and the details about the $^{40}\text{Ar}/^{39}\text{Ar}$ ages mentioned in
300 this study were presented in details in Pereira et al. (2015, 2018) or Moncel et al. (2018). All $^{40}\text{Ar}/^{39}\text{Ar}$
301 ages discussed hereafter are calculated using the potassium total decay constant of Steiger and Jäger
302 (1977) and the monitor standard ACs-2 dated at 1.193 Ma. We are fully aware than other calibrations
303 exist such as the total decay constant of Renne et al. (2011) and the ACs-2 at 1.1891 Ma (e.g. Niespolo
304 et al., 2017) but there is not matter for the purpose of this article, considering that the implied age
305 difference of $\leq 1\%$ is negligible compared to the uncertainties of the ESR method. We therefore in the
306 scope of this contribution do not discuss the various parameters than can be used to calculate $^{40}\text{Ar}/^{39}\text{Ar}$
307 ages. These ages are given with 2σ analytical uncertainty.

308

309 5. Results and discussion

310

311 U, Th and K concentrations of the different sediment samples are shown in table 1 and external dose
312 rates (alpha, beta gamma and cosmic doses), water contents (W%), bleaching rates (Bl%), and
313 equivalent doses with indication of the quality of the ESR growth curve fitting (r^2) are given in table 2.

314

315 5.1. ESR results: general comments

316 The Al centre could be measured in all our samples. Similarly, the Ti-Li centre was measured for
317 almost all these samples, with the exception of Notarchirico 2-6. For this sample, Ti signal intensity
318 was too weak and too close to background noise to be reliably evaluated, even with two scans. It is
319 worth noticing that if Ti signal intensity is extremely low for Notarchirico 2-6 quartz sample, this was
320 not the case for the other Notarchirico samples from levels H1 and H1c, for which the use of multi-
321 centre approach was therefore possible.

322
323 For Ti-Li, the equivalent doses (D_E) were determined following two different approach: firstly, using
324 a coupled exponential and linear fitting function (E+L) (Duval et al, 2009, Duval, 2012; Voinchet et
325 al., 2013). Secondly using a single saturating exponential function by limiting the curve to the first six
326 points (from natural to the 1663 Gy point). The results of the two approaches are relatively similar and
327 are presented in Table 2. We have chosen to use the doses determined using the E+L function for the
328 age calculation. However, since the intensity of Ti-Li does not decrease for high doses, we did not use
329 the Ti-2 function proposed by Duval and Guilarte (2015).

330 The Ti-H centre has only provided useful results for samples from Isoletta and Notarchirico H1 and
331 H1c levels. The Ti-H signal frequently shows a signal-to-noise ratio lower than that of Al or Ti-Li
332 signals, and it is sometimes impossible to obtain meaningful ESR intensities. It is the case for the
333 Lademagne sample for which Ti-H signal cannot be differentiated from the background ESR noise.
334 The shape of the curves led us to test two different approaches for the determination of D_{ES} , firstly,
335 using the Ti-2 fonction (Duval et Guilarte, 2015) by considering all the data points, and secondly using
336 a single saturating exponential (SSE) by considering only the points of the curve corresponding to its
337 increasing part (lowest added doses, between natural and 1663 Gy).

338 For this Ti-H centre, the D_E values obtained using SSE and Ti-2 functions are quite identical and
339 within $1-\sigma$ error (table 2), except for one sample (ESR3). Consequently, the choice of the fitting
340 function has a very limited impact on the dose estimates. The results are extremely close and we have
341 chosen to use only the SSE results, which after Woda and Wagner (2007) describe more the physical
342 filling phenomenon of ESR centres. Consequently, final Ti-H ESR age estimates were therefore
343 calculated in the present study using the SSE function D_E .

344

345

346 5.2 Isoletta

347 At Isoletta, the $^{40}\text{Ar}/^{39}\text{Ar}$ ages of the levels containing tephra constrain the deposition of river
348 sediments between 403 and 365 ka. The ESR results obtained from Ti-Li and Al centres are consistent
349 within 1σ with the available $^{40}\text{Ar}/^{39}\text{Ar}$ ages, with the exception of sample ESR 1. For this sample, the
350 three centres give very different and clearly overestimated results, indicating both a poor bleaching of
351 Al and Ti-Li centers – at least – and raises questions about the dose rate evaluation (Tab. 3).

352 For ESR2 sample, the use of Ti-H centre provides strongly younger ages, while, for ESR4 and ESR3
353 the three ages are close and coherent with $^{40}\text{Ar}/^{39}\text{Ar}$ ages. For these two samples, the equivalent doses
354 obtained using both Al and different Ti centres are lower than 300 Gy. In contrast, the Ti-H yields
355 much smaller De values compared with Al and Ti-Li when De values $>1,000$ Gy, i.e. for sample ESR
356 2. Leaving aside the possibility of incomplete bleaching of the Al and Ti-Li signals, this would suggest
357 that the Ti-H centre tends to saturate for doses above 300-400 Gy and cannot provide reliable dose
358 estimates above this dose. These results agree with previous observations (Tissoux et al, 2007; Duval
359 and Guilarte 2015).

