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Tracing the origin of wood at the regional scale with dendrochemical markers: elemental and strontium and neodymium isotopic composition

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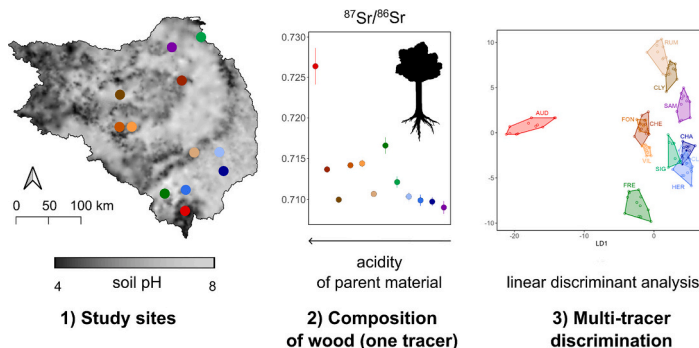
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HIGHLIGHTS

- Multivariable (elemental and isotopic) system is a robust timber tracing tool.
- Discrimination of sites is possible at a regional scale with homogeneous geology.
- Strontium isotope ratio is the most efficient tracer in the system.
- Neodymium isotope ratio is a new relevant tracer for origin of plants.
- Differences between oak species do not have impact on dendrochemical tracing.

GRAPHICAL ABSTRACT



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ABSTRACT

The dendrochemical approach holds significant promise for determining the geographical origin of wood as a complementary tool to dendroprovenancing based on tree-ring width. Tracing the origin of wood based on its elemental and isotopic composition is in particular interesting for provenance studies at the regional scale, as dendrochemical signatures are indicative of geological and pedological characteristics. Although, absorption of nutrients and trace elements reflects the composition of soil bioavailable pools, it is also modulated by multiple environmental and tree related factors. We assess the dendrochemical approach in oak wood provenance studies

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Quercus
Major and trace elements
Seine river catchment

regarding the challenges posed by 1) geochemical variation at a local level, and 2) dendrochemical variation related to oak species, age and social status. A combination of 13 elemental concentrations and 2 isotope – Sr and Nd – ratios was analyzed in oak wood from 12 forests situated in the large Seine river catchment in France. The sampling targeted sites with representative types of geological parent material, where adult trees of two common temperate *Quercus* species (*Quercus petraea* and *Quercus robur*) were selected. The impact of tree characteristics was markedly weaker than that of the site factor and the minimal differences in dendrochemical composition between *Quercus petraea* and *Quercus robur* were considered without effect on determination of the geographical origin. Linear discriminant analysis based on Ca-normalized elemental concentrations and Sr and Nd isotope ratios correctly classified the origin of 93 % of the sampled trees. Strontium isotope ratio $^{87}\text{Sr}/^{86}\text{Sr}$ was the strongest provenance indicator capable of determining the origin of 55 % of wood samples on its own. Our system based on elemental and strontium and neodymium isotopic compositions provides robust indicators for wood tracing and might be applied to provenance studies in environment, physiology, history and archeology.

1. Introduction

Tracing wood origin by means of dendrochemical analysis is a promising alternative to conventional dendroprovenancing *i.e.*, tracing with tree-ring width, but it is far from unfolding its full potential (Boeschoten et al., 2023; D'Andrea et al., 2023; Mortier et al., 2024). Indeed, only 2 % of studies based on dendrochemistry (the elemental, molecular and isotopic composition of wood) address the question of wood provenance (Low et al., 2022). Dendrochemical approaches rely on elemental and isotopic signatures recorded in secondary xylem during or some years after its formation. Among the geochemical signature of wood, the isotopes of hydrogen (H), carbon (C) and oxygen (O), whose proportions depend on local climatic conditions (temperature, precipitation), can be markers of the geographical origin of the trees. However, the wood H, C and O isotopic composition can be influenced by fractionation effects involving biological or physico-chemical processes that are not linked to climatic or geographical factors, making its use as geographical tracers complex. An alternative method relies on the use of the inorganic constituents of wood, which are much less abundant but more closely linked to the local geological context.

1.1. Where do wood inorganic constituents come from, and why are radiogenic isotopes tracers of wood provenance?

In forest soils, available (mobile or potentially mobile) chemical elements, are localised on mineral and organic constituents surfaces and/or in soil solutions and correspond to the main soil bioavailable pool. These elements come from two main sources: (i) release by weathering of soil (and rock) minerals or (ii) brought by atmospheric deposition. Thus, their concentration in soils depends directly on the mineral composition of soils and the underlying geological material.

Chemical elements present in the secondary xylem of tree wood (others than C, O, and H) are mainly taken up by the root system from the bioavailable pool in the soil (Taiz et al., 2014). These chemical elements include both major plant nutrients (*e.g.*, K, Ca, Mg, Mn, Fe) and trace elements (*e.g.*, Ba, Nd, Sr, Rb, Pb) with no known physiological function, which are absorbed and stored in the symplast of the parenchyma cells or in the cell walls of the wood (Meerts, 2002). The inorganic chemical composition of wood therefore reflects characteristics of the soil on which the trees have developed in relation to the geological parent material (Bukata and Kyser, 2008).

Similar to different elements, which can be absorbed at different rates, isotopes of a given chemical element are also absorbed at different rates in plants *i.e.*, they fractionate between soil and plant (von Blanckenburg et al., 2009; Wiggenhauser et al., 2022). The effect of isotope fractionation can be corrected for isotopes of radiogenic origin using the ratio of a stable isotope pair. Therefore, the “radiogenic” isotope ratios of elements such as strontium (Sr), neodymium (Nd), hafnium (Hf), osmium (Os), and lead (Pb) are cleared of biases induced by fractionation of both instrumental and physiological origin (Habfast, 1998; Yang et al., 2018). For this reason, radiogenic isotope ratios have considerable advantage over elemental or stable isotope ratios, which

are significantly affected by biogeochemical processes. These isotope systems have been used as geochemical tracers for many years (Irrgeher and Prohaska, 2016) with application including studies of chemical stratigraphy, geochronology, provenance, and weathering (Banner, 2004).

Among the radiogenic isotope systems listed above, only the Sr isotope ratio ($^{87}\text{Sr}/^{86}\text{Sr}$) has been applied in provenance studies of biomaterials, more specifically for wood (Hajj et al., 2017; Holt et al., 2021). This might be due to 1) low amounts of Nd, Hf, Os and Pb in biomaterials, and 2) a limited variation in their isotopic composition across different types of geological parent material. The joint measurement of several isotope systems is a potentially powerful approach to refine provenancing. The Nd isotope ratio $^{143}\text{Nd}/^{144}\text{Nd}$ holds the most significant potential regarding provenance studies of biomaterials, in particular because of the complementarity with $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in Earth Science studies (Allegre et al., 1979; Nakano, 2016).

