Dating Polygenetic Metamorphic Assemblages along a Transect across the Western Alps

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RECEIVED MARCH 29, 2012; ACCEPTED JANUARY 31, 2014

Multichronometric analyses were performed on samples from a transect in the French–Italian Western Alps crossing nappes derived from the Briançonnais terrane and the Piemonte–Liguria Ocean, in an endeavour to date both high-pressure (HP) metamorphism and retrogression history. Twelve samples of white mica were analysed by 39Ar–40Ar stepwise heating, complemented by two samples from the Monte Rosa nappe 100 km to the NE and also attributed to the Briançonnais terrane. One Sm–Nd and three Lu–Hf garnet ages from eclogites were also obtained. White mica ages decrease from c. 300 Ma in the westernmost samples (Zone Houillère), reaching c. 300°C during Alpine metamorphism, to <48 Ma in the internal units to the east, which reached c. 500°C during the Alpine orogeny. The spatial pattern of Eocene K–Ar ages demonstrates that Si-rich HP white mica records the age of crystallization at 47–48 Ma and retains Ar at temperatures of around 500°C. Paleocene–early Eocene La–Hf and Sm–Nd ages, recording prograde garnet growth before the HP peak, confirm eclogitization in Eocene times. Petrological and microstructural features reveal important mineralogical differences along the transect. All samples contain mixtures of detrital, syn-D1 and syn-D2 mica, and retrogression phases (D3) in greatly varying proportions according to local variations in the evolution of pressure–temperature–fluid activity–deformation (P–T–a–D) conditions. Samples from the Zone Houillère mostly contain detrital mica. The abundance of white mica with Si > 6.45 atoms per formula unit increases eastward. Across the whole traverse, phengite mica grown during HP metamorphism defines the D1 foliation. Syn-D1 mica is more Si-poor and associated with nappe stacking, exhumation, and hydrous retrogression under greenschist-facies conditions. Syn-D2 phengite is very often corroded, overgrown by, or intergrown with, syn-D2 muscovite. Most importantly, syn-D2 recrystallization is not limited to S2 schistosity domains; micrometre-scale chemical fingerprinting reveals muscovite pseudomorphs after phengite crystals, which could be mistaken for syn-D1 mica based on microstructural arguments alone. The Cl/K ratio in white mica is a useful discriminator, as D2 retrogression was associated with a less saline fluid than eclogitization. As petrology exerts the main control on the isotope record, constraining the petrological and microstructural framework is necessary to correctly interpret the geochronological data, described in both the present study and the literature. Our approach, which ties geochronology to detailed geochemical, petrological and microstructural investigations, identifies 47–48 Ma as the age of HP formation of syn-D1 mica along the studied transect and in the Monte Rosa area. Cretaceous apparent mica ages, which were proposed to date eclogitization by earlier studies based on conventional ‘thermochronology’, are due to Ar inheritance in incompletely recrystallized detrital mica grains. The inferred age of the probably locally diachronous, greenschist-facies, low-Si, syn-D2 mica ranges from 39 to 43 Ma. Coexistence of D1 and D2 ages, and the constancy of non-reset D1 ages along the entire transect, provides strong evidence that the D1 white mica ages closely approximate formation ages. Volume diffusion of Ar in white mica (activation energy E = 250 kJ mol–1; pressure-adjusted diffusion coefficient D0 < 0.03 cm2 s–1) has a subordinate effect on mineral ages compared with both prograde and retrograde recrystallization in most samples.

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KEY WORDS: $^{39}$Ar–$^{40}$Ar geochronology; Ar diffusion; eclogite dating; retrograde reaction dating; Western Alps

INTRODUCTION

Quantifying rates of processes during the evolution of orogens requires direct time constraints. However, providing ages for phases of deformation in basement-cover assemblies that have undergone polyphase metamorphism is challenging [see review by Vance et al. (2003); and references therein]. High spatial resolution in situ dating techniques, such as U–Pb age mapping of zircon grains by ion microprobe and of monazite grains by electron microprobe, and U–Pb and $^{39}$Ar–$^{40}$Ar age mapping by laser ablation, complement the well-known petrographic observation that different populations of grains are often present within the same thin section by documenting multimodal age distributions even at the micrometre scale (Villa & Williams, 2013, and references therein). However, in situ dating techniques have their limitations, especially in young metamorphic terrains such as the Alps (Müller et al., 2002) because precision is limited by low concentrations of radiogenic isotopes.

The $^{39}$Ar–$^{40}$Ar stepwise heating technique is preferred for dating polygenetic white mica samples because it provides a control on the chemical composition of the degassed Ar reservoirs (Rex et al., 1993; Villa et al., 1997, 2000; Müller, 2003; Vance et al., 2003); that is, of the identity of the different phases or mineral generations in a sample. This is based on the $^{37}$Ar/$^{39}$Ar ratio (Wartho, 1995), or the combination of $^{38}$Ar/$^{39}$Ar and $^{37}$Ar/$^{39}$Ar ratios (Villa et al., 1996, 2000; Belluso et al., 2000), which reflect the Ca/K and Cl/K ratios. The in situ $^{39}$Ar–$^{40}$Ar laser probe technique cannot be exploited for these samples, despite its potentially high spatial resolution, as the smallest useful volume for analysis is determined by the least abundant isotope/s required for a successful analysis (Villa & Williams, 2013), which, for this study, are $^{32}$Ar and $^{37}$Ar. It has been shown that stepwise heating of polycrystalline mixtures provides better accuracy than laser microprobe ages (Müller et al., 2002), especially when the size of the metamorphic intergrowths is smaller than the effective spatial resolution of the laser ablation volume (Agard et al., 2002). Incremental heating and single-spot fusions are complementary methods capable of producing consistent results (Philippot et al., 2001; Müller et al., 2002; Challandes et al., 2003; Müller, 2003). The $^{39}$Ar–$^{40}$Ar method also benefits from the fact that the Ar retentivity of white mica is empirically well constrained (Di Vincenzo et al., 2004; Allaz et al., 2011, and references therein).

For this study we have analysed rocks with complex multistage metamorphic and structural histories constrained by previous research (Bucher, 2003; Bucher et al., 2003, 2004; Bucher & Bousquet, 2007), combining observations at the microscopic scale and outcrop scale, all the way up to the regional context. The main objective of this combined tectonic, petrological and isotopic study is to enhance our knowledge of the processes controlling the behaviour of various isotopic systems. Twelve of the 14 samples (Table 1) were collected along a segment of a continuous crustal-scale geological–geophysical section (ECORS-CROP seismic section across the Italian–French Western Alps; Roure et al., 1996) crossing the entire

<table>
<thead>
<tr>
<th>Sample</th>
<th>Latitude (N)</th>
<th>Longitude (E)</th>
<th>Rock type</th>
<th>Mineral assemblage</th>
<th>D$_0$ age</th>
<th>D$_1$ age</th>
<th>D$_2$ age</th>
<th>D$_3$ age</th>
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<tr>
<td>Arv007</td>
<td>45°36’34”</td>
<td>6°56’53.8”</td>
<td>Marble</td>
<td>cc, phg, (chl)</td>
<td>&gt;45.4</td>
<td>39.5</td>
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<td>Beu0033</td>
<td>45°34’13”</td>
<td>7°1’51.0”</td>
<td>Gneiss</td>
<td>phg, par, grt, chl, qtz</td>
<td>&gt;90</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Cere0035</td>
<td>45°40’43.1”</td>
<td>7°4’1’3”</td>
<td>Gneiss</td>
<td>ctd, grt, phg, par, chl, czo, qtz</td>
<td>&gt;76</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Cere0035</td>
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<td>7°4’1’1”</td>
<td>Gneiss</td>
<td>ctd, grt, phg, par, chl, czo, qtz</td>
<td>&gt;230</td>
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<td></td>
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<td>Lnd9939</td>
<td>45°36’59.3”</td>
<td>6°57’46.8”</td>
<td>Meta-arkose</td>
<td>phg, chl, qtz, fsp</td>
<td>≤45.5</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Mrk1</td>
<td>46°4’31”</td>
<td>8°3’5”</td>
<td>Gneissic schist</td>
<td>grt, bt, pl, ms, ky</td>
<td>&gt;77</td>
<td>≤47.6±0.1</td>
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<tr>
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<td>46°4’31”</td>
<td>8°3’5”</td>
<td>Mylonite</td>
<td>grt, phg, par</td>
<td>48.2±0.1</td>
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<tr>
<td>SBPT</td>
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<td>7°5’0’2”</td>
<td>Gneiss</td>
<td>ctd, grt, phg, par, chl, czo, qtz</td>
<td>&gt;67</td>
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<td>7°2’48.0”</td>
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<td>&gt;160</td>
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<td>≤43</td>
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<td>&lt;38</td>
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<td>6°59’11.7”</td>
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<td>7°17’54.4”</td>
<td>Metacalcischt</td>
<td>cc, phg, chl</td>
<td>48.3±0.5</td>
<td>39-40</td>
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<td>7°7’51”</td>
<td>Eclogite</td>
<td>omp, grt, phg, par, zoi</td>
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<td>7°0’22.7”</td>
<td>Metaquartzite</td>
<td>qtz, phg, (chl)</td>
<td>40.3±0.5</td>
<td>≤37</td>
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The complete stepwise heating data are given in Electronic Appendix Table 2. Ages are in Ma.
The Zona Interna of Cigolini (1995) corresponds to the Vanoise–Mont Pourri Unit of Caby (1996) and will be referred to as the ‘Internal Unit’ below. Northwards this Internal Unit has been correlated with the Mont Fort Unit (Gouffon, 1993). The Internal Unit is made up of a lower part, formed by paragneiss and micaschist with a polymetamorphic history (Bocquet, 1974b; Cigolini, 1995; Malusà et al., 2005), and a mono-metamorphic upper part, consisting of lower Permian to Mesozoic sequences. The lower part is mainly of volcanoclastic origin (Amstutz, 1955, 1962) and is intruded by Paleozoic granitic and granodioritic bodies (e.g. the Cogne granodiorite, Bertrand et al., 2000). Leucocratic gneisses define the base of the mono-metamorphic upper part. These are followed by a typical Permo-Triassic sequence consisting of conglomerates (‘Verrucano’), quartzitic meta-sandstones, impure quartzites, and ankerite-bearing micaschists. The younger Mesozoic cover is preserved in only the southern part of the study area.