360

361 The relatively large error ranges observed for these ESR ages originate from the D_E evaluation, and are
362 explained by a relatively poor goodness-of-fit achieved for the dose response curves, with r^2 values
363 sometimes lower than 0.99 (Tab 2). For Isoletta samples when D_E values obtained using the different
364 centres were similar, a weighted average age was calculated for the corresponding level. Such
365 weighted average ages were calculated using IsoPlot 3.0 (Ludwig, 2003) and given at 95 % of
366 confidence.

367 For ESR 3 and ESR 4 samples, the weighted average age was calculated using the three different
368 centres, while Al and Ti-Li ages were used for ESR 2 sample.

369 Weighted mean ages of 442 ± 58 ka (2σ , Full external error, MSWD = 0.65 and P = 0.42) 349 ± 26 ka
370 (2σ , full external uncertainty, MSWD = 2.08 and P = 0.059) and 396 ± 41 ka (2σ , full external error,

371 MSWD = 0.27 and P = 0.76) were obtained for Isoletta ESR2, ESR3, associated to the “Acheulian
372 level”, and for Isoletta ESR4 samples, respectively.

373 The ESR age estimates of Isoletta ESR1 sands seems overestimated compared with $^{40}\text{Ar}/^{39}\text{Ar}$ results,
374 whatever the centre considered. In addition, the significant discrepancy between Ti-Li and Al age
375 results precludes the calculation of a weighted mean age value, and the fact that the Ti-Li D_E and age
376 are higher than the Al ones

377 We suspect here an overestimation of the natural signal, related to the difficulty of accounting for
378 background noise and baseline in the case of extremely weak signals. This overestimation directly
379 leads to an overestimation of the D_E . The discrepancy between the ages obtained using the different
380 centres does not allow as the determination of reliable depositional age for this sample.

381 The fact that we observe also a very clear age overestimation using Ti-H for this sample leads us to
382 suppose that the problem may also be related to the annual dose evaluation rather than to only a poor
383 initial bleaching of the quartz grains. Indeed, this level is composed of very coarse elements (blocks,
384 pebbles...) whose sandy matrix constitutes the dated sediment. The absence of an *in situ* gamma
385 measurement means that coarse elements (the main part of the sediment in the level) were not taken
386 into account when determining the annual dose, which could explain the results obtained for this level.
387 It should also be noted that the Th and K content of the sediment sample at this level is extremely low
388 (0.31 ppm and 0.03% respectively; Table 1). For K, an alteration (disappearance) of the potassium-
389 rich minerals (feldspar?) all along the time elapsed between the sediment deposit and the sampling
390 could explain this low content, leading to an underestimation of the annual dose and by extension an
391 overestimation of the age.

392

393 5.3 Lademagne

394 For the sediment from Lademagne upper level, the Ti-H ESR signal was not measurable. The ESR
395 ages using Ti-Li (398 ± 51 ka) and Al (406 ± 51 ka) centres are consistent (table 4). As for the main
396 part of Isoletta's samples, the close D_E obtained using the Ti-Li and Al centres allows us to give a
397 weighted average age of 402 ± 71 ka (2σ , Full external error, MSWD = 0.012 and P = 0.91) for these
398 upper sands. This result agrees with the $^{40}\text{Ar}/^{39}\text{Ar}$ age (389 ± 8 ka) obtained for the same sediment.

399 However, in this case, several grain populations showing different ages have been identified,
400 indicating that the volcanic minerals are not in primary position. Consequently, the $^{40}\text{Ar}/^{39}\text{Ar}$ age of
401 389 ± 8 ka should be interpreted as a maximum age constraint for the deposits, as it was derived from
402 seven crystals showing the most recent ages (Pereira et al, 2018). The corresponding volcanic event
403 being not recorded in the Lademagne lower level sediment in which the youngest recorded eruption
404 was dated of 405 ± 9 ka (Pereira et al, 2018), we can however consider in first approximation that it
405 probably happened shortly before the upper level deposition.

406

407 5.4 Notarchirico

408 Only level 2-6 can be directly compared with an $^{40}\text{Ar}/^{39}\text{Ar}$ result (663 ± 3 ka). However, this level is
409 considered as a secondary deposit, as volcanic minerals seems derive from the reworking of the
410 Notarchirico tephra (level 2.2), the only one real primary deposit of the sequence, located about 60 cm
411 lower in the sequence and directly dated to 661 ± 3 ka (Pereira et al, 2015). The Al ESR age of
412 Notarchirico 2-6 sample (657 ± 31 ka) agrees at 1σ with the $^{40}\text{Ar}/^{39}\text{Ar}$ obtained on the youngest
413 volcanic event reworked into this level. No crystals resulting from a younger eruption dated about
414 614ka and recorded in the upper levels of the sequence are present in level 2-6. The age of this deposit
415 is therefore strictly constrained between 661 and 614 ka.