In the present study, we explore the potential of coupled $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ measurements, along with analyses of inorganic element concentration in tree wood, as tracers of wood provenance, based on the assumption that the chemical and isotopic compositions of tree wood in contrasted geological context are significantly distinct.

1.2. How can we mitigate undesirable influences of factors other than soil and rock type on wood composition?

One of the challenges associated with dendrochemical tracing arises from the fact that trees are not passive samplers and adapt to environmental and ontogenetic constraints in order to maintain a physiological optimum (Hagen-Thorn et al., 2004; Scharnweber et al., 2016).

Some diversity in dendrochemical composition is expected even among trees in the same stand, due both to variations in the micro-environment and to the diversity of physiological and morphological characteristics of the trees themselves. For example, a faster dominant growing tree would require more nutrients than a slower growing tree.

According to their phylogenetics, tree taxa have developed different nutrient acquisition strategies and their biogeochemical composition might diverge considerably even for trees growing in the same environment (Hagen-Thorn et al., 2004). In general, *Angiosperms* tend to have a higher content of mineral nutrients compared to *Gymnosperms* likely because of the enhanced nutrient use efficiency of the latter (Alriksson and Eriksson, 1998; Watmough and Hutchinson, 2002; Meerts, 2002; Augusto et al., 2015). Another example are deciduous species with diffuse porosity (*e.g.*, beech and birch) whose heartwood is richer in mineral nutrients than that of species with annular porosity *e.g.*, oak (Penninckx et al., 2001; Meerts, 2002). These differences might be due to nutrient supply management including root development (Hajek et al., 2014), but also to nutrient storage in wood and to its cation exchange capacity (Bondietti et al., 1990; Herbauts et al., 2002). To limit the effects of plant species, it is preferable to analyze the chemical and isotopic composition of woody species, especially the wood of related tree species.

Wood composition may record traces of past environmental

conditions different than actual ones. Natural events (e.g. drought, fire etc.) or past human activities such as intensive land use (Glatzel, 1991) and/or fertilization (von Oheimb et al., 2008), may have affected the available pool of chemical elements in soils. However, the influence of the past on the chemical and isotopic composition of both soils and trees can be minimized by establishing the referential database on sites with a continuous forest occupation in the past and that have not been subjected to past extreme climatic conditions.

In this study, we test the hypothesis that the chemical and Sr—Nd isotopic compositions of tree wood are significantly distinct when grown on contrasted geological contexts. In order to limit the influence of other factors such as the environmental trajectory of sites, plant physiology and social status of trees, we have carefully selected sites characterized by ancient forests and decided to analyze the chemical and isotopic composition of woods from oak trees with a dominant status and in a limited range of diameters.

1.3. Are chemical and isotopic compositions of wood different between two closely related species?

Quercus robur and *Q. petraea*, two deciduous oak species, are widespread in temperate climate, but occupy specific ecological niches: *Q. robur* is a relatively pioneer species, heliophilous and fairly tolerant of temporary waterlogging (Becker et al., 1996), but vulnerable to water stress, while *Q. petraea*, a more late-successional species, tolerates drained and nutrient-poor soils (Parelle et al., 2007). The resistance of *Q. petraea* to water stress is linked to its higher water-use efficiency (Epron and Dreyer, 1993; Ponton et al., 2002) and its ability to extract water from deeper soil horizons (Bréda et al., 1993), which have potentially different mineral nutrient contents. The high growth rate of *Q. robur* shoots is associated with a high content of nitrogen and non-structural hydrocarbons in its leaves (Li et al., 2013).

Little is known for mineral nutrients in these species, which have received less attention from the scientific community. The two species supposedly adapt their root architecture, including maximum extraction depth to environmental conditions, as has been observed for other tree species (Bakker et al., 2008; Hajek et al., 2014), which should have repercussions on their mineral nutrient content.

Root development also depends on tree age and forest management (Gilman, 1990). The root system extends rapidly in early stages of development in response to high levels of nutrients required by growing biomass. Fine root biomass increases until canopy closure, when the demand decreases and stabilizes (Ericsson, 1994; Jagodzinski et al., 2016). In general, the content of nitrogen and potassium in leaves decreases with age while the content of magnesium and calcium tends to increase, potentially due to deepening of the root system (Jadczuk and Sadowski, 1997).

Most of the fine roots are situated in the surface soil layer of soil (0–30 cm; Jagodzinski et al., 2016), but during their lifetime, trees also access nutrient pools in deeper horizons (Jobbágy and Jackson, 2001). The existence of elemental and isotopic depth gradients in soil can be responsible for dendrochemical variation in wood between trees with different rooting depth (Hajj et al., 2017).

To better assess the effect of tree species on tree nutrition and wood composition, individuals of *Q. robur* and *Q. petraea* have been sampled and their wood analyzed at each study site.

1.4. Test of multi-elemental and multi-isotopic analysis approach for determination of wood origin

The present work illustrates the application of a multi-elemental and multi-isotopic analysis for the determination of wood origin at the scale of the Seine river catchment in France. The two common oak species *Q. petraea* and *Q. robur* were identified as model species of temperate deciduous forests with considerable interest for heritage and archeology. The area was selected within the scope of a provenance study of the

timber wood from Notre-Dame de Paris cathedral, damaged during the fire on April 15, 2019. The approach was tested on oak wood cores ($n = 140$) collected in 12 forests growing on contrasting types of soil within the zone of interest. The study area is characterized by a relatively homogeneous geology made of mostly calcareous - and to lesser extent siliceous - sedimentary rocks. Their deposition age increases progressively from the most recent layers (Holocene) around Paris, towards Middle Jurassic at the south-eastern edge, in the Yonne department (Guillocheau et al., 2000). One site, in the south, is located on Paleozoic granites.

As explained earlier in the text, dendrochemical provenancing has two major limitations: 1) the range of geochemical variation within the zone of interest, and 2) the impact of site-independent variables on wood chemical composition. The main objective of the present study is to assess the capacity of the dendrochemical approach, when based on a combination of elemental and isotopic tracers, to discriminate trees having grown on different types of soil and geological parent material. This ability to distinguish sites on the basis of dendrochemical variations may be influenced by the extent of intra-site variations related to the characteristics of the selected trees: oak species, age, and social status.

To reduce intra-site variation and optimize the approach, we assessed the effect of 1) normalization (division) by a reference element, and 2) tree characteristics on elemental and isotopic tracers. Normalization is applied because absolute concentrations of elements in wood are dependent on the biochemical properties of the lignocellulosic matrix whose variations are controlled by physiological processes (for example, causing variations in cation binding capacity with cambial age; Herbauts et al., 2002; Momoshima and Bondiotti, 1990) more than by soil composition. Normalizing the concentration of one given nutrient to another's should mitigate the effects linked to the physiological processes and amplify the influence of the site.