The P–L Unit predominantly consists of calcareous, which are interlayered with variable amounts of metabasite (Elter, 1972; Cigolini, 1995). Two types of metabasite occur: eclogites, which are retrogressed in most places, and prasinites. Some researchers have proposed a subdivision of the P–L Unit within our study area into an eclogitic (‘Zermatt–Saas Fee’) and a non-eclogitic (‘Combin’) part (Droop et al., 1990; Ballèvre & Merle, 1993; Dal Piaz, 1999). However, our observations indicate that both sub-units represent a mélangé consisting of mafic boudins metamorphosed in eclogite or blueschist facies, embedded in a matrix of metasediments that underwent the same degree of metamorphism, whereby this mélange formed during exhumation (Bousquet, 2008).

The tectono-metamorphic evolution of the portion of the internal Western Alps imaged by the ECORS-CROP profile (Bucher; 2003; Bucher et al., 2003, 2004, and references therein) consists of three phases of Alpine deformation (D1–D3), associated with different P–T conditions prevailing in the various units (Bucher & Bousquet, 2007; Bousquet, 2008). The D1 structures have largely been overprinted by subsequent deformation. Occasionally, relics of D1 are preserved on the macroscopic and microscopic scale; for example, in eclogitic boudins from the P–L Unit surrounded by a matrix of mainly greenschist-facies calc schist. Here an S1 foliation and syn-D1 mineral assemblage are preserved. During this first phase of deformation, associated with subduction in the Western Alps (Fig. 2b), the P–L Unit reached eclogite-facies conditions (P>20 kbar, T>500°C). Detailed petrological investigations (Bousquet, 2008) indicate some complexity within the long-lasting subduction history referred to as D1 (Bucher et al., 2004). The peak-P mineral assemblage consists of garnet, omphacite and glaucophane, and corresponds to an early stage of D1. Si-rich white mica occurs in many
samples from the study area, including all of the samples dated by $^{39}$Ar–$^{40}$Ar. As white mica is not stable under eclogite-facies conditions in the studied mafic rocks, its formation post-dates the pressure peak. Because it is also clearly seen to pre-date $D_2$ microstructures, we assign it to a later stage of $D_1$. In the Internal and Ruitor Units (Fig. 2) the pressures prevailing during $D_1$ are in the range of 10–14 kbar at c. 400–450°C (Fig. 2b; Bucher et al., 2003; Malusà et al., 2005). More externally (internal part of the Zone Houillère Unit close to the tectonic contact with the Ruitor Unit), $P$–$T$ estimations suggest 5 kbar and 350 ± 25°C, whereas the most external part never exceeded 300 ± 25°C, as indicated by the vitrinite reflectance of coal (Bucher et al., 2003).

North-northwestward nappage stacking and exhumation during $D_2$ took place under greenschist-facies conditions (Ceriani et al., 2001; Bucher, 2003; Ceriani & Schmid, 2004). $D_2$ is the dominant deformation event, characterized by isoclinal folds on all scales. Owing to intense transposition the main foliation is usually a composite of $D_1$,

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**Fig. 1.** Paleogeographical domains of the Western Alps after Bucher et al. (2003), with the study area outlined. The trace of the ECORS-CROP transect (Roure et al., 1996) is indicated. The black dot indicates the location of additionally analyzed samples from the Monte Rosa nappe.
Fig. 2. (a) Geological map of the study area after Bucher et al. (2003) showing the locations of the samples. B–B’ indicates the trace of the cross-section shown in (b). (b) Schematic cross-section B–B’ modified after Bucher et al. (2003) and P–T path of different tectonic units in the study area. P–T conditions were calculated using Geo-Calc software (for details see Bucher et al., 2003; Bucher & Bousquet, 2007). All samples were projected onto this cross-section to show their structural position. V, Valaisan oceanic Unit; ZH, Zone Houillère Unit; RU, Ruitor Unit; IU, Internal Unit; GP, Gran Paradiso massif; P–L, Piemont–Liguria oceanic Unit; ETC, enigmatic tectonic contact.
and D₃. The abundance of the pre-Alpine relicts generally decreases eastwards owing to the eastward increase in D₂ strain magnitude (Bucher et al., 2004). In the external parts of the Ruitor Unit pre-Alpine relicts are common (Baudin, 1987), and they gradually become rare in the internal parts of the Ruitor Unit and in the Internal Unit (Cigolini, 1995).

The last ductile deformation phase, D₃, produced large-scale post-nappe folds (Bucher et al., 2003, 2004); its final stages coincide with a change from top-to-the-NNW to top-to-the-west movements in the Western Alps (Fuegoschuh et al., 1999; Ceriani et al., 2001; Ceriani & Schmid, 2004; Loprieno et al., 2011) some 32 Myr ago (Fuegoschuh & Schmid, 2003; Simon-Labric et al., 2009). D₃ also developed under greenschist-facies conditions, but in the absence of discrete syn-D₃ mineral parageneses (Cigolini, 1995).

Representative analyses are shown in Table 2, and the full dataset is reported in Electronic Appendix Table 1 (supplementary data are available for downloading at http://www.petrology.oxfordjournals.org).

All samples were crushed with a jaw crusher and a roll mill, then sieved in different grain size fractions between 125 and 500 μm. The sieving opening is a good approximation of the diameter of the mica platelets. All analysed minerals (white mica, garnet, glaucophane, pyroxene, epidote) were enriched by standard magnetic and gravimetric techniques, then further purified by hand-picking. The detailed procedure of our ³⁹Ar⁻⁴⁰Ar analyses has been described by Villa et al. (2000). The ⁴⁰K decay constants followed Steiger & Jäger (1977), and the age of the FCs fluence monitor followed Kuiper et al. (2008). A summary of the ages is given in Table 1; the complete dataset is reported in Electronic Appendix Table 2. The Lu–Hf and Sm–Nd procedures followed Kleinhanns et al. (2002); the decay constants for ¹⁴⁷Sm and ¹⁷⁶Lu were taken as 0·00654 Ga⁻¹ (Lugmair & Marti, 1978) and 0·01865 Ga⁻¹ (Scherer et al., 2001).
The complete results are shown in Electronic Appendix Table 3.

**AGE RESULTS**

The spatial distribution of the ages obtained in this study follows a systematic regional pattern. Figure 3 shows all the K–Ar ages obtained in this study (identical to the 39Ar–40Ar total-gas ages in Electronic Appendix Table 2) plotted against the temperature of Alpine metamorphism, which is independently constrained by petrological data (Bucher et al., 2003). In this section we refer to only 39Ar–40Ar total-gas ages; age spectra and other diagrams displaying Ar isotope systematics will be discussed in a later section. Isochrons can be plotted from the data in Electronic Appendix 2; they will not be further considered, as they do not provide additional information to the stepwise heating age spectra of phyllosilicates (Foland, 1983).

From the most external unit, the Zone Houillère Unit, which underwent the lowest grade Alpine metamorphism, we analysed three samples spanning the entire unit. All three yield total-gas ages ranging between 261 and 51 Ma, from the most external to the most internal sample. The data show a negative correlation between K–Ar (total-gas) age and maximum metamorphic temperature (Fig. 3). A similar correlation was found in the Ruitor Unit, from which five analysed samples give total-gas ages decreasing from 94 to 50 Ma (Fig. 3). One surprising observation is that sample Cere0035 yields a much older total-gas age than Rui9958, despite having been metamorphosed at higher temperature, giving the age–temperature correlation an unpredicted sawtooth pattern. The sample from the Internal Unit has the lowest total-gas age of the whole traverse, 40 Ma. The total-gas ages of the three samples from the P–L Unit are nearly constant (43–47 Ma) and do not correlate with the metamorphic peak temperature.

**CONVENTIONAL ‘THERMOCRONOLOGICAL’ INTERPRETATION**

The conventional ‘thermochronological’ interpretation (Jäger, 1967) requires that only tectonic units that were heated to $T > 350^\circ C$ may be used for an estimation of the
age of HP metamorphism, because higher-grade white mica should record 'cooling ages' only. In this approach the HP event must always be older than the $^{39}\text{Ar} - ^{40}\text{Ar}$ mica ages from samples that did not exceed 330°C during Alpine metamorphism. It should be noted that the 350°C 'closure temperature', $T_c$, of white mica for Ar loss according to Purdy & Jäger (1976) cannot be freely modified, as the entire interpretative edifice that seeks to explain regional patterns of mica ages as 'cooling ages' relies decisively on a tight correspondence to mineral isograds. Any modification of $T_c$(mica) creates a conflict with this correspondence, causing the whole edifice to collapse (Villa, 1998).