416 For samples from H1 and H1c levels, the three ESR centres have been measured. As for the Isoletta
417 site, the ESR ages obtained using the Ti-Li and Al centres are consistent with each other and with the
418 $^{40}\text{Ar}/^{39}\text{Ar}$ ages (table 4) of the neighboring levels, whereas the Ti-H ages are significantly younger.
419 This result is probably related to the high D_E values (> 400 Gy) and the probable aforementioned Ti-H
420 centre saturation. The close D_E values obtained for the Al and Ti-Li centres led to weighted mean ages
421 of 743 ± 67 ka (2σ , Full external error, MSWD = 0.024 and P = 0.88) and 736 ± 70 ka (2σ , Full
422 external error, MSWD = 0.013 and P = 0.91) for Notarchirico H1 and Notarchirico H1c samples,
423 respectively. We can also notice that the Al and Ti-Li ESR ages obtained for the lower levels of the
424 Notarchirico sequence are significantly older than the date determined for level 2-6. Nevertheless, as
425 quite the whole sequence (levels J to B) was developed within the same climatic stage according to the
426 palaeoenvironmental data (that $^{40}\text{Ar}/^{39}\text{Ar}$ dates place during MIS16, Pereira et al., 2015 and as the

427 error range of the ESR ages is relatively wide, the ages of levels H1 and H1c can be compared with the
428 $^{40}\text{Ar}/^{39}\text{Ar}$ results of 670 ± 3 ka (Pereira et al., 2015) obtained for level F (table 5). This result then sets
429 a minimum age limit for H levels. ESR results may seem incoherent with this estimate, but
430 considering the error range associated with ages, this is still consistent with it. Moreover, the results of
431 the H1 levels are much older than the $^{40}\text{Ar}/^{39}\text{Ar}$ ages of the levels that cover them. Nevertheless, the
432 estimated $^{40}\text{Ar}/^{39}\text{Ar}$ ages obtained for F levels gave minimum ages for H1 and H1c and therefore do not
433 disagree with those actually obtained by ESR for these levels. It would be desirable in the future to
434 constrain this chronology by $^{40}\text{Ar}/^{39}\text{Ar}$ dating of sanidines extracted from these lower layers.

435

436 **6. Conclusion**

437 A multi-centre ESR approach was used on quartz grains extracted from Middle Pleistocene fluvial
438 deposits of central Italy that were also dated by the $^{40}\text{Ar}/^{39}\text{Ar}$ method. For most of the samples
439 analyzed, except one sample from the Isoletta site (ESR1), the ages determined both from Ti-Li and Al
440 signals are in agreement with each other and consistent with the $^{40}\text{Ar}/^{39}\text{Ar}$ ages (Fig. 8). As mentioned
441 in previous works, the use of the Ti-Li centre is therefore appropriate for this time range (Tissoux et al,
442 2007; Duval et Guilarte, 215) and this use is here validated by comparison with a totally independent
443 method, based on totally different physical principle. Furthermore, the results derived from Al signal
444 clearly show the usefulness of this centre when the fluvial sediments sampled are made of fine sand
445 carried by clear water river (without any fine particles in suspension). An evidence of this transport
446 condition is showed by the absence of silt or clay in the sampled sandy layers.

447 Our results strengthen the validity of ESR-MC method to accurately date sedimentary successions in
448 fluvial context proposed in previous studies (Tissoux et al, 2007; Bartz et al. 2018, 2019; del Val et al.
449 2019; Duval et al. 2015, 2017, this volume; Gouveia et al. 2020; Kreutzer et al. 2018; Mendez Quintas
450 et al. 2018; Sahnouni et al. 2018). The only discordant sample, Isoletta ESR1, was carried out from
451 extremely coarse and poorly sorted sediments probably of colluvial origin, in which quartz grains
452 could not have been completely bleached,
453 or in relation with a poor dose rate reconstruction in the age calculation process. The not well bleached
454 grains, which prevents the use of the Al centre. Furthermore, the difficulty of accurately measuring the

455 Ti-Li signal intensity of natural aliquots (high background noise and baseline), seems to have led to an
456 overestimation of the age obtained using this centre.