The effects of normalization and tree characteristics are evaluated through a linear mixed model with species, age and social status as explanatory variables and with varying reference element used for normalization. The influence of the three tree characteristics (species, age and social status) on wood elemental and isotopic composition is discussed with respect to their potential implication for the uptake of mineral nutrients. Altogether, this study puts forward several recommendations regarding the relevance of individual elemental and isotope tracers and sampling strategy for regional referential databases.

2. Material and methods

2.1. Study sites

The sampling sites represent the major types of soil encountered in forested areas of the Seine river catchment (76,674 km², 14 % of the metropolitan French territory). The diversity of soil types expected across the Seine catchment was first assessed with the help of the geological map (BRGM, n.d.) and of the map of bioindicated pH (Gégout et al., 2005). The sampling sites were then identified by considering forests with simultaneous presence of *Q. petraea* and *Q. robur*, with a minimum tree cover of 25 % for each species, according to forest maps and inventory databases from the National Institute of Geographic and Forest Information. The selected forests were located on the Cassini map from the 18th century to avoid recent plantations. We looked for sites that were homogeneous from the topographical, geological, pedological and silvicultural points of view, with the two species in an intimate mixture. In half of the selected sites, the mixture could not be found, and the two oak species were sampled in separate areas a few hundred meters apart. The sampling site of Fontainebleau did not have any *Q. robur* trees in its vicinity so that only *Q. petraea* trees were sampled at this site. The soil typology predicted from geological and pH maps was checked on site and completed or revised if needed. The sites were characterized for geological parent material, pH in topsoil horizon and degree of mixing between the two oak species (Table 1). For each site

Table 1

Study sites identified by the name of the forest, the number of the French department and a three-letter ID. The description of geological parent material is based on on-site observations. Sites are ordered in approximate increasing order of acidity of geological parent material.

Name (department)	ID	Geological parent material	Topsoil pH	Oak species	Area sampled (ha)
Au-Duc (89)	AUD	Sandy regolith on granite	4.3–5.0	Mixed* (72 m)	1.52
Chêne à la Vierge (51)	CHE	Siliceous upland silt	4.4–4.6	Mixed* (202 m)	3.67
Claye-Souilly (77)	CLY	Siliceous colluvium and silt	5.0	Separated (408 m)	0.37
Fontainebleau (77)	FON	Ancient alluvions, sand and gravel	4.7–5.1	–	0.94
Villefermoy (77)	VIL	Decarbonated loess	4.8–5.6	Separated (245 m)	0.69
Rumilly (10)	RUM	Silt on clay	4.0	Mixed	0.36
Fretoy (89)	FRE	Decarbonated clay and silt	5.9–6.3	Separated (637 m)	0.23
Signy-l'Abbaye (8)	SIG	Sandy clay or argillaceous sand, carbonated at QP	5.2–5.5	Separated (227 m)	0.23
Clairvaux (10)	CLA	Sublithographic compact limestone (Jurassic)	5.1–6.3	Mixed	2.15
Hervaux (89)	HER	Compact limestone or clay and decarbonated clay (Triassic)	5.4–6.8	Mixed	0.55
Samoussy (2)	SAM	Sandy carbonates (Cenozoic)	4.5–8.0	Separated (689 m)	0.43
La Chaume (21)	CHA	Compact limestone and decarbonated clay (Triassic)	6.7–7.6	Separated (392 m)	0.41

and each species, a composite sample was taken to represent the topsoil horizon from one to three samples, depending on the soil variability encountered. Soil pH was measured in the laboratory using soil suspensions (air dried sieved soil fractions <2 mm) diluted in water with a weight ratio 1 (soil) to 5 (solution). Stand mixing was evaluated based on distances (Table 1) between the centroids of the areas occupied by *Q. petraea* and *Q. robur* at each site. Mixed* refers to stands where the two populations are in contact, but not in intimately mixed. The sites were grouped in four categories defined by their overall increasing acidity approximated by on-site observations and descriptions of (i) geological parent material, (ii) type of soil and pedological processes, (iii) presence of carbonates or quartz in soils and (iv) plant indicators. A color palette attributed to the categories (“red” for crystalline silicate rocks, “brown” for silty silicate sediments, “green” for silicate sediments with marl or clay and “blue” for calcareous rocks) is used in the following.

2.2. Wood sampling and description

Ten trees of *Q. petraea* and ten trees of *Q. robur* were selected among individuals with stem diameter 35–50 cm at breast height (1.30 m) and no apparent health problem. Limits on tree size and health were set to avoid juvenile and declining trees whose absorption mechanisms are controlled by specific nutrition needs significantly different from those of mature and prospering trees. Wood cores of 0.5 cm diameter were sampled at breast height with a Haglőf increment borer driven by a battery-powered electric drill. To characterize the forest plot, a dendrometric inventory was realized in the middle of the sampled population where trees with diameter > 7.5 cm located within a circle of 700 m² in area (equivalent to 14.9 m in diameter) were described for their

taxon and circumference. The 1st, 3rd and 5th largest trees in diameter from the dendrometric inventory were measured for height and their average was considered as the dominant height of the stand. The height of trees was assessed by two independent observers using an ultra-sonic system (Vertex 5, Haglőf). The social status of the sampled trees was determined as the ratio (expressed in %) between their height and the dominant height of the stand. The ratios were distributed into four equally populated classes: 75–95, 95–100, 100–105 and 105–115 % for subsequent analyses.

2.3. Sample preparation

After surface preparation using a sledge microtome, the cores were scanned at 2400 dpi, ring widths were measured using the software CooRecorder 9.8.1 (CybisElektronik & Data AB) and age at breast height was determined. From the 20 trees cored at each site, 12 were selected for geochemical analyses: eight *Q. petraea* and four *Q. robur* trees, except at Fontainebleau where only eight *Q. petraea* were sampled ($n = 140$ in total). The imbalance in species representation was justified by the more frequent occurrence of *Q. petraea* in the Seine river catchment. Wood cores were freeze-dried, ground, weighed (total mass between 2 and 3 g) and dissolved in ultra pure HNO₃ (70 %, VWR Chemicals) using a microwave digestion system (Imbert Štůlc et al., 2023). Elemental and Sr isotopic analyses were carried out only on heartwood to circumvent dendrochemical differences between heartwood and sapwood (Meerts, 2002). Each tree was analyzed in 4–6 aliquots and the aliquot with the Sr concentration closest to the average was selected for Sr isotopic analysis. The remaining aliquots were pooled for Nd isotopic analysis. Sixty-two samples used for Nd isotopic analysis were complemented with sapwood to reach the quantity of Nd necessary for isotopic analysis (ca. 0.1 ng). Elemental concentrations and Sr isotope ratios were acquired for 140 trees and 132 trees, respectively. Neodymium isotope ratios were measured for a subset of 6–8 *Q. petraea* per site, except at Clairvaux and Au-Duc where all 12 trees were analyzed ($n = 75$ in total).