Conventional 'thermochronology' thus requires an age of c. 100 Ma for HP metamorphism (i.e. Mid-Cretaceous; 'Eo-Alpine'), with white mica in the Internal and P–L Unit recording post-metamorphic 'cooling'. A difficulty with this interpretation is that the mica 'cooling ages' should decrease eastward as metamorphic grade increases (as it should take longer for higher-grade samples to be exhumed through their 'closure isotherm'), which is not observed (Fig. 3). Most importantly, a supposed Cretaceous eclogitization is incompatible with Lu–Hf and Sm–Nd data on garnet samples from the P–L Unit (Electronic Appendix Table 3), which require a Paleocene–Eocene age for the growth of prograde garnet, and thus an Eocene eclogitic event. Although both the plate motion constraints in the Western Mediterranean and the stratigraphic record in sedimentary basins surrounding the Alps are consistent with an Eocene eclogitic event in the axial belt (Malusà et al., 2011), earlier studies (e.g. Dewey et al., 1989) did not envisage this hypothesis, as the prevailing view for decades had been that eclogites in the whole Alps were of Cretaceous age.

The internal inconsistency of the 'thermochronological' approach at the 100 km scale requires a different approach to interpret the data. We will focus on the mineral geochronometers at the micrometre scale using microchemistry and petrology to constrain the significance of $^{39}\text{Ar} - ^{40}\text{Ar}$ ages of white mica.

**MICROSTRUCTURAL OBSERVATIONS AND EMP ANALYSES OF MULTIPLE WHITE MICA GENERATIONS**

To understand the large-scale regional pattern of the white mica $^{39}\text{Ar} - ^{40}\text{Ar}$ data we need to first understand the role of microstructure and heterogeneous mica composition at the subgrain scale in controlling the Ar isotope record. The different microstructural mica populations were analysed by EMP to relate them to micrometre-scale chemical variations. This procedure allows the chemical fingerprinting of three mica populations: (1) detrital grains; (2) grains formed during D1; (3) grains formed during D2. The celadonite content varies significantly in these three populations. The general trend from a dominance of detrital mica in the less deformed external part to the dominance of metamorphic mica in the frequently mylonitic internal part is systematic. The Zone Houillère Unit is dominated by detrital mica in the most external parts of the study area, where metamorphic conditions never exceeded sub-greenschist-facies conditions. Mixed detrital and newly grown mica coexist in the internal part of the Zone Houillère Unit. Even in the immediately adjacent Ruitor Unit inherited grains are still present in all samples, showing that mixed populations are common in the metamorphic portions of orogens, and that detrital mica can survive during subsequent deformation and metamorphism (Bousquet et al., 1998; Agard et al., 2002).

We focus the discussion of the EMP data on the Si content, because it can be used as a geobarometer (Massonne & Schreyer, 1987). In principle, additional indicators can be used to discriminate heterochemical mica generations (e.g. the Mg/Na or F/Fe ratios: Heri et al., 2013), but the Si content is sufficient to illustrate this diversity, with the added bonus of providing qualitative pressure constraints in the higher-grade units. However, in lower-grade units, such as the Zone Houillère Unit, a pyrophyllite component may contribute to high Si contents (Valente & Borghi, 2000).

In the most external part of the Zone Houillère Unit, close to the Houiller Front (Rui9978; Fig. 2a and b), the very weak Alpine foliation is defined by fine-grained mica (Fig. 4a), whereas the detrital mica grains are much larger, show no preferred orientation and are randomly distributed in the matrix (Fig. 4a). The clear textural dichotomy is mirrored by the EMP analyses (Fig. 4b): mica grains identified as detrital on the basis of purely textural criteria have Si contents below 85 atoms per formula unit (a.p.f.u.); whereas metamorphic micas have Si contents as high as 85 a.p.f.u. At first sight, the Si contents would appear to define a continuous variation between 64 and 85 a.p.f.u. In fact, the presence of two discrete intergrown mica generations will result in a bimodal Si distribution with two narrow concentration clusters only if the size of the intergrown phases is much larger than the excitation volume of the EMP beam [such as, for example, the sample of Villa (2006, fig. 3)]. If the intergrowth scale is smaller than the excitation volume (Livi & Atad, 2013), a smeared distribution of concentrations and element ratios is obtained (Heri et al., 2013). In that case, the textural context reveals that accurate compositional information is given only by the two extremes of the data distribution.

In the intermediate Zone Houillère Unit the Alpine deformation is more intense. Neocrystallized white mica in sample Ln9939 is still subordinate, but it is larger than in sample Rui9978. Figure 4c shows a three-dimensional
Fig. 4. (a) Thin section of sample Rui9978 from the external Zone Houillère Unit, showing the difference between detrital and metamorphic white mica. (b) Composition of the mica from sample Rui9978 measured by EMP (data in Electronic Appendix Table 1). The limit between the metamorphic high-Si and the detrital low-Si population is based on correlated microstructural and EMP analyses of this study. (c) Three-dimensional distribution of metamorphic and detrital white micas in sample Ln9939 from the intermediate Zone Houillère Unit. (d) Detrital white mica in sample Cere0033. (e) D1 microlithons in sample Cere0033. (f) Detrital white mica in sample Cere0035. (g) Back-scattered electron (BSE) image of one detrital white mica grain from sample Cere0035 (dark grey). (h) Si false-colour concentration map showing a clear zonation in the detrital mica grains. Blue (highest), green, yellow and red (lowest) represent decreasing concentrations. (i) Al false-colour concentration map verifying the Si zonation. Relative colour coding as in (h). (j) K false-colour concentration map. Relative colour coding as in (h). K concentrations are high across the whole mica grain and show no visible zonation. (k) EMP analyses of the three mica populations in sample Cere0035.
(3D) view of thin sections parallel and perpendicular to the stretching lineation. Newly grown micas are particularly clearly visible in the section parallel to the stretching lineation, where they are well aligned in the foliation. A population of larger and non-aligned grains is best seen in the section perpendicular to the stretching lineation, where they appear together with smaller and well-aligned new micas. Being non-aligned the larger grains are interpreted to be of detrital origin. This sample illustrates that 3D microstructural analysis is needed for accurate interpretation of the age data.

In the Ruitor Unit (Fig. 2a and b) grains belonging to all three identified mica populations are found (Cere0035, Cere0033; Fig. 4f–l). The youngest population, the horizontally aligned micas defining the S2 foliation (Fig. 4d and e), is interpreted to have recrystallized syn-kinematically with D2. Microlithons oriented perpendicular to the S2 foliation (Fig. 4d and e) contain an older population of mica interpreted to have formed during D1. Much larger grains in comparison with those found within D1 microlithons and the D2 micas (Fig. 4d) are interpreted as relict detrital grains and form the oldest population. D1 micas are also often preserved in fold hinges (Fig. 4e). Sample Cere0035 also contains small detrital grains in addition to the large ones typical in other samples (Fig. 4f). EMP mapping reveals chemical zoning in these smaller detrital micas (Fig. 4g–k).

The P–L Unit exhibits strongly contrasting microstructures as a function of rock competence. We describe here Vaud003, an eclogite boudin, and Traj005, a calecschist forming the matrix of such eclogitic boudins. Sample Vaud003 was chosen as it predominantly contains D1 (HP) mica and remained undeformed during D2; it shows an internal foliation, which is discordant to the main foliation defined by the second phase of deformation (S2), and hence has to be classified as S1. The attribution to D1 is independently confirmed by the mineral assemblage Grt–Px–Qz, implying P > 15 kbar. In contrast, calecschist Traj005 is strongly overprinted by S2 (Fig. 5), and it could appear at first sight that all micas are synkinematic with S2. However, omnipresent microlithons, relict D1 fold hinges (Fig. 5a and b) and (large) relict D1 grains, showing an internal foliation discordant to the main S2 foliation (Fig. 5c), are clear evidence for the preservation of D1 relics. Electron microprobe analyses of Traj005 white micas again show different compositions for different white-mica populations (Fig. 6). A relict D1-fold hinge (Fig. 6a and b) shows high Si contents (up to 6.8 a.p.f.u.) across the fold hinge, the scatter being part of the apparent variation of the D1 mica composition whenever the scale of the relict D1 mica intergrowth is smaller than the EMP excitation volume (see above). A relict D1 mica is shown in Fig. 6c. The textural difference from the mica of the S2 foliation is visible in Fig. 5, and is confirmed by the Al concentration map (Fig. 6d). Si contents are >6.45 a.p.f.u. for D1 mica, whereas they range from 6.45 to 6.40 a.p.f.u. for D2 mica (Fig. 6b–c). Mica with Si < 6.15 a.p.f.u. post-dates the D2 micas (Fig. 6e), but its occurrence is occasional.

These observations illustrate two general principles, which apply to the entire studied traverse. First, only the inherited micas are zoned, whereas newly formed mica shows no significant compositional heterogeneity. Second, neoformed D1 and D2 micas have distinct compositions, suggesting that diffusive re-equilibration of major elements was negligible during Alpine metamorphic events at 450 ± 25°C. The zoning of detrital mica pre-dates Alpine metamorphism, as confirmed by findings of pre-Alpine parageneses in the Ruitor basement (Baudin, 1987; Giorgis et al., 1999). The chemical differences between the three mica populations (detrital, D1 and D2) cause a large spread in mica compositions (Fig. 4k; Electronic Appendix Table 1).

