

occurs in a similar fashion to the so-called benzoin condensation³¹. As shown in Fig. 4, cyanide ion first adds to C₆₀ to form C₆₀(CN)⁻ (3), which can react with the closely located molecule of C₆₀ in the 1,4-addition mode to minimize steric congestion and gives anion 4. Then an intramolecular S_N2' reaction of 4 furnishes the [2 + 2] dimer 1. A further reaction of dimer 1 with cyanide ion could occur, but this would make 1 acquire a negative charge together with a cyano group, and would cause the rupture of its [2 + 2] bonds as inferred from the above-mentioned electrochemical behaviour of 1. Thus the overall reaction results in the highly selective formation of dimer C₁₂₀ instead of oligomers and polymers.

In single crystals of 1 obtained in the present study, the C₁₂₀ molecules are arrayed in highly ordered layers, different from the face-centred cubic arrangement of C₆₀. Photo-irradiation of this crystalline material should lead to the formation of a C₆₀ polymer, which might have a more well-defined structure than previously reported ones^{7,32}. The present result indicates that a thermally forbidden [2 + 2] process of a highly electron-deficient and strained double bond such as that in fullerenes can take place under solid-state reaction conditions catalysed by cyanide ion. Application of the present method to C₇₀ is expected to lead to another new carbon allotrope, C₁₄₀. □

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The Lu–Hf dating of garnets and the ages of the Alpine high-pressure metamorphism

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It remains controversial whether burial and exhumation in mountain belts represent episodic or continuous processes^{1–20}. Regional patterns of crystallization and closure ages of high-pressure rocks may help to discriminate one mode from the other but, unfortunately, metamorphic geochronology suffers from several limitations. Consequently, no consensus exists on the timing of high-pressure metamorphic events, even for the Alps—which have been the subject of two centuries of field work. Here we report lutetium–hafnium (Lu–Hf) mineral ages on eclogites from the Alps as obtained by plasma-source mass spectrometry. We find that the Lu/Hf ratio of garnet is particularly high, which helps to provide precise ages. Eclogites from three adjacent units of the western Alps give (from bottom to top) diachronous Lu–Hf garnet ages of 32.8 ± 1.2, 49.1 ± 1.2 and 69.2 ± 2.7 Myr. These results indicate that the Alpine high-pressure metamorphism did not occur as a single episode some 80–120 Myr ago^{6,7,10,18}, but rather that burial and exhumation represent continuous and relatively recent processes.

With the discovery of the coesite-bearing quartzites of Dora Maira in the western Italian Alps¹, the exhumation history of rocks that had been buried to ~100 km depth during the formation of the Alps provided fresh insight into alpine tectonic processes. Published data, however, emphasize both the extent of inconsistency of the chronological data on high-pressure metamorphism and its far-reaching geodynamic implications^{2–5}. The Eoalpine age (100–120 Myr) inferred from a discordant array of zircons⁶ and from ³⁹Ar–⁴⁰Ar dating in phengites^{7,8} seems to support a widely accepted view that the exhumation of eclogites is coeval with the continuing subduction of the oceanic Tethyan lithosphere under the African plate⁹. Eclogite burial and exhumation also appear to be Eoalpine in age in the Sesia-Lanzo unit with Rb–Sr, K–Ar and U–Pb ages in the range 60–114 Myr (refs 10–12). In contrast, the Late Eocene–Early Oligocene age found for Dora Maira^{13,14}—as a lower concordia intercept defined by zircons and as a U–Pb isochron on ellenbergerite, which was later confirmed by U–Pb ion-probe data on zircons¹⁵—rather suggests that burial and exhumation are far more recent and coeval with the collision between the Apulian and European plates. Sm–Nd and U–Pb Eocene ages are also known from other eclogite localities in the western and central Alps^{16–18}. As these eclogites seem to have been overprinted in the greenschist facies during the Oligocene (25–35 Myr ago) at the latest^{7,19}, the value of the exhumation rate may vary from a fraction of a millimetre to several centimetres per year depending on which age is accepted for the high-pressure metamorphism.