2.4. Elemental analyses

Elemental concentrations were quantified by ICP-MS (Thermo iCap TQ, Germany) tuned to minimize the occurrence of oxides and double charged ions. The SQ-KED (Single Quadrupole – Kinetic Energy Discrimination) mode and TQ-O2 (Triple Quadrupole – Oxygen) reaction and mass-shift modes were used to limit potential interferences. An external calibration was carried out using synthetic multi-elemental solutions (Techlab) acidified with 2 % HNO₃ (v/v). The accuracy of the calibration was checked with a certified reference surface water material (SPS-SW1, Spectrapure Standards) and the instrumental drift was monitored by a combination of running SPS-SW1 every 10–20 samples and addition of Rh and Ir to the samples as internal standards. Each digestion run was controlled for contamination by two blanks and one reference material (NIST-1515, apple leaves, Sigma-Aldrich). Aliquot measurements of elemental analysis and repeated measurements of isotopic analyses were cleared from outliers determined as values out of interval mean ± 2 standard deviations. Values obtained for SRM NIST 1515 ($n = 46$) are reported in Table A. 1 in the Appendix.

2.5. Isotopic analyses

Strontium and neodymium were separated from the digestion solution by extraction chromatography, based on specific resins: the Sr-SPEC resin (50–100 μm size; Eichrom) for Sr (Hajj, 2017) and the TRU-SPEC and Ln-SPEC resins for Nd (Eichrom; Caro et al., 2006; Cogež et al., 2015). The yield of the chromatographic separation was on average 61.6 % for Nd and 73.0 % for Sr. Digestion blanks ($n = 96$ for both) measured by ICP-MS indicated a contribution of 2.0 ± 3.1 % for Sr and 7.4 ± 7.5 % for Nd to amount in samples. This non-negligible contribution of the digestion blank for some samples might have resulted in a

measurable bias in the isotope ratios especially for Nd. However, given the good reproducibility of Nd isotope measurements on reference materials subjected to digestion (see below), such bias would most likely have affected all sample equally, maintaining the validity of comparison between samples. The Sr and Nd blank contribution resulting from the chromatographic separation step ($n = 6$) was estimated using the signal yield on the multi-collector mass spectrometer (see below). This contribution corresponded to a maximum contribution to total sample signal of <0.1 % (Sr) and 1 % (Nd), resulting in a negligible bias on the measured isotope ratios.

Isotope ratios $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ were acquired during separate measurements sessions by Multi-Collector Inductively Coupled Plasma Mass Spectrometer (MC-ICP-MS; Neptune Plus ThermoFisher Scientific) in low-resolution mode and corrected for interferences and mass-dependent fractionation (Imbert Štulc et al., 2023). A time-dependent drift was observed in $^{143}\text{Nd}/^{144}\text{Nd}$ ratio values of standard reference material (NIST-3135a, Sigma-Aldrich) during one measurement session. For this particular session, the $^{143}\text{Nd}/^{144}\text{Nd}$ ratio of samples was further corrected by a factor determined as the ratio between the true $^{143}\text{Nd}/^{144}\text{Nd}$ value of NIST-3135a (0.511418 from Caro et al., 2006) and its average measured value before and after block of sample measurements ($n \in [5;6]$).

Measurement uncertainty was quantified as the 95 % interval of confidence for samples with $n > 2$ measurements using Student's law ("type A" uncertainty; BIPM et al., 2008) and with two standard deviations over repeated measurements of the standard reference material SRM-1515 (Sigma-Aldrich) for samples with $n < 3$ measurements ("type B" uncertainty; BIPM et al., 2008). The $^{87}\text{Sr}/^{86}\text{Sr}$ value of the reference material NIST-987 (Sigma-Aldrich) acquired during six measurements sessions was 0.710283 ± 0.000012 (0.7102467 from Luu et al., 2022). The $^{143}\text{Nd}/^{144}\text{Nd}$ value of the standard reference material NIST-3135a measured during six independent sessions was 0.511418 ± 0.000050 (0.511418 from Caro et al., 2006). Occasionally, the accuracy of Nd isotopes analyses was assessed through repeated measurements ($n = 3$ and 4, respectively) of AMES-Rennes with $^{143}\text{Nd}/^{144}\text{Nd}$ value equal to 0.511985 ± 0.000014 (0.511954 from Luu et al., 2022) and JnDi-5 with 0.512145 ± 0.000044 (0.512102 from Das et al., 2022). Random error introduced by sample preparation was evaluated through measurement of six independently processed (digestion and chromatographic separation) aliquots of NIST-1515 whose $^{87}\text{Sr}/^{86}\text{Sr}$ value was 0.714165 ± 0.000081 (0.71398 from Liu et al., 2016) and $^{143}\text{Nd}/^{144}\text{Nd}$ value was 0.512500 ± 0.000015 (reference data not available). We attributed the higher measurement uncertainty for Sr isotopes in NIST-1515 to a variable degree of contamination during digestion and chromatographic separation.

Ratios $^{143}\text{Nd}/^{144}\text{Nd}$ were normalized to the $^{143}\text{Nd}/^{144}\text{Nd}$ ratio of the chondritic uniform reservoir (CHUR, equal to 0.512638) and expressed as ϵNd units:

$$\epsilon\text{Nd} = \left[\frac{\left(\frac{^{143}\text{Nd}}{^{144}\text{Nd}} \right)_{\text{sample}}}{\left(\frac{^{143}\text{Nd}}{^{144}\text{Nd}} \right)_{\text{CHUR}}} - 1 \right] \cdot 10^4$$

2.6. Data analysis

The relative effects of site, oak species, tree age and social status on elemental concentrations and isotope ratios were assessed using a linear mixed model. The site factor was considered as a random effect as the sampled sites represented only a limited segment of variation within the Seine river catchment, the species factor was considered as a categorical fixed effect with two levels (*Q. petraea* and *Q. robur*), the tree age was considered as a continuous fixed effect, and the social status was considered as a categorical fixed effect with four levels (see Section 2.2). The significance of these four effects was tested using restricted likelihood ratio tests of model reductions, removing each factor from the

model, one after the other (type II tests). The relative part of variation (*i.e.*, semi-partial R^2 , hereafter referred to as *part* R^2) explained by factor, corresponding to the ratio between the variance of the considered effect and the total variance, was determined following Nakagawa et al. (2017).

We tested the normalization of elemental data using several elements (Table A.4) by dividing the given elemental concentration by the concentration of an element of high abundance in wood (Ca and K) or of high apparent sensitivity to the site effect (Mn, Sr). Additionally, we tested absolute elemental concentrations and elemental concentrations normalized to the sum of all measured elements (mineral mass of the wood). Both normalized and absolute concentrations were transformed to logarithms to allow for linearization and to rectify skewed distribution of elemental data. Calcium was retained as the reference element for normalization (see Section 4.1).