**FACTORS CONTROLLING K–Ar AGES**

We now compare the insight gained on the petrogenesis of the mica samples with their geochronology. First we present systematic case studies on six selected samples, each illustrating a single issue. We then use the resulting assessment of the respective importance of mixing, diffusion and recrystallization to derive a robust and accurate interpretation of the regional age pattern.

**The influence of hand-picking on 39Ar–40Ar ages**

To quantify the influence of white-mica purity on 39Ar–40Ar ages we compared the Ar isotope fingerprint of the mechanical separate (magnetic and gravimetric) with its extensively hand-picked counterpart for three samples. Hand-picking is an unquestioned routine practice in many geochronology laboratories, including ours; what we set out to quantify was its effect on samples that are evidently mineralogically heterogeneous. The studied samples represent typical petrogenetic varieties encountered in the area: (1) Ln9939 from the Zone Houillère Unit contains predominant detrital mica grains; (2) Vga0120 from the Internal Unit is a mylonite containing mostly D2 mica; (3) Traj005 from the P–L Unit contains a mixture of D1 and D2 mica populations, lacking detrital grains. Stepwise heating data were obtained on these samples by using very similar laboratory heating schedules. A detailed discussion of these results is presented in Electronic Appendix Text I; a summary is shown in Fig. 7a–c, which shows that hand-picking indeed generally leads to smaller contamination by extraneous phases degassed in the low-T steps. However, hand-picking may provoke selective
Fig. 5. Thin section of sample Traj005 showing different mica generations (crossed polarizers). (a) Enlargement of a relict D1 fold hinge. (b) Close-up view of (a); the inset shows the area chosen for the detailed EMP analysis shown in Fig. 6a. Point analyses are given in Table 2 and Electronic Appendix Table 1. (c) Enlargement showing relict detrital mica grains. The location of Fig. 6c is the 200 × 200 μm square outlined between/below (a) and (c).
Fig. 6. (a) BSE image of the area shown in Fig. 5b. Field of view 0.3 x 0.3 mm. (b) Contour map of the Si concentration with individual quantitative analyses. (c) BSE image of the area shown in Fig. 5c. Field of view 0.2 x 0.2 mm. (d) Al false-colour concentration map; colour coding as in Fig. 4h. (e) Contour map of the Si concentration. It should be noted that although D1 mica grains and D2 mica grains show similar orientation they are texturally different, as is visible in Fig. 5.
enrichment if two populations are present. In particular, if the age difference between the two populations (detrital pre-Alpine and Alpine mica) is large, hand-picking may lead to unrepresentative results (see Villa, 2006, p. 166).

The influence of grain size on $^{39}$Ar–$^{40}$Ar ages

To test the role of diffusion, we dated different grain-size fractions of white mica taken from two samples that reflect entirely different processes (Fig. 8). Sample Vaud003 almost exclusively consists of $D_1$ phengite grown during eclogite-facies metamorphism and its age is expected to mirror the closure to Ar loss (independently of the exact Ar-loss mechanism, which will be discussed below) at, or after, the metamorphic peak. Sample SBPT, on the other hand, is dominated by detrital mica; its age is controlled by.

Fig. 7. Age spectra comparing picked and unpicked mica fractions; the grain size for all fractions was 125–160 μm. (a) Ln9939. The hand-picked aliquot consistently yields step ages that are older by 10–15 Ma than the unpicked aliquot, suggesting a subjective sampling bias. (b) Vga0120. This single-generation $D_2$ mica shows no major differences in the age spectra between picked and unpicked aliquots, except for the first two steps. As for Ln9939, this difference is best explained by the contamination of Cl-rich minerals other than mica in the unpicked aliquot. (c) Traj005. The age spectra of both aliquots display an upward-convex shape. As established by Wijbrans & McDougall (1990), this pattern clearly identifies two mica populations, whereby the oldest step of the age spectrum of a mixture defines the minimum age for the older phengite population and the youngest steps define the maximum age for the muscovite population. The width of the ‘hump’ pertains to the mass balance between the $D_1$ and $D_2$ generations. It appears that hand-picking of Traj005 has enriched $D_1$ phengite preferentially.

Fig. 8. (a) Age spectra of samples Vaud003.1, Vaud003.2 and Vaud003.3; the sieved size fractions are 125–160 μm, 160–250 μm and 250–500 μm, respectively. The age spectra are almost parallel, with an age difference of c. 0.5 Ma. (b) Age spectra of samples SBPT1 and SBPT2; the size fractions are 160–500 μm and 125–160 μm respectively. The two age spectra coincide within 1 Ma over 80% of the $^{39}$Ar release.
by (partial) resetting of the ages of pre-Alpine grains. If diffusive Ar loss had played an important role during either exhumation or rejuvenation, different ages for different grain sizes would be expected, whereby it is necessary to ensure that (1) the sieve fraction reflects natural grain size and not just mechanical comminution of a uniform size distribution larger than the largest analysed grain size, and (2) the effective grain size controlling diffusion is larger than the smallest analysed grain size. Point (1) holds true for our samples, whose natural grain-size variations range from >500 to <50 \( \mu \)m. Point (2) also holds true, as it is well known (Villa et al., 1996, and references therein) that the effective grain size for diffusion coincides with the crystallographically coherent mineral structure, which in the present case coincides with the whole grain.

Sample Vaud003 is an undeformed eclogitic boudin, as described above. The analysed grain-size fractions were 125–160 \( \mu \)m (Vaud003.1), 160–250 \( \mu \)m (Vaud003.2) and 250–500 \( \mu \)m (Vaud003.3). The corresponding age spectra are nearly identical (Fig. 8a), all spectra displaying a weak but statistically significant upward-convex shape; this fingerprint of heterochronous mica generations can be used to qualitatively estimate the relative abundance of phengite and muscovite. In this sample phengite is predominant and muscovite is subordinate; each size fraction is (slightly) heterochronous. The same identical age spectra for all three size fractions rules out that 40\(^{\text{Ar}}\) inherited from detrital grains and “excess” 40\(^{\text{Ar}}\) play an important role; diffusion theory would predict the grains with different radii to be affected to different degrees. We also point out that whenever recrystallization is only partial, the smallest grains are most affected by it; the effects of diffusion and of recrystallization parallel each other.

In each size fraction of sample Vaud003, the steps most closely representing \( D_\text{s} \) phengite are identified on the basis of two criteria: their position as the oldest steps of the hump-shaped age spectra (Wijbrans & McDougall, 1986), and their nearly constant Cl/K ratio of 4–5 \( \times \) 10\(^{-4} \). In all three size fractions these criteria are met by the 760 °C step, which accounts for over 40% of the 39\(^{\text{Ar}}\) release in each fraction. The 760 °C steps of the three size fractions display a small but significant, regular age difference: for the smallest, intermediate, and largest grain size (Vaud003.1, Vaud003.2 and Vaud003.3) the respective ages are 46.86 \pm 0.06 Ma, 47.27 \pm 0.07 Ma, and 47.61 \pm 0.06 Ma (Electronic Appendix Table 2).

The age comparison between size fractions of Vaud003, whose median grain radii vary between 71 and 187 \( \mu \)m, allows the calculation of the role of diffusion. The maximum possible diffusivity can be constrained in the limiting case of zero recrystallization (even if in fact this deformed sample contains multiple, heterochronous, recrystallized mica generations). A mathematical formulation of Ar retention is provided by the equations of Dodson (1973) defining \( T_c \) for Ar loss as a function of the activation energy, \( E \), the diffusion coefficient at infinite \( T \), \( D_\infty \), and the cooling rate, \( dT/dt \). The quantification of the diffusion parameters, however, is problematic. As hydrothermal laboratory experiments with added water always are subject to recrystallization of the experimental charge (Hess et al., 1987; Villa & Puxeddu, 1994; Harrison et al., 2009), their results are not applicable to those natural systems for which an estimate of the true volume diffusivity is required. To derive the latter, it is necessary to infer it from indirect evidence.

The diffusivity of Ar in white mica has been constrained by the case study by Hames & Cheney (1997) of a polymetamorphic, centimetre-sized muscovite porphyroclast. Those authors showed that Ar diffusion is very slow. From the data of those researchers, Villa (2010, p. 10) calculated that the diffusion coefficient \( D \) ranged between 4 \( \times \) 10\(^{-21} \) and 4 \( \times \) 10\(^{-20} \) cm\(^2\) s\(^{-1} \) at 450 °C. This agrees with the estimation of Graham (1981), based on an experimental study on the diffusion coefficient of hydrogen, who argued that \( D(\text{Ar}) \) must be orders of magnitude smaller than the estimated \( D(\text{H}) \) at 450 °C, 10\(^{-19} \) cm\(^2\) s\(^{-1} \). This Ar diffusion coefficient can be used to calculate a \( T_c \) following Dodson (1973).

The equation of Dodson (1973) contains four unknowns: \( T_c \), \( E \), \( D_\infty \), and \( dT/dt \). If \( T_c \) and \( E \) can be independently constrained on the basis of field estimates, the other two follow from the given boundary conditions. In the case of Vaud003, the boundary condition is provided by the grain-size fractions: the sample having \( a = 0.087 \) cm is older than that having \( a = 0.071 \) cm by 0.75 \pm 0.08 Ma. The cooling rate that results from the difference in the calculated \( T_c \) for Vaud003.3 and Vaud003.1 divided by their age difference is iteratively fed into the equation of Dodson (1973).