Other than K–Ar, of which the significance is obscured by the

Table 1 Lu–Hf and Sm–Nd data

| | Lu (p.p.m.) | Hf (p.p.m.) | ¹⁷⁶ Lu/ ¹⁷⁷ Hf | ¹⁷⁶ Hf/ ¹⁷⁷ Hf | Sm (p.p.m.) | Nd (p.p.m.) | ¹⁴⁷ Sm/ ¹⁴⁴ Nd | ¹⁴³ Nd/ ¹⁴⁴ Nd |
|---------------------------------------|----------------|----------------|--------------------------------------|--------------------------------------|----------------|----------------|--------------------------------------|--------------------------------------|
| Sesia (Lillianes-Fontainemore) | | | | | | | | |
| Whole rock | 0.211 | 0.262 | 0.116 | 0.282632 (72) | 4.62 | 19.61 | 0.1422 | 0.512106 (26) |
| | 0.205 | 0.221 | 0.132 | 0.282877 (95) | 4.61 | 19.53 | 0.1424 | 0.512178 (27) |
| | 0.197 | 0.267 | 0.105 | 0.282769 (32) | 4.64 | 19.57 | 0.1428 | 0.512093 (24) |
| Garnet | 1.02 | 0.0390 | 3.69 | 0.287667 (74) | 0.203 | 0.253 | 0.4840 | 0.510662 (52) |
| Garnet (impure) | 0.833 | 0.0511 | 2.31 | 0.286051 (84) | 0.619 | 1.96 | 0.1906 | 0.512003 (23) |
| Clinopyroxene | 0.0128 | 0.185 | 0.0798 | 0.282535 (42) | 2.21 | 8.43 | 0.1581 | 0.513154 (27) |
| Phengite | 0.00315 | 0.0239 | 0.0187 | 0.282731 (151) | 3.33 | 7.60 | 0.2643 | 0.513198 (22) |
| Monviso (Lago Superiore) | | | | | | | | |
| Whole rock | 0.643 | 0.454 | 0.192 | 0.283234 (32) | 7.55 | 25.17 | 0.1807 | 0.513012 (22) |
| Garnet | 1.75 | 0.0311 | 8.00 | 0.290696 (91) | | | 0.65 | 0.513131 (24) |
| Clinopyroxene | | | | | 3.80 | 12.58 | 0.1823 | 0.513041 (21) |
| Dora-Maira (Parigi) | | | | | | | | |
| Whole rock | 0.267 | 0.144 | 0.263 | 0.282828 (22) | 8.55 | 41.96 | 0.1228 | 0.512189 (18) |
| Garnet | 1.67 | 0.107 | 2.21 | 0.284067 (28) | | | 0.089 | 0.511738 (31) |

The replicates of Sesia-Lanzo whole rocks represent different powder aliquots. The numbers in parentheses are twice the standard error. The Nd and Hf isotopic compositions of the Monviso whole rock sample plots in the field of mid-ocean-ridge basalts, whereas those of the Dora Maira massif and the Sesia-Lanzo zone plot in the field of continental rocks.

unpredictable presence of excess argon, high-temperature paths of eclogite exhumation have so far been dated using only two methods. U–Pb dating of zircons gives, in principle, reliable crystallization ages, although zircon is not a mineral specific to high-pressure assemblages. In addition, as best shown in the case of Dora Maira^{6,14}, linear arrays defining concordia lower intercepts indicate the presence of inherited lead and therefore do not provide unambiguous crystallization ages. Ion-probe dating can recognize old discordant areas in zircons, but the youngest part of the concordia is linear, making mixing between young populations difficult to identify. The second method, which is that of Sm–Nd internal isochrons in garnet-bearing rocks, often fails when isotopic equilibration between clinopyroxene and garnet has not been achieved²⁰. In addition, the small spread of Sm–Nd ratios severely limits the precision of this method of dating. The closure temperature of Sm–Nd in garnet is still debated but is supposed^{20–22} to be higher than 600 °C, which should provide valuable information on the timing of eclogite exhumation.

Sguigna *et al.*²³ determined a value for the decay constant of ¹⁷⁶Lu of $(1.93 \pm 0.03) \times 10^{-11} \text{ yr}^{-1}$. An advantage of the Lu–Hf method of dating is therefore a relatively fast radiogenic ingrowth of ¹⁷⁶Hf which in particular is three times faster than that of ¹⁴³Nd. The uncertainty on the decay constant affects Lu–Hf ages by no more than 1.5%. The advent of plasma-source mass spectrometry, which combines a magnetic sector double-focusing mass spectrometer with a plasma source, has brought within reach for the first time precise Lu–Hf geochronology on small or Hf-poor samples. The Plasma 54 in Lyon can determine the isotopic composition of Hf on small quantities (20 ng) with an excellent external reproducibility (40 p.p.m.). Separation of Lu and Hf, blanks, standard values, and mass spectrometry are described elsewhere²⁴. Internal precision on Hf isotope compositions is usually in the range of 20–40 p.p.m. and isotope dilution produces Lu/Hf ratios currently precise to ~1%. Isolation of Sm and Nd is reduced to the separation of a rare-earth-element-enriched fraction by cation exchange chromatography (B.L. and F.A., manuscript in preparation).