The capacity of the measured dendrochemical variables to classify a tree to a site was assessed using linear discriminant analysis. Three datasets were tested to build linear discrimination functions: 1) elemental composition only, 2) elemental and Sr isotopic composition, and 3) elemental and Sr and Nd isotopic composition. In the three models, the elemental composition was introduced in the form of logarithms of Ca-normalized concentrations. The first dataset included $n = 140$, while the second and the third were reduced by 6 % to $n = 132$ and by 46 % to $n = 75$ because of missing values for Sr and Nd isotope ratios, respectively. The correctness of site prediction was evaluated by leave-one-out cross validation, removing tree by tree.

The data were processed with R software (version 4.3.1) and figures were plotted with help of the package "ggplot2". Statistical models were fitted with the "lm" function from the basic package "stats" for linear models, and with the "lmer" function from the package "lme4" for mixed models. The significance of fixed effects was assessed using the "Anova" function in "car" package, and with "ranova" from "lmerTest" for the random site effect. Variance explained by each factor was calculated with the function "partR2" from the package "partR2". Linear discriminant analysis was carried out with the "lda" function from the package "MASS".

3. Results

3.1. Dendrochemical composition as a proxy of wood origin

3.1.1. Isotopic and elemental composition of wood

Results of geochemical analyses are reported in the Appendix in Table A.2 for Sr and Nd isotopic composition and Table A.3 for elemental composition. Among the 13 elements measured in wood, Ca was the most abundant in 56 % of samples and on average at eight out of 12 sites, with a general mean of 702 ± 503 $\mu\text{g/g}$. The content of elements in wood decreased on average in the following order: potassium (K, 570 $\mu\text{g/g}$), sulfur (S, 79 $\mu\text{g/g}$), iron (Fe, 43 $\mu\text{g/g}$), aluminium (Al, 40 $\mu\text{g/g}$), magnesium (Mg, 25 $\mu\text{g/g}$), manganese (Mn, 20 $\mu\text{g/g}$) and phosphorus (P, 10 $\mu\text{g/g}$). The content of trace elements in wood was between 1 $\mu\text{g/g}$ and 2 $\mu\text{g/g}$ for strontium (Sr), copper (Cu), rubidium (Rb), and zinc (Zn) and 10^{-2} $\mu\text{g/g}$ for neodymium (Nd). Trees from a given site were homogeneous regarding their Al, Cu, K, S and Sr content (mean RSD across sites <30 %), but rather heterogeneous in Fe, Mg, Mn and Zn content (mean RSD > 40 %). Concentrations of other elements in wood varied within a given site between 30 and 40 %.

Mean and intra-site variability of elemental and isotope ratios with expected strong potential for site discrimination (Mn/Ca, Sr/Ca, $^{87}\text{Sr}/^{86}\text{Sr}$ and ϵNd according to Imbert Štulc et al., 2023) are presented in Fig. 1. The Mn/Ca ratio varied between 0.0018 ± 0.0014^3 and 0.20 ± 0.08 for trees in the Samoussy and Au-Duc forests, respectively, and the Sr/Ca ratio varied between 0.0010 ± 0.0002 and 0.0090 ± 0.0014 for trees in the Hervaux and Au-Duc forests respectively. The $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratio varied between 0.709740 ± 0.000526 and 0.726372 ± 0.002264 in wood from the La Chaume and the Au-Duc forests,