As starting values we choose \( T_c = 500 \) °C and \( E = 250 \) kJ mol\(^{-1} \). The former value was established in a field study in the Central Alps (Allaz et al., 2011) for samples that record a pressure of 6–7 kbar. It may be a conservative underestimate, as retention of 40\(^{\text{Ar}}\) in white mica near or above 530 °C is well documented in the literature (Hammerschmidt & Frank, 1991; De Sigoyer et al., 2000; Di Vincenzo et al., 2001, 2004; Philippot et al., 2001; Villa, 2006; Warren et al., 2012). If we take into account a pressure dependence of \( T_c \) of 6–7 °C kbar\(^{-1} \) (Dahl, 1996a), in the present samples \( T_c \) would increase by c. 40–50 °C relative to the Barrovian muscovites from the Central Alps. The value for \( E \) is based on the phlogopite diffusivity data of Giletti (1974), increased slightly to take into account the lower ionic porosity of muscovite compared with phlogopite (Dahl, 1996b). Our aim is to derive the diffusivity for geologically realistic situations; therefore, we can introduce the pressure-adjusted diffusion coefficient, \( D'_p \),
which already incorporates the pressure dependence for the natural conditions studied by Allaz et al. (2011). This has the advantage of a greater robustness with respect to possible systematic errors in the estimate by Dahl (1996a) of the pressure dependence. Very few muscovites will record pressures <8 kbar at 500°C; this means that very few natural muscovite samples have a diffusivity higher than that calculated here. For muscovite formed in the 8–16 kbar range, the systematic bias will only be at most half of any possible bias of the estimate of Dahl (1996a).

The calculated values of $D'_0$ and $T_c$ are $0.1 \text{cm}^2 \text{s}^{-1}$ and 494°C, respectively, for sample Vaud003. The calculated $T_c$ for Vaud003.1 is 460°C, lower by 34°C than that of the coarser size fraction. The resulting ‘cooling rate’ during the initial post-eclogitic decompression stage is thus $45 \pm 5 \text{°C Ma}^{-1}$. The combination of the values for $D'_0$ and $E$ assumed here can be extrapolated to temperatures of geological interest (e.g. 450°C). Our $D'_0$ and $E$ predict a diffusivity $D_{450°C} = 10^{-19.4} \text{cm}^2 \text{s}^{-1}$. This value is too high, as it is identical to the diffusivity of hydrogen in muscovite (Graham, 1981), and higher by a factor between two and 20 than the diffusivity of Ar calculated from the muscovite of Hames & Cheney (1997) (Villa, 2010, p. 10). This suggests that the starting values for $T_c$ and $E$ we used for our simple model calculation actually overestimate the diffusivity of Ar. Reducing $D'_0$ by half an order of magnitude, $D'_0 = 0.03$, leads to $T_c = 535°C$ and 482°C in Vaud003.3 and Vaud003.1, respectively. The additional $P$-dependent increase of $T_c$ by $10^4°C$ (see above) means that the $T_c$ for the coarsest and finest size fractions is 560°C and 520°C, respectively, higher than or equal to the temperature prevailing during the metamorphic peak ($500 \pm 30°C$). This suggests that the apparent age difference between the small and the large grains reflects, at least in part, the preferential preservation of non-retrogressed cores in the larger grains. Taking into account that the partial retrograde recrystallization in Vaud003 (which we had set to zero when modelling all Ar losses as if they had been diffusive) has the effect of decreasing the importance of diffusion, further reducing $D'_0$, which will lead to even higher $T_c$. We thus conclude that the age of the metamorphic peak is very closely approximated by fraction Vaud003.3 at 47.61 ±0.06 Ma, with a total systematic uncertainty smaller than 1 Ma.

Finally, the hypothesis that Vaud003 might provide a record of 40Ar diffusion needs to be reconciled with the observation that the shape of the spectra of the three grain-size fractions does not change as a function of incomplete 40Ar retention. Not even the smallest grain size shows a staircase-shaped age spectrum, which is often viewed as a reflection of diffusive Ar loss. In fact, it is well known that in vacuo degassing of phyllosilicates does not mirror the geometrical distribution of 40Ar in the crystals (Hodges et al., 1994), and that staircase-shaped spectra instead originate from a mixture of two diachronous mineral generations (Villa & Hanchar, 2013).

Sample SBPT, the second sample analysed for grain-size effects, was collected from the Permo-Triassic cover of the Avice synform, near the contact between the Ruitor Unit and the P–L Unit (Fig. 2; Caby, 1996). The analysed grain-size fractions were 160–500 µm (referred to as SBPT1) and 125–160 µm (SBPT2). The two total-gas ages are indistinguishable (60.9 ±0.1 and 60.9 ±0.1 Ma). The age spectra are similar, yielding two geologically meaningless plateaux at 62–63 Ma (Fig. 8b; see also Electronic Appendix Text 1). During the Eocene HP event, resetting the detrital mica population purely by volume diffusion would require much longer than 500 Ma, implying that diffusion of 40Ar has been negligible in controlling the Ar isotope record of sample SBPT. Similar conclusions had already been reached by Poland (1979), Chopin & Maluski (1980), Chopin & Monié (1984) and Monié (1985).

In cases where Ar diffusion is slow, 40Ar inheritance is expected. In turn, if inherited 40Ar plays a significant role, the K–Ar age is not that of the metamorphic crystallization, but is excessively old. Accordingly, Lanphere & Dalrymple (1976) gave a rigorous definition of the terms ‘inherited 40Ar’ and ‘excess 40Ar’. Inherited 40Ar was produced by $40K$ decay in the mineral’s prehistory and was never completely lost during the formation of the mineral observed at present. Excess 40Ar was introduced into a mineral during or after its formation. These two terms describe two entirely different geochemical processes: the former amounts to (partial) 40Ar loss, the latter to 40Ar gain. Nevertheless, Kelley (2002) proposed to explain all data that deviate from the assumption by Jäger (1967) of very high diffusivities and very low $T_c$ by excess 40Ar, thereby clouding the profound difference between 40Ar loss and introduction of 40Ar from outside. ‘Excess 40Ar’ often becomes a term used to explain problematic ages (in the absence of multichronometric controls). Unfortunately, the choice of what ages are defined as ‘problematic’ merely depends on the chosen value for $T_c$; by doing so, one effectively follows a circular argument. We propose that, because mixed ages are normal for minerals that grew below their $T_c$, a shift of $T_c$ to higher $T$ changes ‘problematic’ ages attributed to excess 40Ar to normal mixed ages with inherited 40Ar, but without excess 40Ar. The distinction between excess and inherited radiogenic isotope concentrations is not merely a semantic one, but one of essence. It can be achieved by multichronometric control [e.g. comparing the K–Ar and Rb–Sr systems (Villa et al., 2006), or the K–Ar and Lu–Hf systems, as done here], which immediately eliminates the ambiguities inherent in the use of a single isotopic system. It can also be achieved by correlating the chemical and microstructural evidence for petrological relics with the isotope record.
The influence of deformation on $^{39}$Ar–$^{40}$Ar ages

Two samples from the Bottarello glacial cirque (Monte Rosa nappe) were analysed to examine the influence of deformation on $^{39}$Ar–$^{40}$Ar ages. The median temperature in the investigated part of the Monte Rosa nappe during the early stages of Alpine metamorphism was 650°C (Engi et al., 2001). According to the $T_c$ approach, the $^{39}$Ar–$^{40}$Ar ages should date the time when these samples cooled below 350°C during exhumation. As samples Mrlk1 and Mrlk3 were collected about 1 m apart (Table 1), they should be the same age. Instead, Mrlk1 has a hump-shaped age spectrum (Fig. 9) and a total-gas age of 62.9 ± 0.3 Ma, whereas Mrlk3 has a much flatter age spectrum and a total-gas age of 45.9 ± 0.3 Ma. This age difference was not caused by the thermal history and can be explained only by the petrological differences. Mrlk1 was taken from the pre-Alpine wall-rock of a shear zone and largely preserves the pre-Alpine paragenesis, whereas Mrlk3 was taken from the shear zone itself (Keller et al., 2004, fig. 2); its garnet–phengite–paragonite assemblage was formed during HP shearing or recrystallization. We therefore consider c. 48 Ma as a reliable age estimate of D1 deformation in the relevant sector of the Monte Rosa nappe (see Electronic Appendix Text 1).

The comparison of these two samples indicates that at a metamorphic peak temperature ≥600°C (Engi et al., 2001; Keller et al., 2004) Mrlk1 retained some of its $^{40}$Ar whereas Mrlk3 retained none. This proves that petrological, structural and microstructural control is essential in determining whether or not mica will retain inherited $^{40}$Ar during recrystallization. Attributing the inheritance of pre-metamorphic ages at $T_c$ > 400°C only to the lack of an intergranular Ar sink (Warren et al., 2012) does not explain the context of the present samples. First, the diffusivity of Ar in white mica assumed by Warren et al. (2012) is unrealistically high, as the hydrothermal laboratory experiments with added water cannot separate the effects of diffusion from Wood–Walther dissolution–recrystallization (Villa, 2010, pp. 5–6) and, therefore, must not be exported to the geological reality. Second, the observation that sheared sample Mrlk3 gives an Eocene age, unlike Mrlk1, may well be compatible to some extent with different intergranular fluid conditions. However, what is most obvious in the comparison between Mrlk1 and Mrlk3 is that the mineral composition of the sheared sample is different from that of the unshaped one, which is certain evidence of recrystallization.