High-pressure rocks are found in three internal units of the Alps known, from bottom to top, as Pennine, ophiolitic and Austro-Alpine²⁵ (Fig. 1). In the western Alps, the Dora Maira massif, the Monviso, and the Sesia-Lanzo zone each belong to one of these units (in the order as mentioned) and offer extensive outcrops of low-temperature eclogitic rocks. We have measured the Hf and Nd isotopic compositions and the Lu/Hf and Sm/Nd ratios of one eclogitic sample from each locality and in some of their constituent minerals, notably garnet, phengite and clinopyroxene. The Dora Maira coesite–pyrope–quartzite assemblage described by Chopin¹

was sampled in the classical locality of Parigi. This eclogite was equilibrated at ~700 °C and >30 kbar (ref. 1). The Monviso sample is a mafic garnet–omphacite–glaucophane eclogite equilibrated at ~450 °C and 15 kbar (ref. 26). The Sesia-Lanzo sample is a felsic eclogite equilibrated at 550 °C and >14 kbar (ref. 27). In each case, the decompression took place with no noticeable reheating.

The Lu–Hf data (Table 1) attest to the large ¹⁷⁶Lu/¹⁷⁷Hf ratio of garnets which reaches 3 for felsic rocks and 8 for the mafic eclogite of Monviso. Because the samples were not dissolved in pressurized bombs, the reproducibility of Lu–Hf replicate analyses of felsic

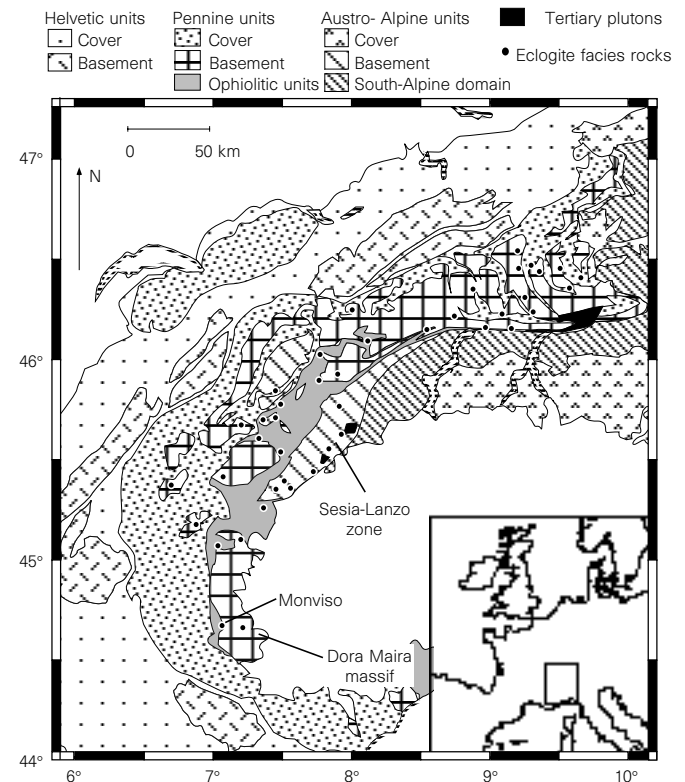


Figure 1 Sketch map of the structure of the western and central Alps with the distribution of eclogite facies rocks and sample localities indicated. The Helvetic units represent the European mainland, the Pennine units the European margin and the Tethyan oceanic crust, and the Austro-Alpine units the Apulian margin.