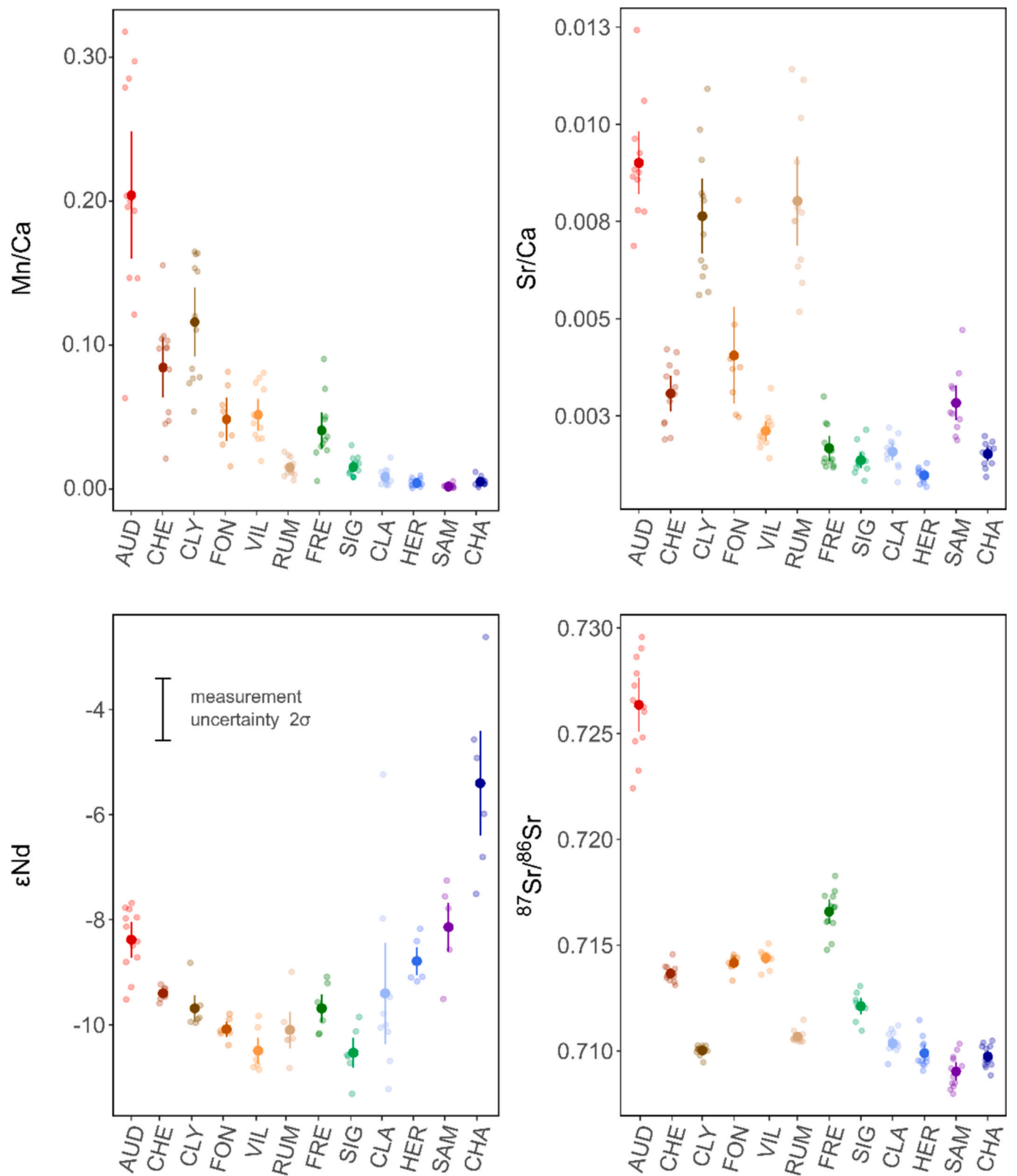


Fig. 1. Mean \pm 95 % confidence interval of elemental and isotope ratios (Mn/Ca, Sr/Ca, $^{87}\text{Sr}/^{86}\text{Sr}$ and ϵNd) in oak woods of referential sites ($n = 12$) ordered in approximate increasing order of acidity of parent material. The color palette used here introduced in Table 1. The measurement uncertainty expressed as two SD is shown for ϵNd , and is smaller than the size of the dots for the other tracers. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

respectively. The ϵNd of samples varied between -10.5 ± 0.6 and -5.4 ± 1.8 in wood from the Signy l'Abbaye and the La Chaume forests, respectively. The relationship between the elemental or isotope ratios and acidity of the parent material differed according to the elements (Fig. 1): it was exponentially decreasing for the Mn/Ca ratio (Spearman rank $r = -0.62$, $P = 0.03$, $n = 12$, between the Mn/Ca ratio and the soil pH), parabolic for ϵNd (adjusted- $R^2 = 0.70$, $P = 0.002$, $n = 12$, in a polynomial model of order 2) and variable depending on the site for Sr/Ca and $^{87}\text{Sr}/^{86}\text{Sr}$. The differences in tracer responses to the acidity of the parent material indicate the potential of combining these variables to discriminate wood provenance between sampling sites.

3.1.2. Effect of normalization on inter-site variation

According to linear mixed models, normalized concentrations were more tightly related to the site factor than absolute elemental

concentrations, except for K-normalized concentrations (Table A.4 in the Appendix). The $\text{part } R^2$ of site increased on average from 50 % for absolute elemental concentrations to 72 % for Mn-normalized concentrations and the strength of the site effect varied according to the element used for normalization. Normalized concentrations of Ca, Mn, Nd, Rb and Sr were systematically observed to be strongly site-dependent. The $\text{part } R^2$ of the site effect was >0.70 whatever the normalization based on these elements. This was in contrast to Al, Mg, P and Zn, whose variation was explained only to a limited extent ($\text{part } R^2 < 0.5$ on average) by the site variable. The $\text{part } R^2$ was 50 % only with non-normalized element concentrations. The normalization to Ca concentration was finally chosen based on arguments explained in Section 4.1.

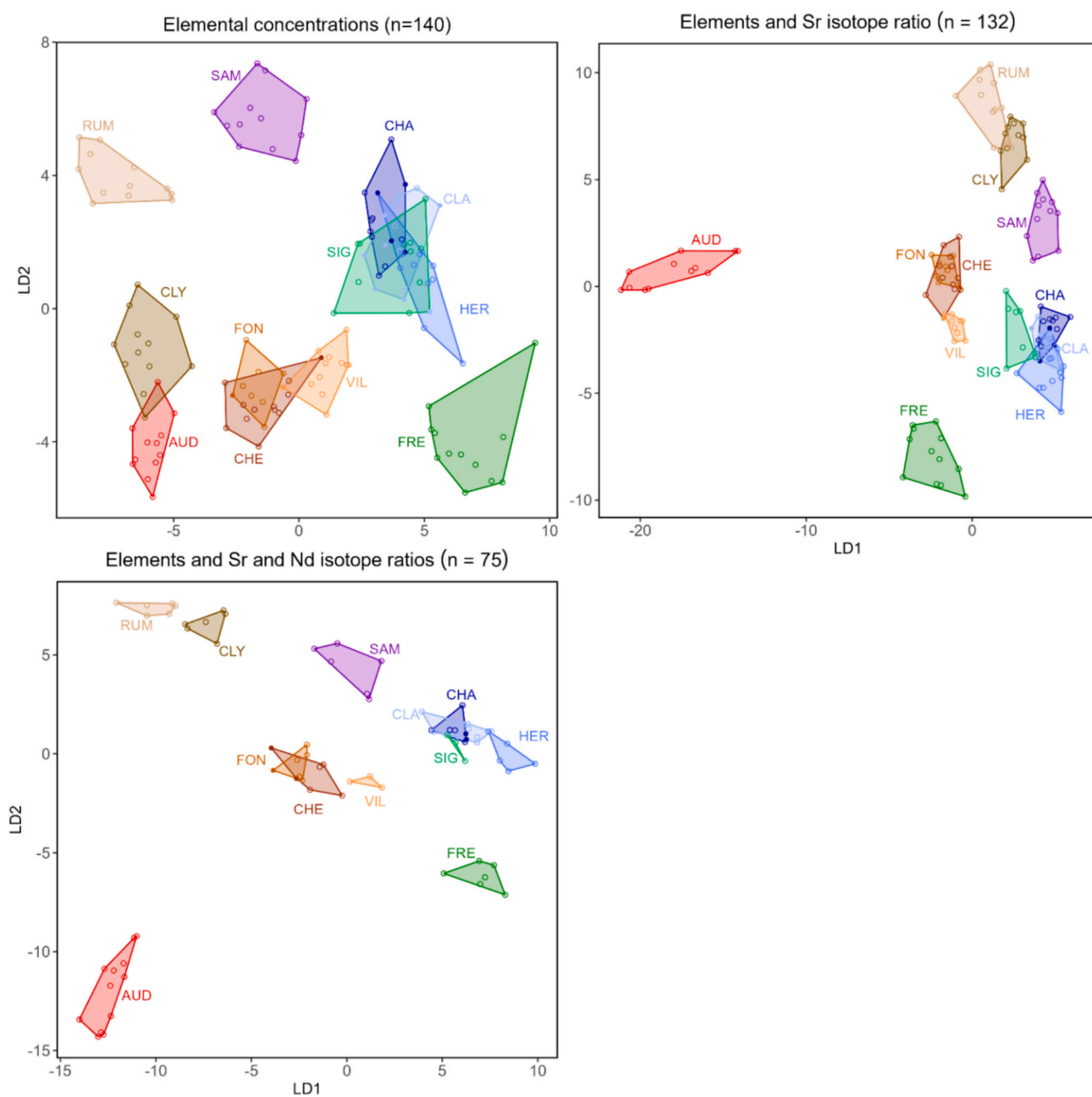


Fig. 2. Elemental and isotopic signatures of woods from referential forests projected on first two axes of linear discriminant analysis. Void \circ and full \bullet points are used for trees classified correctly and incorrectly respectively. The color palette used here is introduced in Table 1. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