For $T_c$ to be the only parameter controlling isotope exchange, the $T_c$ of a mineral would need to be lower than the lower boundary of the stability field of that mineral. This leads to a natural classification of mineral geochronometers into two classes.

'Class I' chronometers are those minerals for which $T_c$ is lower than the stability field of the mineral; diffusion is
fast enough to reset the isotopic clock constantly during mineral growth, so that old inherited minerals and newly grown ones have the same age signatures at any time. They never display heterochronous generations, as all grains grew above Tc. Examples are fission-track and (U + Th + Sm–He) chronometers.

Class II chronometers are those minerals for which Tc is higher than the lower boundary of the mineral's stability field. In Class II minerals, heterochronous generations co-exist as overgrowths without isotope resetting, and polygenetic disequilibrium assemblages retain their isotopic disequilibrium. Within-grain disequilibria (sensu Villa & Williams, 2013) have been documented for biotite, K-feldspar, monazite, muscovite and zircon (and most other mineral geochronometers as well). This means that these minerals are all Class II chronometers.

Temperature does play a role in enhancing reaction kinetics, leading to more or less thorough recrystallization of a mineral (including dissolution–repliciation, new growth, reaction). However, T is not the sole parameter uniquely controlling isotope transport. The age of a Class II mineral, as defined above, cannot be used to solve the inverse problem (given a fractional loss, what was the temperature that caused this loss?), as thermally activated diffusion is always slower than competing processes such as fluid-induced recrystallization and deformation-induced recrystallization (Cole et al., 1983; Lasaga, 1986; Villa, 1998, 2006, 2010; Allaz et al., 2011; Villa & Williams, 2013).

REGIONAL PATTERN OF MICA AGES

Zone Houillère Unit
Samples from the Zone Houillère Unit consist of a mixture between metamorphic and detrital mica populations. Partial recrystallization and ensuing preservation of detrital mica is also revealed by staircase-shaped spectra (Fig. 10a, c and e), by the tell-tale anticorrelation of Cl/K with age (Fig. 10b and f), and by the EMP analyses (Fig. 10d; see also Electronic Appendix Text I).

Ruitor Unit
The increase in intensity of deformation towards the SE continues across the Ruitor Unit and is responsible for a decreasing amount of detrital pre-Alpine mica and an increasing amount of metamorphic mica. All samples from the Ruitor Unit contain multiple mica generations. The age spectra of the five analysed samples (Fig. 2) show common features (Fig. 11a).

Samples Cere0033 and Rd1009 display staircase-shaped age spectra. The mixture between Alpine metamorphic mica and pre-Alpine detrital grains indicated by our petrological and microstructural observations (see also Baudin, 1987; Giorgis et al., 1999) is confirmed by the variations in Cl/K (Fig. 11b). In contrast, Cere0033, SBPT and BEZ0033 display 'plateau' age spectra. As discussed above, these apparent 'plateaux' are artefacts due to the simultaneous degassing of two generations of mica, an inherited one and an Alpine metamorphic one, which in this series of samples degas over very similar temperature intervals. A precise quantification of the 'end members' on the basis of the age spectrum alone is impossible, as already demonstrated by Hodges et al. (1994). Total-gas ages of single samples show a systematic eastward decrease from 93 Ma to 55 Ma in relation to their structural position (Fig. 11a). To display the common patterns of these mixtures, all samples are plotted together in a Cl/K vs age correlation diagram (Fig. 11b). The data define a minimum triangle with vertices defined by the envelope of all steps of all samples. The resulting ages of the three vertices, interpreted to represent the three microstructurally observed populations, can be visually estimated from Fig. 11b. The vertex corresponding to the oldest age suggests an apparent age of c. 135 Ma for the inherited (detrital) mica. This is younger than the age of the inherited population of sample Rui9978, suggesting that the pre-Alpine micas in the Ruitor zone were partly recrystallized. This is supported by the microstructural observation of chemically zoned detrital mica grains. The vertex with the highest Cl/K ratio defines an age of c. 47–50 Ma, which is compatible with the observation from sample Rd1009, and it is interpreted to represent the age of D2. The vertex corresponding to the lowest age points to a population with an age of c. 40 Ma, compatible with the estimate for D2 provided by sample Vga0120 discussed below.

Internal Unit
Vga0120 is a mylonitic Triassic quartzite collected at the tectonic contact between the Internal Unit and the P–L Unit (Fig. 2). These mylonites formed during D2 (Bucher et al., 2003, 2004). Our microstructural and chemical data show neither an abundant inherited mica population nor substantial retrogression. Therefore, the age of this sample can be interpreted as the age of D2. The age spectrum is almost flat, with slightly increasing ages (Fig. 7b). In the literature the average of such a quasi-flat age spectrum is sometimes interpreted as a reliable plateau age (e.g. Dal Piaz et al., 2001), despite small but significant differences of the step ages. The Cl/K–age correlation diagram (Fig. 12) reveals a V-shaped trend, indicating heterochemical mixtures of three components. This requires that only the step with the end-member chemical signature should be considered as closely approximating the true age of one specific reservoir and not the average of several heterochemical steps.

The crystallization age of the D2 mica in sample Vga0120 is estimated from the steps with the lowest Cl/K ratio (940°C in both hand-picked and unpicked
Fig. 10. $^{39}$Ar-$^{40}$Ar results from the Zone Houillère Unit. (a) Staircase-shaped age spectrum of sample Rui9978, with a youngest step at 116.9 ± 0.8 Ma and step ages continuously increasing up to 292.2 ± 0.5 Ma. In the literature such staircase-shaped age spectra are sometimes described as being due to diffusive loss (e.g. Markley et al., 1998). However, it is known that intra-grain age gradients in mica result in plateaux, not staircases (Hodges et al., 1994). Instead, staircases such as that of (a) are best interpreted as mixed ages. A pre-Alpine detrital mica population with an age ≥ 292 Ma is mixed with an Alpine metamorphic population. (b) Cl/K–age correlation diagram for Rui9978. The negative linear correlation is evidence for a binary mixture between heterochemical, diachronous mica populations (Villa, 2001). (c) Staircase-shaped age spectrum of sample Ln9939. (d) Mica compositions of sample Rui9958: EMP analyses reveal different mica populations. (e) Staircase-shaped age spectrum of sample Rui9958. (f) Cl/K–age correlation diagram. As in (b), the negative correlation is evidence for a binary mixture.

The three steps defining an apparent ‘plateau’ in Fig. 7b (steps 5–7 of the hand-picked fraction; Electronic Appendix Table 2) have Cl/K ratios of $(1.5–2.3) \times 10^4$, much higher than that $(1.9 \times 10^3)$ of the 940°C step, which we used to infer the D$_2$ vertex. This means that these three steps contain a detectable proportion of Ar from the D$_1$ mica and/or D$_3$ retrogression phases, making the ‘plateau’ statistically valid but petrologically meaningless. We conclude that the clear attribution of this quartzite mylonite to D$_2$
suggests an age of $39.7 \pm 0.1$ Ma for $D_2$ in the Internal Unit.

**Piemont–Liguria Oceanic Unit (Schistes lustrés)**

The age of late $D_k$, closely approximating the metamorphic peak, can be estimated as $c. 47.6$ Ma on the basis of eclogitic boudin Vaud003 (Fig. 8a), which contains an almost pure $D_1$ mica population. In contrast, calcschist Arv007 contains both $D_1$ and $D_2$ mica populations (Fig. 13a and b), whose ages can be estimated from the Cl/K correlation diagram as $c. 39.5$ Ma for the younger and $\geq 45.4$ Ma for the older population.

The Cl/K–age correlation diagram for Traj005 (Fig. 13c) indicates ages of $c. 48$ Ma for $D_1$ phengite and of $c. 40$ Ma for $D_2$ muscovite. The end-member determination in the Cl/K–age diagram and the visual estimation of the age
When studying the mixed D1–D2 micas by using Cl/K–age correlations it is observed that the end-members with ages of 47–48 Ma have higher Cl/K ratios than those with ages around 40 Ma (Fig. 13b and c). It is especially remarkable that eclogitic fluids have often been documented to be hypersaline (Frezzotti et al., 2004, p. 212), which gives further support for our identification of high-Cl/K mica as the HP D1 generation. Additional effects, such as a high partition coefficient for Cl in HP mica (Nazzareni et al., 2008; J. Glosny, personal communication, 2013), can increase the effect of fluid chemistry.

In the samples from the Internal and P–L Units we found no detrital mica. Samples containing two populations of heterochemical Alpine metamorphic mica can be unravelled to give end-member ages for D1 (c. 47–48 Ma) and D2 (c. 40 Ma). These end-member ages coincide with the ages of samples having a single predominant population (Vaud003, Vga0120), which accordingly are characterized by flat age spectra (Fig. 14). We find no indications for excess or inherited 40Ar.

Garnet from three samples from the P–L Unit was dated by Lu–Hf. One sample, for which we also obtained an 39Ar–40Ar age, was additionally dated by Sm–Nd (Electronic Appendix Table 3). The choice of a suitable co-genetic mineral having a low parent/daughter ratio is necessary to accurately estimate the isochron age. For Vaud003, a garnet–omphacite pair gave a Lu–Hf age of 59.6 ± 5.2 Ma and an indistinguishable Sm–Nd age of 45.7 ± 1.2 Ma. For Lan003, a garnet–glauconite pair gave 54.9 ± 4.3 Ma. Both Vaud003 and Lan003 display a prograde HP assemblage. In contrast, Lev008 was extensively retrogressed in the upper greenschist facies; a garnet–epidote pair gave 41.3 ± 7.1 Ma, significantly younger than the two HP assemblages.