457 For the considered Middle Pleistocene time range (i.e. 700-300 ka), the Ti-H ages are underestimated
458 (Fig. 8) when D_E exceed 300-400Gy, suggesting a saturation of the Ti-H traps. That leads to an
459 underestimation of the ages by comparison with $^{40}\text{Ar}/^{39}\text{Ar}$. This is verified for our samples except for
460 ESR1 Isoletta sample, for which low dose rate value leads to obtain an age Ti-H older than the
461 $^{40}\text{Ar}/^{39}\text{Ar}$ age, and for ESR4 Isoletta sample for which a value of about 300 Gy was obtained allowing
462 the calculation of an age close to the $^{40}\text{Ar}/^{39}\text{Ar}$ one.

463 It seems therefore preferable to avoid the use of Ti-H centres to date early Middle Pleistocene levels,
464 especially if the D_e derived from Ti-Li and Al centres are greater than 300 Gy. It would be interesting
465 in the future to conduct similar approach, combining $^{40}\text{Ar}/^{39}\text{Ar}$ and multi-centre ESR, on deposits
466 containing both fluvial quartz and volcanic minerals, from late Middle Pleistocene to Upper
467 Pleistocene (300-50 ka) as well as late Lower Pleistocene times (1.0-0.7 Ma) to further test and
468 validate the MC approach over a longer period of time.

469

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479

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651 Figures Caption

652 Fig.1. Location of Isoletta, Lademagne and Notarchirico sites (Italy)

653 Fig.2. Cross section of Isoletta site and location of ESR and $^{40}\text{Ar}/^{39}\text{Ar}$ samples– Picture from Biddittu
654 modified.

655 Fig.3: Cross section of the upper part of Lademagne site and location of $^{40}\text{Ar}/^{39}\text{Ar}$ and ESR samples

656 Fig.4: Notarchirico site and location of ESR samples

657 Fig.5: Stratigraphic sections of Isoletta, Lademagne and Notarchirico sites and $^{40}\text{Ar}/^{39}\text{Ar}$ results.
 658 $^{40}\text{Ar}/^{39}\text{Ar}$ ages from primary and secondary volcanic deposits from Pereira et al, 2015 and 2018.

659 Fig 6: Isoletta ESR2 quartz grain ESR spectra (combination of two scans on the 431Gy irradiated
 660 aliquot) with Al, Ti-Li and Ti-H signals and indication of the peaks used for the intensity
 661 measurements.

662 Fig.7: Some example of dose response curves obtained for Al, Ti-Li and Ti-H ESR centres.
 663 Comparison between D_E determined using Ti-2 and exponential+linear function for Ti-H centre.

664 Fig.8: correlation between ESR ages obtained by different paramagnetic centres and $^{40}\text{Ar}/^{39}\text{Ar}$ ages.
 665 Solid line corresponds to the 1:1 ratio. ESR age close to this line (or with error range crossing the line)
 666 are considered as accurate, result below this line are underestimated, ages above the line are
 667 overestimated.

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 669 Fig.SM1: Dose response curves for the different ESR studied centres - Isoletta
 670 Fig.SM2: Dose response curves for the different ESR studied centres - Lademagne and Notarchirico

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676 Tables caption

677 Tab.1. Radionuclide contents, obtained from High Resolution Gamma Spectrometry, for analyzed
 678 sediments of Isoletta, Lademagne and Notarchirico Sites. Analytical uncertainties are given at $\pm 1\sigma$
 679 confidence level.

680
 681 Tab. 2. ESR results obtained on quartz extracted from sediments. Analytical uncertainties and ages are
 682 given with $\pm 1\sigma$. Water contents (W%) were estimated by the difference in mass between the natural
 683 sample and the same sample dried for a week in an oven at 50°C (323.15 K). Dose rates were
 684 determined using dose rate conversion factor updated by Guerin et al (2011). Alpha and beta
 685 attenuations estimated for the selected grain sizes from the tables of Brennan (2003); k-value of 0.15
 686 (Yokoyama et al., 1985), cosmic dose rate calculated from the equations of Prescott & Hutton (1994).
 687 For Ti-H centres, the D_{ES} and ages marked by an asterisk were calculated using the Ti2 function while
 688 the other Ti-H ages and D_{ES} were calculated using the SSE function. For Ti-Li centres the D_{ES} and
 689 ages in italics were calculated using the SSE function while the other Ti-Li ages and D_{ES} were
 690 calculated using the exponential+linear function.

691
 692 Tab. 3. Isoletta Site, Comparison between ESR and $^{40}\text{Ar}/^{39}\text{Ar}$ ages. $^{40}\text{Ar}/^{39}\text{Ar}$ ages are given with 2σ
 693 analytical uncertainty and are already published in Pereira et al 2018. Ti-H ages are used for mean
 694 ages calculation of ESR 3 and 4.

695
 696 Tab. 4. Lademagne Site, Comparison between ESR and $^{40}\text{Ar}/^{39}\text{Ar}$ ages; $^{40}\text{Ar}/^{39}\text{Ar}$ ages are given with
 697 2σ analytical uncertainty and are already published in Pereira et al 2018.