3.1.3. Site discrimination based on wood composition

The proportion of trees which were correctly attributed to their site of origin by linear discriminant analysis was 90 % for model 1 ($n = 140$), 93 % for model 2 ($n = 132$) and 93 % for model 3 ($n = 75$). Using the same trees in dataset, the model 2 was as performant as the model 1 (93 % compared to 92 % for $n = 132$) and the model 3 was more performant than models 1 and 2 (93 % compared to 85 % and 89 % respectively for $n = 75$). Using all the data available for each model, the totality of trees was classified correctly at five sites using model 1 and at eight sites using models 2 and 3 (Fig. 2). Sites at which the trees were determined with 100 % correctness were those on acid soils (Au-Duc, Claye-Souilly, Rumilly) or with particular pedogenetic processes (paleosol at Fretoy and podzolization on limestone at Samoussy). The most often misclassified trees were those located on limestone (Clairvaux, Hervaux and La Chaume). Trees from Clairvaux were misattributed in 50, 33 and 10 % of cases with models 1, 2 and 3 respectively, mostly to the La Chaume and Signy l'Abbaye forests.

The first two axes representing at least 75 % of the dataset variation relied mainly upon $\log(\text{Sr}/\text{Ca})$, $\log(\text{S}/\text{Ca})$, $\log(\text{Al}/\text{Ca})$ and $\log(\text{Nd}/\text{Ca})$ for model 1 and upon $^{87}\text{Sr}/^{86}\text{Sr}$ in addition to the four aforementioned variables for models 2 and 3. The bivariate model based on $^{87}\text{Sr}/^{86}\text{Sr}$ and $\log(\text{Sr}/\text{Ca})$ ratios alone ($n = 132$) was capable of correct classification of 73 % of trees, while model based only on $^{87}\text{Sr}/^{86}\text{Sr}$ ($n = 132$) achieved a correct classification of 55 % of trees. However, the reduction to univariate model considerably deteriorated discrimination of sites situated on limestone (La Chaume, Clairvaux, and Hervaux) and of the Fontainebleau forest. When considered alone, the other potential site tracers did not exceed 40 % of correctly predicted trees, specifically 39 % for $\log(\text{Sr}/\text{Ca})$, 38 % for $\log(\text{Mn}/\text{Ca})$, 26 % for $\log(\text{S}/\text{Ca})$, 19 % for $\log(\text{Al}/\text{Ca})$ and 16 % for ϵNd .

The soil pH was correlated with either LD1 or LD2, depending on the model ($R = 0.73$, $P = 0.007$; $R = 0.59$, $P = 0.04$; $R = 0.78$, $P = 0.003$; for model 1, 2 or 3, respectively; $N = 12$).

3.2. Impact of tree characteristics on wood tracing

Compositional variables were modeled as a function of site, oak species, age of trees and their social status (Section 2.6). The explanatory variables were tested for interdependency: species, age and social status variables were uncorrelated, but age and social status were controlled by the site variable (p -value < 0.01 in a one-way ANOVA and Chi-squared test respectively with site as the explanatory variable). The effect of including sapwood in some of the ϵNd samples was non-significant (p -value < 0.05) and weak ($\text{part } R^2 = 0.006$). The interaction between the site variable and tree characteristics was tested but rejected because non-significant. The site variable had a significant effect (p -value > 0.05) on all compositional variables and was responsible for > 50 % of variation for seven out of 13 (Table A.4 in Appendix) and ten out of 12 (Table 2) elements based on absolute concentrations and Ca-normalized ratios, respectively. Conversely, tree characteristics were mostly without effect on elemental (absolute and normalized) concentrations and isotopic ratios in wood, with a few exceptions whose effects were otherwise weak ($\text{part } R^2 \in [0; 0.2]$). Only $\log(\text{P}/\text{Ca})$ was subjected to a significant and strong impact from species ($\text{part } R^2 = 0.11$) and $\log(\text{Mg}/\text{Ca})$ to a significant and strong impact from both species ($\text{part } R^2 = 0.05$) and age ($\text{part } R^2 = 0.18$) comparable to that of site ($\text{part } R^2 = 0.44$ and 0.47 respectively, Table 2). Variations in Sr isotope ratio and Sr/Ca, Mn/Ca, Nd/Ca and Rb/Ca ratios (log-transformed) were determined by the site variable at a semi-partial R^2 level of at least 70 %. The residual variation (i.e., not explained by the model) varied between 6 % for the $^{87}\text{Sr}/^{86}\text{Sr}$ and 29 % for Rb/Ca ratio and was inferior to 20 % for the other elements. Therefore, log-transformed Sr/Ca, Mn/Ca, Nd/Ca, Rb/Ca ratios, and $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratio were the most robust tracers of the geographical origin within the present dataset and were designated as "primary tracers" in the following. However, given the low impact of tree characteristics on compositional variables, all of the elemental and

Table 2

Semi-partial R^2 and p -values yielded by linear models of compositional variables (log of elemental ratios to Ca for all elements except Ca, log of absolute values for Ca, and isotope ratios) as a response to site, species, age and social status. Variables in decreasing order of semi-partial R^2 of site. ***: $P < 0.001$, **: $P < 0.01$, *: $P < 0.05$, ns: $P > 0.05$.

Composition	Site	Species	Age	Social status
$^{87}\text{Sr}/^{86}\text{Sr}$	0.96***	0.00**	0.00 ^{ns}	0.00 ^{ns}
Sr	0.89***	0.00*	0.01 ^{ns}	0.00 ^{ns}
Mn	0.85***	0.00 ^{ns}	0.03 ^{ns}	0.00 ^{ns}
Nd	0.81***	0.00**	0.03 ^{ns}	0.00 ^{ns}
Rb	0.70***	0.00 ^{ns}	0.01 ^{ns}	0.02*
Fe	0.63***	0.00 ^{ns}	0.00 ^{ns}	0.02 ^{ns}
Cu	0.63***	0.02***	0.06*	0.00 ^{ns}
S	0.61***	0.04***	0.04 ^{ns}	0.01 ^{ns}
Zn	0.60***	0.00 ^{ns}	0.03 ^{ns}	0.01 ^{ns}
Ca	0.57***	0.01**	0.10**	0.02*
K	0.57***	0.00 ^{ns}	0.01 ^{ns}	0.03*
Al	0.55***	0.01*	0.09*	0.03**
ϵNd	0.55***	0.01 ^{ns}	0.10*	0.00 ^{ns}
P	0.47***	0.11***	0.05 ^{ns}	0.01 ^{ns}
Mg	0.44***	0.05***	0.18***	0.00 ^{ns}

isotope ratios considered here might be used as potential tracers of origin.