The garnet ages allow us to round off the chronology of the Alpine metamorphic cycle in the study area. Lu–Hf and Sm–Nd data are usually interpreted as dating prograde garnet growth prior to the eclogite peak-P conditions. Our data show that the subduction of the P–L Unit (early D1 sensu Bucher et al., 2004) started c. 59 Ma ago. The late stage of D1 is dated at 47–48 Ma by white mica grown syn-kinematically. Greenschist-facies conditions during exhumation (D2) were reached between 43 and 39 Ma ago; this diachronism was caused by an east-to-west migration of deformation (Bucher et al., 2004). Ages of c. 35 Ma are observed around the tectonic contact between the Ruitor and Zone Houillère Units, indicating deformation during a late stage of D2 (Bucher et al., 2004). Nappe refolding (D3) not being associated with neoformed K-bearing minerals, could not be dated in the area of our study. The timing of D3 is inferred from the regional context, which indicates that thrusting at the front of the Penninic units (Roselend Thrust; Loprieno et al., 2011) in the western sector of the ECORS-CROP profile (Fig. 1) overlapped with the late stages of D2 in our area. This thrust was dated at 34–30 Ma (Fügenschuh & Schmid,
D2 mylonites with eclogitic boudin
high strain during D1, almost undeformed during D2
high-Si micas >> low-Si recrystallization

D2 mylonitization -> high strain during D2, no D1 relics

(b) D1 & D2 strongly overprinted during D2, but high Si relics still present (D1)

(c) D2 mylonite D2 mylonitization -> high strain during D2, no D1 relics

Fig. 14. Schematic compilation illustrating the major influence of deformation on the recorded ages. (a) Samples containing only D1 mica (evidenced by microstructural and EMP analysis) show isochemical ages of 47 ± 1 Ma. (b) D1 and D2 mica, both present in the matrix of the boudins, yielding discordant age spectra typical for mixtures. (c) D2 mylonites without D1 relicts showing isochemical ages of 40 Ma.
Comparison with literature

The literature on other sectors of the Western Alps provides time constraints on their tectono-metamorphic evolution that are easily harmonized with the petrological-geochronological framework proposed here. Dal Piaz et al. (2001) analysed white mica from metabasic eclogites in the most internal part of the P–L Unit by the ^39Ar–^40Ar incremental heating technique. Those researchers, not discussing Cl/K systematics, interpreted all their ages in the range between 41 and 46 Ma as representing HP formation ages, because Rb–Sr dating yielded the same age range. This interpretation has interesting implications. First, if one adopts the T_c approach, the statement of Dal Piaz et al. (2001) amounts to assigning a value for T_c to the K–Ar system that is not very different from that of the Rb–Sr system, and moreover, substantially above 500°C. Second, if the HP mineral ages are interpreted as formation ages, the possibility of obtaining mixed ages produced by the subsequent retrograde tectono-metamorphic evolution is very likely [albeit not mentioned by Dal Piaz et al. (2001)], because mica that was newly formed during the post-HP exhumation–retrogression must be retaining its Ar signature as well. For an equivalent of the P–L Unit, the Voltri Group eclogite (150 km SE of our study area), Federico et al. (2005) found ages around 49 Ma for eclogitic parageneses and ages <40 Ma for the retrogression. This suggests that the average age around 43 Ma reported by Dal Piaz et al. (2001) may record a mixture of eclogitic mica (with an age of ~47 Ma, compatible with the HP age proposed here) and partially retrogressed micas younger than 41 Ma. The mafic rocks analysed by Dal Piaz et al. (2001), by analogy to sample Vaud003, date only the late stages during D_3.

White mica ^39Ar–^40Ar ages between 25 and 300 Ma were reported by Markley et al. (1998) for the Siviez–Mischabel nappe, which corresponds to the NE continuation of the Ruitor Unit of this study according to Gouffon (1993). Although their data do not show an age difference for different grain sizes (Markley et al., 1998, pp. 420–421), those researchers proposed that diffusion controls the total gas K–Ar ages of white mica in the central Siviez–Mischabel nappe. Furthermore, Markley et al. stated that Hercynian mica is rimmed by 60 Ma old mica and concluded that these samples overestimate the timing of deformation by 20 Ma. Giorgis et al. (1999) reported pre-Alpine ages and proposed a Variscan P–T path from the ^39Ar–^40Ar data. Within our interpretative scheme, their staircase-shaped age spectra represent multiple mica generations and cannot be used to infer the ages of the pure D_1 or D_2 mica growth in the absence of petrological–chemical studies at the micrometre scale.

Chopin & Maluski (1980) reported discordant ^39Ar–^40Ar age spectra, interpreted as Cretaceous mica ages, from the Gran Paradiso Unit (a southwestern equivalent of the Monte Rosa nappe, both being parts of the most internal Briançonnais). It is likely that their samples, like some of the present study, record mixed ages between detrital and metamorphic mica generations.

Freeman et al. (1997) proposed an interpretation of the greenschist-facies evolution on the basis of Rb–Sr micro-sampling ages on white mica. They proposed 34 Ma as the age of back-thrusting along a shear zone (their Entrelor Shear Zone). However, we consider this shear zone as a refolded D_3 nappe contact rather than a back-thrust (Bucher et al., 2003) because the stretching lineation used by Freeman et al. is related to a D_3 thrust that was overturned by D_3 back-folding (Bucher et al., 2003; Bousquet, 2008).

In the Zone Houillère Unit, adjacent to the Houiller Front (Fig. 2) and the Valaisan domain (Fugenschuh et al., 1999; Loprieno et al., 2011), Freeman et al. (1998) reported Rb–Sr white mica ages for other samples from the same area. Even if, strictly speaking, their isochrons for detrital minerals do not rigorously meet the requirement that all phases be in equilibrium at time zero, most of their mica samples are sufficiently radiogenic that the calculated ages are not over-sensitive to the isotopic composition of the initial Sr. Freeman et al. obtained pre-Alpine ages varying from 324 ± 7 Ma close to the front of the Zone Houillère Unit to 188 ± 3 Ma towards more internal positions. Our sample Rui9978 (from an intermediate position with respect to the regional distribution of their samples) confirms this trend, which further supports evidence for a mixture between metamorphic and detrital populations. This trend is also compatible with the observation that intensity of deformation and metamorphic temperature increase towards the SE (Fig. 2; Bucher et al., 2003, 2004). Both Rui9978 and the samples of Freeman et al. (1998) are well below the T_c values of Jäger (1967) for the respective isotopic systems, and yet they underwent loss of radiogenic 40Ar and 87Sr. The fact that the Rb–Sr and K–Ar systems yield identical ages contradicts ‘thermochronology’, which does not predict any 87Sr diffusion in white mica at such low temperatures. On the contrary, our data indicate that it is deformation-induced recrystallization, rather than diffusion, that is responsible for the exchange of both 40Ar and 87Sr, which are therefore expected to correlate (Villa et al., 2006).

Reddy et al. (1999) concluded that Rb–Sr data for recrystallized white mica indicate that the Gressoney Shear Zone (GSZ), associated with top-to-the SE kinematics, was active between 43 and 35 Ma. Those researchers interpreted the GSZ as the upper boundary of an extrusion channel active during D_2 exhumation. In our study D_2 is interpreted to have been active between 43 and 35 Ma,
consistent with the study of Reddy et al. (2003), and with the dating at 39 Ma of the retrograde shearing during exhumation in the neighbouring Gran Paradiso Massif (Rosenbaum et al., 2012).

Agard et al. (2002) dated white mica from the P–L Unit c. 60 km to the south of our sampling area. The ages that those workers proposed for the eclogitic and retrogressive metamorphic stages are similar to the results of our study. All along strike in the Western Alps arc, Cretaceous apparent mica ages were observed (Monte Rosa, Gran Paradiso, etc.; Agard et al., 2002, fig. 3). Monié (1990) also observed 40Ar inheritance in HP phengite. It seems likely that the observations made in the present study are not limited to our study area, but probably also hold true for corresponding units further north and south. Our work provides a straightforward explanation for the excessively high (60–130 Ma) ages recorded only by mica in most of the HP portions of the Alps. These Cretaceous apparent ages are due to relic pre-Alpine micas, which were incompletely degassed owing to a combined effect of low temperatures (<50°C) and incomplete neocrystallization. We also reach two important methodological conclusions that agree with the results of Agard et al. (2002): (1) we argue that the 39Ar–40Ar isotopic system in HP phengite normally records formation and/or deformation ages; (2) our incremental heating and their laser ablation data yield consistent results. The compatibility of the data presented by Agard et al. (2002) with our data, together with the consistency of our data throughout the tectonic units along the ECORS-CROP transect, reinforces the correspondence between microstructures and 39Ar–40Ar ages obtained for each sample. Those researchers also found consistency between 39Ar–40Ar mica age and relative age of the white mica as inferred from macro- and microstructural studies, and stated that this makes the hypothesis of excess 40Ar at the scale of the whole orogen very unlikely (Agard et al., 2002, p. 612–613). Whereas the study of Agard et al. (2002) applies to the more internal P–L Unit, our study extends these findings to the more external Briennois paleogeographical domain. The Lu–Hf age of the epidote–garnet retrograde assemblage (413 ± 71 Ma, Lev008) further reduces the likelihood that excess 40Ar had a major effect. In our study area, excess 40Ar plays a negligible role compared with that of recrystallization and/or inheritance. Hence, we disagree with internally inconsistent criteria (e.g. Reddy et al., 2003) to reject the age of some of the samples.