698
 699 Tab. 5 Notarchirico Site, Comparison between ESR and $^{40}\text{Ar}/^{39}\text{Ar}$ ages. $^{40}\text{Ar}/^{39}\text{Ar}$ ages are given with
 700 2σ analytical uncertainty and are already published in Pereira et al 2015. Ti-H ages are not used for
 701 mean age calculation.

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	U(ppm)	Th (ppm)	K (%)
Isoletta ESR1	1.58 ± 0.07	0.31 ± 0.07	0.03 ± 0.01
Isoletta ESR2	1.62 ± 0.14	9.37 ± 0.22	2.39 ± 0.03
Isoletta ESR 3	1.79 ± 0.09	2.43 ± 0.13	0.44 ± 0.01
Isoletta ESR 4	1.40 ± 0.06	1.07 ± 0.07	0.23 ± 0.01
Lademagne Upper	1.04 ± 0.11	2.91 ± 0.06	0.80 ± 0.02
Notarchirico 2-6	4.69 ± 0.08	4.87 ± 0.04	1.45 ± 0.01
Notarchirico H1	2.72 ± 0.08	4.48 ± 0.04	0.83 ± 0.01
Notarchirico H1-c	3.22 ± 0.09	5.89 ± 0.05	1.07 ± 0.01

Tab.1. Radionuclide contents, obtained with High Resolution Gamma Spectrometry, for analyzed sediments of Isoletta, Lademagne and Notarchirico Sites. Analytical uncertainties are given at $\pm 1\sigma$ confidence level.

		D_α $\mu\text{Gy/a}$	D_β $\mu\text{Gy/a}$	D_γ $\mu\text{Gy/a}$	D_{cos} $\mu\text{Gy/a}$	D_A $\mu\text{Gy/a}$	W %	BI %	D_E (Gy)	r^2	Age (ka)
Isoletta											
ESR1	Al	19 \pm 1	190 \pm 11	168 \pm 10	24 \pm 1	401 \pm 15	15	48	462 \pm 24	0.992	1154 \pm 109
	Ti-Li							100	715 \pm 75	0.986	1786 \pm 327
	Ti-H								803 \pm 100	0.981	
ESR2	Al	57 \pm 2	1786 \pm 36	1008 \pm 28	33 \pm 1	2884 \pm 15	15	42	1315 \pm 62	0.991	456 \pm 34
	Ti-Li							100	1155 \pm 110	0.989	401 \pm 59
	Ti-H								1059 \pm 120	0.979	
ESR3	Al	30 \pm 2	497 \pm 20	354 \pm 16	53 \pm 3	934 \pm 26	15	46	338 \pm 60	0.981	362 \pm 64
	Ti-Li							100	314 \pm 73	0.979	336 \pm 66
	Ti-H								401 \pm 45	0.987	
ESR4	Al	20 \pm 1	303 \pm 12	220 \pm 10	101 \pm 5	644 \pm 16	15	44	252 \pm 40	0.984	391 \pm 72
	Ti-Li							100	275 \pm 25	0.989	426 \pm 59
	Ti-H								296 \pm 38	0.984	
Lademagne											
Lad Sup	Al	77 \pm 3	980 \pm 35	919 \pm 52	111 \pm 6	2087 \pm 70	5	44	847 \pm 100	0.981	406 \pm 51
	Ti-Li							100	831 \pm 70	0.985	398 \pm 51
Notarchirico											
2-6	Al	84 \pm 1	1999 \pm 24	1803 \pm 21	166 \pm 8	4052 \pm 32	10	57	2658 \pm 122	0.991	657 \pm 31
H1	Al	115 \pm 2	1203 \pm 20	1215 \pm 18	95 \pm 5	2628 \pm 27	17	66	1942 \pm 60	0.995	739 \pm 43
	Ti-Li							100	1972 \pm 110	0.995	750 \pm 57
	Ti-H								1895 \pm 161	0.989	
H1-c	Al	146 \pm 2	1521 \pm 23	1551 \pm 22	95 \pm 5	3313 \pm 32	17	69	2425 \pm 85	0.993	732 \pm 49
	Ti-Li							100	2453 \pm 100	0.989	740 \pm 52
	Ti-H								2515 \pm 200	0.991	
									887 \pm 71	0.981	267 \pm 28
									810 \pm 82*	0.978*	245 \pm 26*

Tab. 2. ESR results obtained on quartz extracted from sediments. Analytical uncertainties and ages are given with $\pm 1\sigma$. Water contents (W%) were estimated by the difference in mass between the natural sample and the same sample dried for a week in an oven at 50°C (323.15 K). Dose rates were determined using dose rate conversion factor updated by Guerin et al (2011). Alpha and beta attenuations estimated for the selected grain sizes from the tables of Brennan (2003); k-value of 0.15 (Yokoyama et al., 1985), cosmic dose rate calculated from the equations of Prescott & Hutton (1994). For Ti-H centres, the D_{ES} and ages marked by an asterisk were calculated using the Ti2 function while the other Ti-H ages and D_{ES} were calculated using the SSE function. For Ti-Li centres the D_{ES} and ages in italics were calculated using the SSE function while the other Ti-Li ages and D_{ES} were calculated using the exponential+linear function.