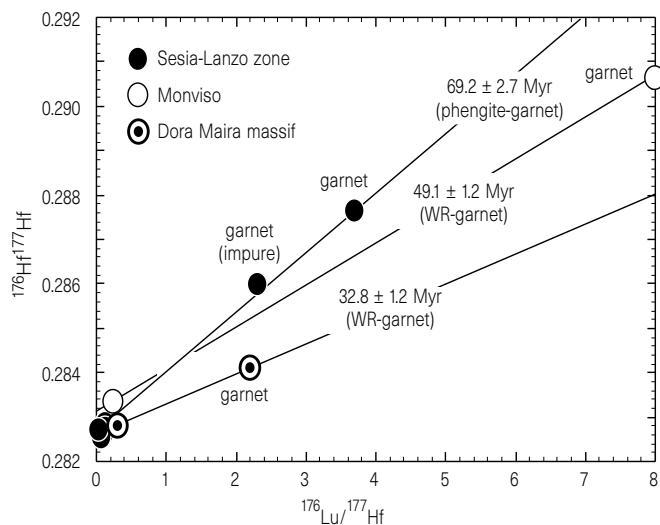


Figure 2 Lu-Hf isochrons (WR, whole rock). Phengite, clinopyroxene and whole rocks plot in the bottom left part of the diagram. Note the high value of the Lu/Hf ratio of garnets. Error bars are significantly smaller than the symbols. The rather scattered results for three replicates of a Sesia-Lanzo whole rock sample probably reflects the presence of inherited zircons. The ages, however, are well constrained by the garnet fractions.

whole rocks is not very good, suggesting that some refractory minerals may be escaping dissolution. This problem, however, should not affect the dating of mineral pairs. Because of the high Lu/Hf ratio, Hf in garnet of even very young samples is fairly radiogenic, making Lu-Hf chronology of garnet-bearing assemblages a promising technique.

The whole-rock garnet age of the Dora Maira sample is 32.8 ± 1.2 Myr (Fig. 2), which compares well with earlier 35 Myr U-Pb zircon ages¹⁵, a Sm-Nd age of 31.8 Myr on garnets from sample 15623a, and a U-Pb age of 31.4 ± 1.3 Myr on ellenbergerite^{13,14}. The whole-rock garnet age of the Monviso sample of 49.2 ± 1.2 Myr (Fig. 2) is in excellent agreement with the ⁴⁰Ar-³⁹Ar ages found on phengite²⁸. The phengite-garnet age of 69.2 ± 2.7 Myr (Fig. 2) obtained on the Sesia-Lanzo sample is only marginally older than the U-Pb ages reported from zircons (65 Myr)¹¹ and sphene (66 Myr)¹². A less-purified fraction of the same garnet gives a slightly older age of 74.6 ± 4.1 Myr (Fig. 2) though still consistent within errors. The Sm-Nd data on the felsic eclogites of Dora Maira and Sesia-Lanzo are of little chronological value, most likely because of inadequate mineral purity. This shows that, owing to the high Hf content of garnets with respect to other eclogitic minerals, Lu-Hf dating is far less sensitive to the quality of mineral separation than Sm-Nd. The Monviso sample was inadvertently underspiked. The 63 ± 7 Myr Sm-Nd age obtained from the clinopyroxene-phengite pair from the Sesia-Lanzo sample and the crude 40 ± 10 Myr clinopyroxene-garnet Sm-Nd age acquired through a calibration of the Sm/Nd beam ratio using standard solutions are, however, consistent with the Lu-Hf data.

The significance of ages depends on whether the temperature at which exchanges of parent and daughter isotopes are frozen, the closure temperature T_c (ref. 29), is higher or lower than the temperature of crystallization. U-Pb ages of concordant zircons date the crystallization of this mineral. By contrast, K-Ar ages generally date closure at low temperature. Because little is known about diffusion of Hf in common minerals, it is not clear whether Lu-Hf ages of eclogitic garnets reflect a closure temperature or the time of crystallization. Hafnium in granitic liquids diffuses more slowly than neodymium³⁰. The ionic radius³¹ of six-fold-coordinated Hf⁴⁺ (0.083 nm) in crystals is intermediate between that of Mg²⁺ (0.072 nm) and that of the trivalent rare-earth elements (0.11 nm). Comparison with the closure temperature of Fe-Mg thermometers³² and Sm-Nd chronometers²⁰⁻²² suggests that the closure temperature of the Lu-Hf system in garnet-bearing assemblages is most probably in excess of 600 °C. This chronometer therefore dates the early stage of exhumation in Dora Maira, and the

high-pressure metamorphic event itself in the low-temperature eclogites of Monviso and Sesia-Lanzo.