Other areas of the Western Alps can be constrained by the 39Ar–40Ar data of Agard et al. (2002) from an area further south, and by the Rb–Sr data for the GSZ of Reddy et al. (1999), to a similar time frame to that of the transect studied here. Underplating of the South Penninic suture zone by the Briennois units in Eastern Switzerland started at c. 50 Ma as indicated by Rb–Sr white mica ages (Bachmann et al., 2009). This is consistent with the 47–48 Ma age for the eclogitic mica crystallization proposed here.

Agreement regarding the P–T evolution, the kinematics and the geochronological data between these studies indicates that the geodynamic model of Bucher et al. (2003) might be valid for larger parts of the Western Alps. Further detailed studies that combine field, petrological and geochronological analyses will be needed to improve our understanding of the timing of the Alpine orogeny.

In summary, a general pattern consisting of three key points can be recognized in all available white mica age data from the Western Alps, in combination with the Lu–Hf and Sm–Nd garnet ages: (1) excess 40Ar is negligible, whereas inherited 40Ar is abundant because Ar diffusion is very slow; (2) Ar is lost by temperature-independent mica recrystallization anywhere between 250 and 600°C; (3) monogenetically recrystallized, single-generation neo-formed mica gives reliable constraints on D1 and D2 ages, consistent with those of mica samples having the same microstructural setting, the same homogeneous chemical composition, and the same petrogenetic significance.

Mounting evidence for the same three-point pattern is forthcoming from other HP terrains. From the Attic–Cycladic HP rocks, Bröcker et al. (2013) also found mixed mica generations with ubiquitous Ar inheritance; they further observed that Ar retention is Sr retention. This reinforces our suggestion that, in the absence of recrystallization, 87Sr and 40Ar loss are both minor if T is <500°C.

Our three-point pattern has general implications for the mechanisms controlling K–Ar ages. Because the radiogenic 40Ar recoils away from the mica interlayer site occupied by 40K into the T–O–T framework (Hetherington & Villa, 2007), the limiting factor for its transport is the mobility of the structure-forming cations (Villa, 2010), which is also rate-limiting for 87Sr transport. This explains the observations of similar 40Ar and 87Sr retention (Bröcker et al., 2013). The low intrinsic mobility of 40Ar and 87Sr, however, needs to be reconciled with the observation that 40Ar and 87Sr loss occurs at 250–300°C in the Zone Houlèire Unit (this study; Freeman et al., 1998). The factors controlling recrystallization during HP retrogression have been explained in detail by Parra et al. (2002). White mica–chlorite pairs in retrogressed HP rocks from Tinos (Attic–Cycladic belt) exhibit compositional variability that stems from the achievement of equilibrium only at the local mm-scale. Crystallization of new grains was fast, freezing in different segments of the retrogressive P–T path; equilibrium assemblages were achieved by crystallizing new grains showing progressive composition changes, whereas diffusive re-equilibration of relic grains was negligible, so that mineral compositions did not readjust to the changing P–T conditions (Parra et al., 2002, pp. 54–55).
**P–T** conditions alone were evidently not sufficient to reset mineral compositions, it is necessary to take into account the presence of aqueous fluids (\(a_{\text{H}_2\text{O}}\)), the availability of solutes \((X)\), and the intensity of \(D\), and to consider that the actual control on mineral compositions is a function of \(P, T, a_{\text{H}_2\text{O}}, X\), and \(D\). An aqueous fluid is always required, as it is 'the principal catalyst of metamorphic reactions' (Parra et al., 2002, p. 54; Putnis, 2009), and therefore of isotope exchange (Villa, 2010). Strain focusing localizes deformation-enhanced reactions to a progressively smaller volume, leaving the rest of the rock unaffected; thus deformation vastly prevails over diffusion. As documented by Worley et al. (1997), diffusion is detectable only at \(T\) much higher than 520°C. This additional, independent argument rounds off the evidence reviewed here that \(Ar\) retention in white mica is nearly complete at \(T < 500 \text{°C}\) as long as the mineral is not recrystallized.

The regional distribution of eastward decreasing mica ages (Fig. 3) could be mistaken for a temperature-dependent pattern amenable to thermochronology. To the extent that more deformed rocks also generally record a higher metamorphic grade, the younger samples in the east indeed also experienced higher temperatures. However, when examined in close detail, the east–west age gradient is neither smooth nor decreasing throughout the easternmost unit, as would be expected if temperature alone were controlling \(K–Ar\) ages in mica. Instead, the context of all the independent lines of evidence reviewed above forces us to a very different interpretation. Diffusion of \(Ar\) in white mica is extremely slow. In most or all samples it is overrun by recrystallization, which mainly depends on \(a_{\text{H}_2\text{O}}, X\), and \(D\), and only marginally on \(T\). This dependence provides the required explanation for why the \(K–Ar\) ages of detrital mica were reset (in unison with \(Rb–Sr\) ages) at 230–300°C in the Zone Houillère Unit, but were not reset to zero at 600°C in the Monte Rosa samples.

**CONCLUSIONS**

The early phase of HP metamorphism in the P–L Unit is indicated by Lu–Hf and Sm–Nd ages of \(\sim 50–60 \text{ Ma}\) for prograde garnet growth. The age of the eclogitic peak is closely constrained by \(^{39}\text{Ar}–^{40}\text{Ar}\) dating of white mica, which grew at 10–15 kbar during the final stages of \(D_1\), at 47–48 Ma in all tectono-metamorphic units. Exhumation related to \(D_2\) (Bucher et al., 2003, 2004) took place diachronously around 40 Ma. The \(P–T–t\) evolution of \(D_1\) and \(D_2\) proposed here is compatible with data from the P–L Unit further south in the Western Alps (Agard et al., 2002). The comparison between the \(^{39}\text{Ar}–^{40}\text{Ar}\) laser ablation data of Agard et al. (2002) and the data of this study confirms that mixed populations are correctly unravelled with the chemical information provided by the \(^{39}\text{Ar}–^{40}\text{Ar}\) incremental heating technique. The Cl/K vs age common denominator isotope correlation diagrams allow the identification of heterochemical mica generations and of their ages.

Consistency within fractions of the same sample, between samples within a given tectonic unit, and also along the entire studied sector of the ECORS-CROP transect requires that neither temperature-dependent diffusive loss of \(^{40}\text{Ar}\) nor gain of excess \(^{40}\text{Ar}\) played an important role in the case of our samples. The K–Ar isotopic record of all samples from the ECORS-CROP transect and the Monte Rosa nappe was mainly controlled by the following processes. (1) \(^{40}\text{Ar}\) inheritance is observed in preserved petrographic pre-Alpine reliefs that are mixed with Alpine mica populations, and in \(D_1\) relics that are mixed with a \(D_2\) population. Inherited \(^{40}\text{Ar}\) is retained even in relict grains subjected to metamorphic temperatures \(\geq 500 \text{°C}\). In the only sample showing permissible evidence for \(^{40}\text{Ar}\) diffusion, the inferred diffusion parameters \((E = 250 \text{ kJ} \text{ mol}^{-1}, D'_0 < 0.03 \text{ cm}^2 \text{ s}^{-1})\) confirm that diffusion is a very slow and hence very inefficient way to reset K–Ar ages. (2) \(^{40}\text{Ar}\) loss from mica occurs instead by temperature-independent, deformation-induced and fluid-assisted recrystallization between 250 and 600°C. (3) \(^{39}\text{Ar}–^{40}\text{Ar}\) stepwise heating data with a chemically homogeneous signature and a uniform age are observed only in samples containing mica of a single generation (\(D_1\) or \(D_2\)), which are often highly deformed. This contrasts with samples where grain-scale microstructural and chemical observations indicate incomplete recrystallization and preservation of multiple populations, which are always the cause of staircase-shaped and/or upward-convex age spectra. In weakly deformed and poorly recrystallized samples the mass fraction of inherited grains is very high. The successful recognition of mixtures as a prerequisite for their reliable dating underscores that microstructural, microchemical and petrological analyses must not be viewed as optional ‘accessory information’, because they are as essential for any geochronological interpretation as the mass spectrometric analyses.

**ACKNOWLEDGEMENTS**

We thank all our colleagues from the ‘Groupe Brianconnais’, as well as Rainer Abart, Annett Büttner, Stefano Ceriani, Christian de Capitani, Martin Engi, Alexandra Heri, Lukas Keller, Jan Kramers and Marco Malúsa for stimulating discussions. Mica samples Mrlk1 and Mrlk3 were separated and provided by Lukas Keller. Reviews by R. Schuster and W. Müller on an earlier version of this paper, as well as those by J. Glodny, M. Flowerdew and an anonymous reviewer, helped to improve the presentation. The editorial handling by R. Gierè was especially constructive.
FUNDING

The Swiss National Science Foundation provided support for this work through grant 20-63391.00 to S.M.S.

SUPPLEMENTARY DATA

Supplementary data for this paper are available at Journal of Petrology online.

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