	Al ESR ages	Ti-Li ESR ages	Ti-H ESR ages	Mean ESR ages	$^{40}\text{Ar}/^{39}\text{Ar}$ ages
ESR1	1154±109ka	1786 ± 327 ka	810 ± 47 ka	Not possible	403 ± 8 ka
ESR2	456 ± 34 ka	401 ± 59 ka	102 ± 16 ka	442 ± 58 ka	375 ± 10 ka
ESR3	362 ± 64 ka	336 ± 66 ka	374 ± 17 ka	349 ± 26 ka	365 < expected < 375
ESR4	391 ± 72 ka	426 ± 59 ka	377 ± 84 ka	396 ± 83 ka	365 ± 19 ka

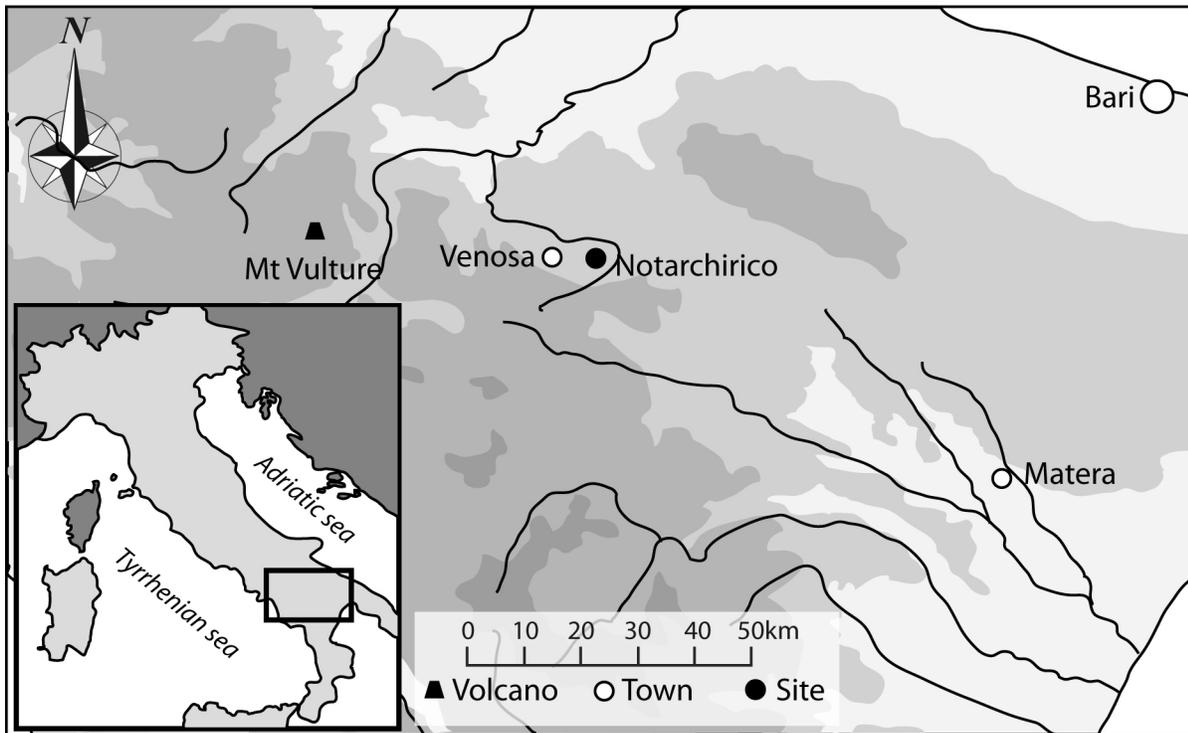
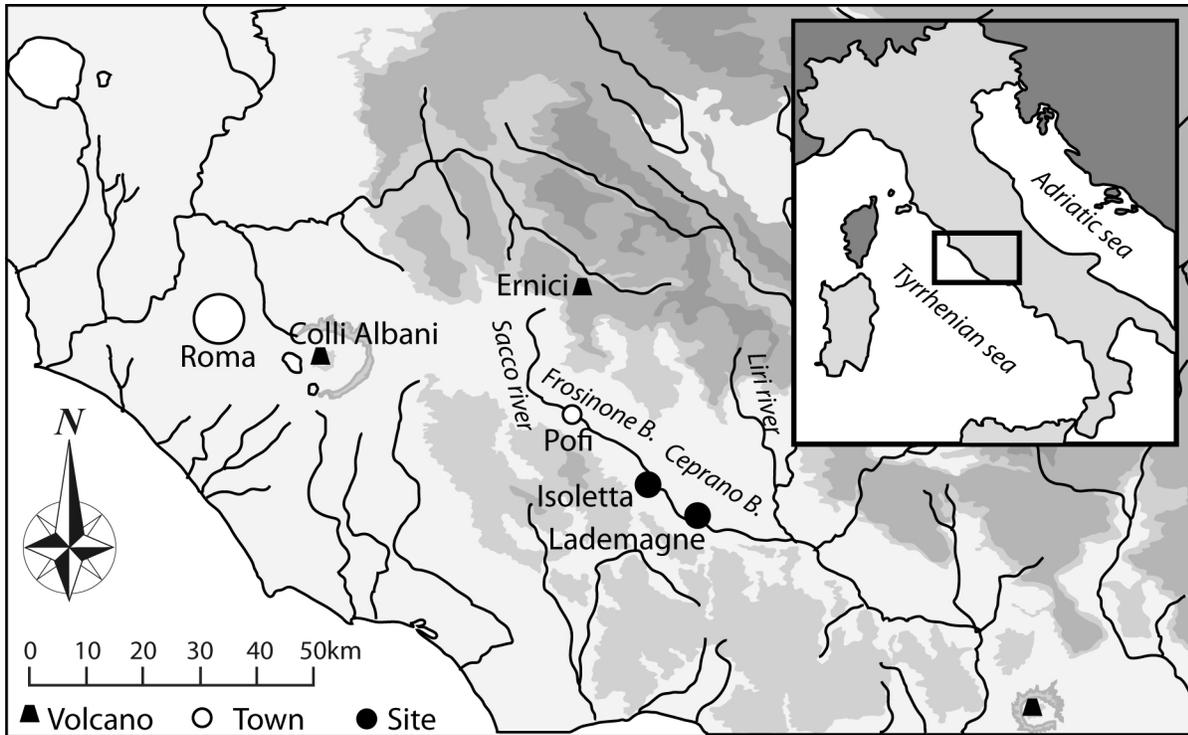
Tab. 3. Isoletta Site, Comparison between ESR and $^{40}\text{Ar}/^{39}\text{Ar}$ ages. $^{40}\text{Ar}/^{39}\text{Ar}$ ages are given with 2σ analytical uncertainty and are already published in Pereira et al 2018. Ti-H ages are used for mean ages calculation of ESR 3 and 4.