The exhumation of eclogites seems to be very rapid. At Dora Maira, the U-Pb crystallization age of zircons, the high-temperature Sm-Nd and Lu-Hf closure ages, and the K-Ar age of the retrogressive phengites crystallized in the greenschist facies, all coincide within error (~3 Myr). The coesite-pyroxene quartzites therefore seem to have been decompressed from 30 to 3 kbar at a rate of the order of 3 centimetres per year, well outside the range accepted for erosion rates. Similar arguments also support fast exhumation for the Sesia-Lanzo zone and Monviso.

The age of the early stage of exhumation obtained by the Lu-Hf method on the same type of mineral is older when the structural position of the units that host the eclogites is higher. The Lu-Hf ages at Monviso and Sesia-Lanzo clearly predate the Late Eocene-Early Oligocene collision between the European and Apulian plates, which is dated as the time when material from either continental margin engaged into the Pennine and Austro-Alpine nappes^{25,33,34}. The youngest record of eclogite exhumation actually coincides within errors with the collision and is found in the Pennine unit at Dora Maira and Alpe Arami in the central Alps¹⁸. It predates by less than a few Myr the intense 31-Myr-old magmatic activity represented by the emplacement of the granitic pluton at Bergell³⁵ and other localities³⁶, and by the eruption of the widespread andesites found as clasts in the Tavayannaz and Champsaur formations³⁷. The suggestion that at 30 kbar eclogite-facies rocks could partially melt³⁸ is supported by the contemporaneity of their exhumation with magmatism and by the similarity of Nd isotopic compositions in the felsic eclogites and in Alpine granites³⁹.

The geochronological evidence indicates that the process of burial and exhumation of crustal rocks is rapid with respect to the overall duration of the high-pressure conditions. Some eclogites are already brought to the surface well before the protolith of others even become buried. The exhumation of the Sesia-Lanzo zone was complete ~35 Myr before the Dora Maira massif was metamorphosed in the eclogite facies. Some eclogites therefore rise through a near steady-state mechanism apparently unrelated to the collision, possibly through prism flow⁴⁰ in a subduction environment. □

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A sexually selected character displacement in flycatchers reinforces premating isolation

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Theory suggests that natural selection against the production of unfit hybrids may reinforce barriers to gene flow, eventually leading to reproductive isolation of differentiated populations^{1–4}. This mode of speciation may be achieved by female choice selecting for a divergence in male secondary sexual traits that facilitates species recognition. Although intuitively appealing, conclusive evidence for such reinforcement is generally lacking^{5–8}, and serious doubts have been raised about its validity^{9–11}. We have tested key predictions of the reinforcement hypothesis on the European, black-and-white, *Ficedula* flycatchers, using molecular techniques, field observations and mate choice experiments. In populations where two species coexist, we show that female choice selects for a divergence in male plumage colour and that the resulting character displacement reduces the frequency of hybridization.

The current geographical distribution of European *Ficedula* flycatcher forms has led researchers to suggest that a sympatric divergence in secondary sexual characters has occurred^{12–14}. In a large area in Central and Eastern Europe the breeding distribution overlaps for two clearly differentiated flycatchers, the brown form of

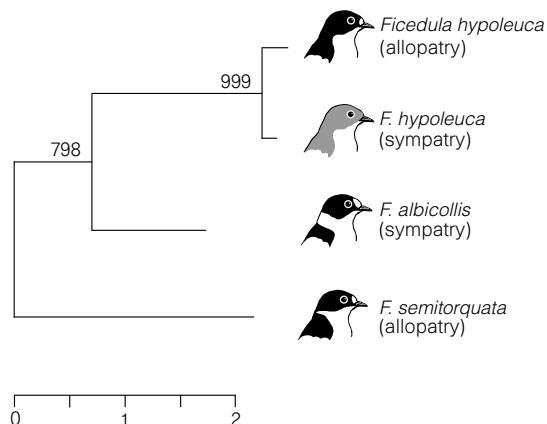


Figure 1 Phylogenetic relationships among sympatric and allopatric flycatchers based on mitochondrial DNA sequences. A neighbour-joining tree is presented with genetic distances drawn to scale. The scale refers to Kimura 2-parameter distances (%). Values at the nodes represent bootstrap replication scores based on 1,000 resamplings. The phylogenetic reconstruction suggests that the plumage characters in sympatry are derived traits, supporting the argument of a sympatric character divergence.

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