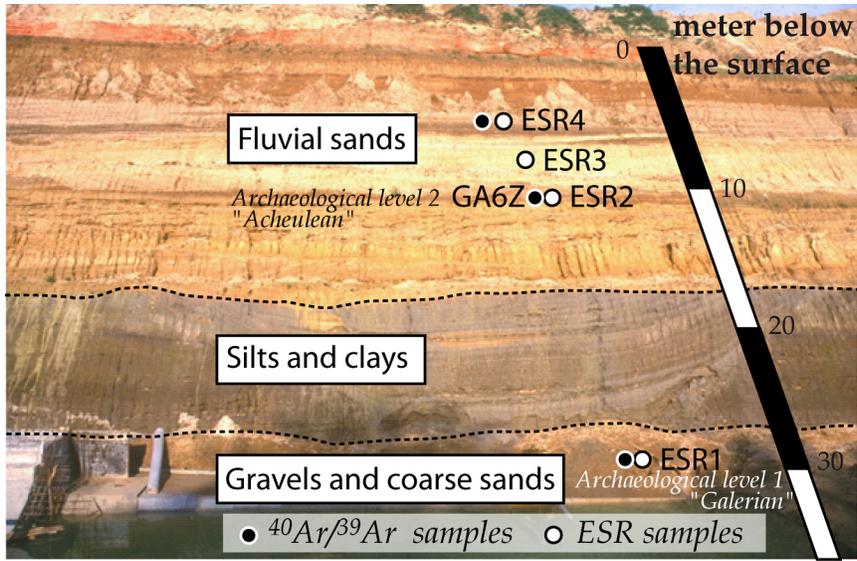
	Al ESR age	Ti-Li ESR age	Mean ESR age	Ti-H ESR age	$^{40}\text{Ar}/^{39}\text{Ar}$ age
Lad Sup	406 ± 51 ka	398 ± 51 ka	402 ± 71 ka	inapplicable	389 ± 8 ka

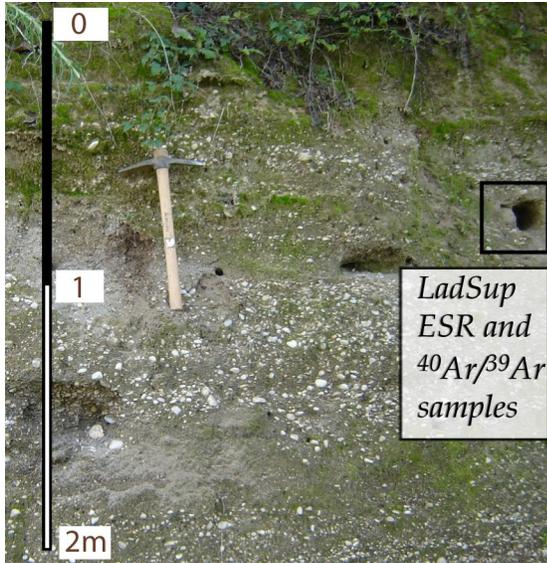
Tab. 4. Lademagne Site, Comparison between ESR and $^{40}\text{Ar}/^{39}\text{Ar}$ ages; $^{40}\text{Ar}/^{39}\text{Ar}$ ages are given with 2σ analytical uncertainty and are already published in Pereira et al 2018.

	Al ESR ages	Ti-Li ESR ages	Mean ESR ages	TiH ESR ages	$^{40}\text{Ar}/^{39}\text{Ar}$ ages
Notarchirico 2-6	657 ± 31 ka	-	-	-	663 ± 13 ka
Notarchirico H1	739 ± 43 ka	750 ± 57 ka	743 ± 67 ka	119 ± 35 ka	$> 670 \pm 14$ ka
Notarchirico H1c	732 ± 49 ka	740 ± 52 ka	736 ± 70 ka	267 ± 28 ka	$> 670 \pm 14$ ka

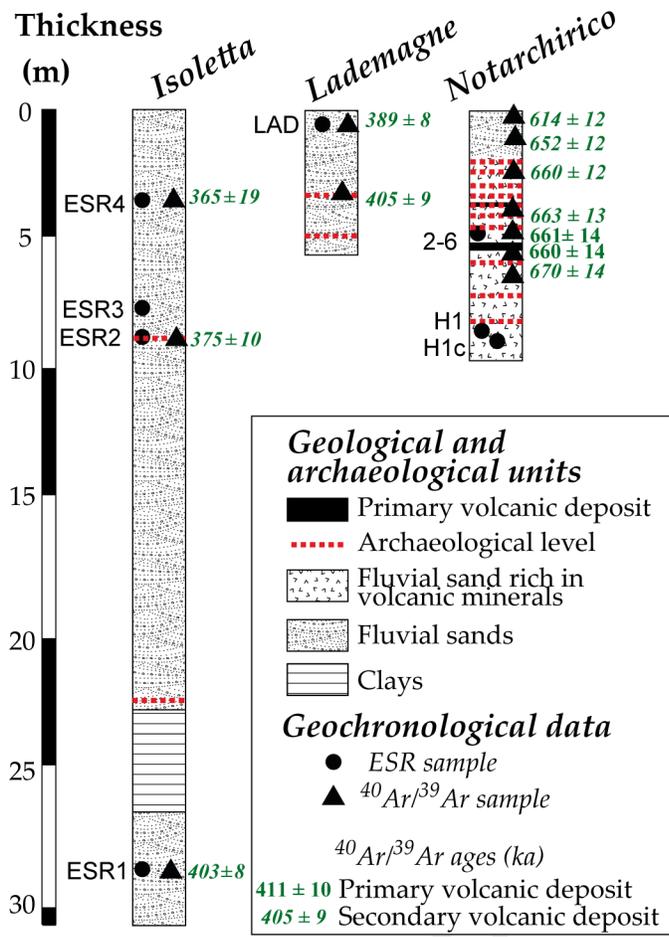
Tab. 5 Notarchirico Site, Comparison between ESR and $^{40}\text{Ar}/^{39}\text{Ar}$ ages. $^{40}\text{Ar}/^{39}\text{Ar}$ ages are given with 2σ analytical uncertainty and are already published in Pereira et al 2015. Ti-H ages are not used for mean age calculation.

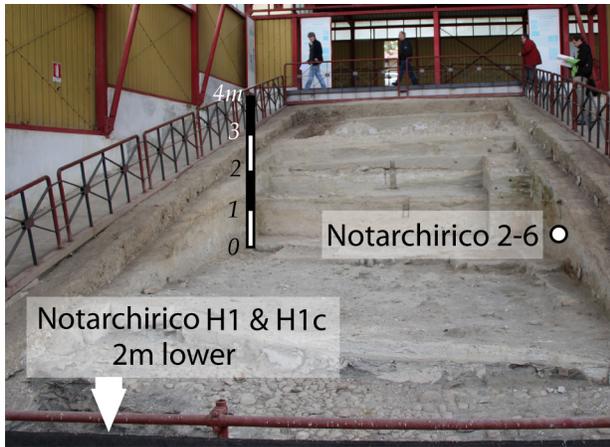






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