3.2.1. Effect of oak species

The species composition of sampled trees at each site was 2/3 of *Q. petraea* (eight trees) and 1/3 of *Q. robur* (four trees), except for the Fontainebleau forest where only *Q. petraea* ($n = 8$) was sampled. Although very weak, the species effect was significant for primary tracers Sr/Ca, Nd/Ca (log-transformed) and $^{87}\text{Sr}/^{86}\text{Sr}$. For $^{87}\text{Sr}/^{86}\text{Sr}$ ratio, slightly higher values were observed in *Q. petraea*, in particular in the Au-Duc forest (Fig. 3). Conversely, elemental ratios Mg/Ca and P/Ca reached higher values in *Q. robur* compared to *Q. petraea*. The two species-sensitive tracers attained higher levels in *Q. robur* particularly at Au-Duc, Fretoy, Signy l'Abbaye and Clairvaux for P/Ca and at Signy l'Abbaye for Mg/Ca.

The model including only *Q. petraea* ($n = 96$) produced similar statistical results as that including both species. The coefficients of determination for the site factor yielded by a model based only on *Q. robur* ($n = 44$) were slightly reduced for most of the elements, likely because of dataset shrinkage. The relative order of elements according to their $\text{part } R^2$ remained almost unchanged with exception of S/Ca which was particularly indicative of site ($\text{part } R^2 = 0.95$), but only in the model with *Q. robur*. Due to the weak species effect, trees of the two oak species were considered equivalent and used together indistinctly in the following.

3.2.2. Effect of social status

The average height of sampled trees per site varied between 75 and 116 % of the stand dominant height, for the La Chaume and the Au-Duc forests, respectively. In four forests (La Chaume, Chêne à la Vierge, Samoussy and Rumilly), the sampled population was slightly underdeveloped compared to the stand dominant height with at least five trees in the lowest class ([75; 95] %), while in the Au-Duc and the Hervaux forests, five and nine of the sampled trees were higher ([105; 115] %) compared to dominant trees at the plot. In the remaining forests, the sampled population followed a normal distribution with the majority of trees included within the central interval [95; 105] %. The social status of sampled trees was significantly and moderately related to the site (p -value < 0.01 and contingency coefficient = 0.54 in a Chi-squared test of social status variations according to site). Throughout our dataset, the compositional variables were not or only weakly (Rb, Ca, K, and little more Al) depending on social status (Table 2) and that even in the subset constituted only of sites with deep and multi-horizon soil profiles where the effect of rooting depth would be more expected.

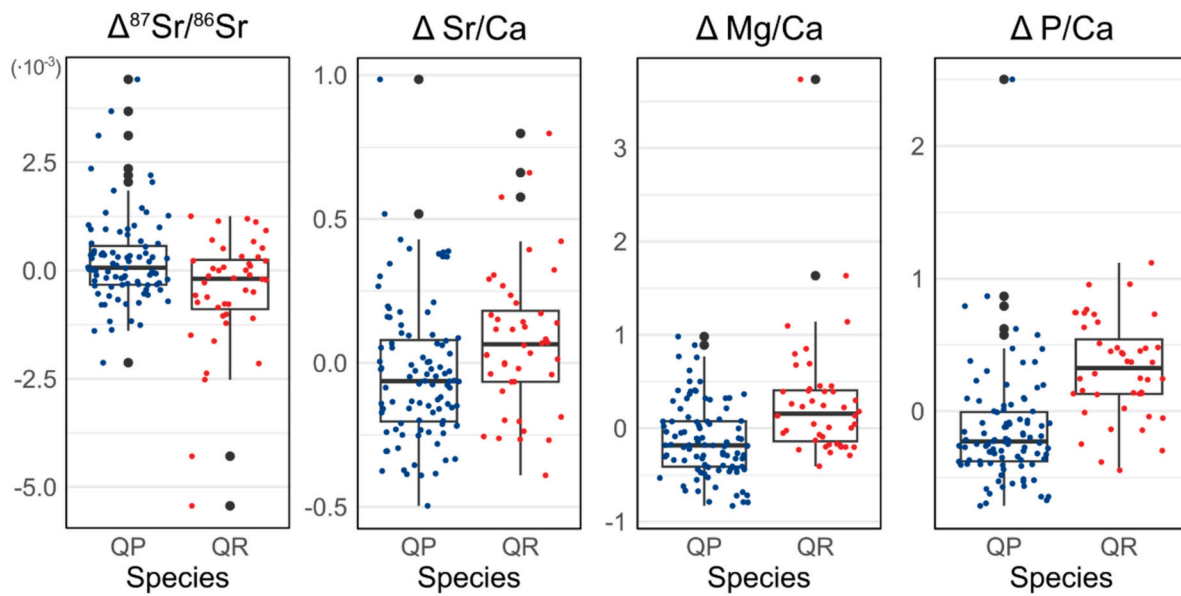


Fig. 3. Difference between *Q. petraea* (QP, in blue) and *Q. robur* (QR, in red) for primary tracers $^{87}\text{Sr}/^{86}\text{Sr}$ and Sr/Ca , and for two elemental tracers sensitive to inter-species differences, Mg/Ca and P/Ca . Δ stands for the relative difference between each sample and the average site value, in proportion of the average site value. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

3.2.3. Effect of age

The age of trees varied between 49 and 209 years in the Villefermoy and the La Chaume forests, respectively. The difference between the youngest and the oldest tree, for a given site, was between 4 years (at Auduc and Fontainebleau) and 105 years (at La Chaume). Among the sampled stands, three populations were young (Villefermoy, Signy l'Abbaye and Fretoy with average tree age around 60 years), six populations were mature (with average tree age between 86 and 126 years) and three populations were old-growth (Chêne à la Vierge, Clairvaux and La Chaume with average tree age around 140 years). Tree age was significantly and strongly linked to the site (p -value < 0.001 and $\text{part } R^2 = 0.85$ in a one-way ANOVA of tree age according to site), but the effect of the site did not appear to be indicative of geo-pedological

characteristics, but rather of stand management. According to field observations, stands were managed as even-aged high forests (with $\text{SD} < 10$ years) or were currently undergoing conversion from previous coppice-with-standards system to high forest.

The compositional variables were not or only weakly (Cu and Al) depending on tree age except for $\log(\text{Mg}/\text{Ca})$ and ϵNd whose variations were explained by age at 18 and 10 %. At five plots, the age difference between trees was higher than 25 years, such that these stands were considered multi-generational. A linear regression of selected tracers against tree age was performed for three of these sites where the tree age was approximately normally distributed – Clairvaux, Herveaux, and La Chaume (Fig. 4). A decrease in values with age was significant ($p < 0.05$) only for $^{87}\text{Sr}/^{86}\text{Sr}$ and Mg/Ca ratios at Clairvaux and was not related to

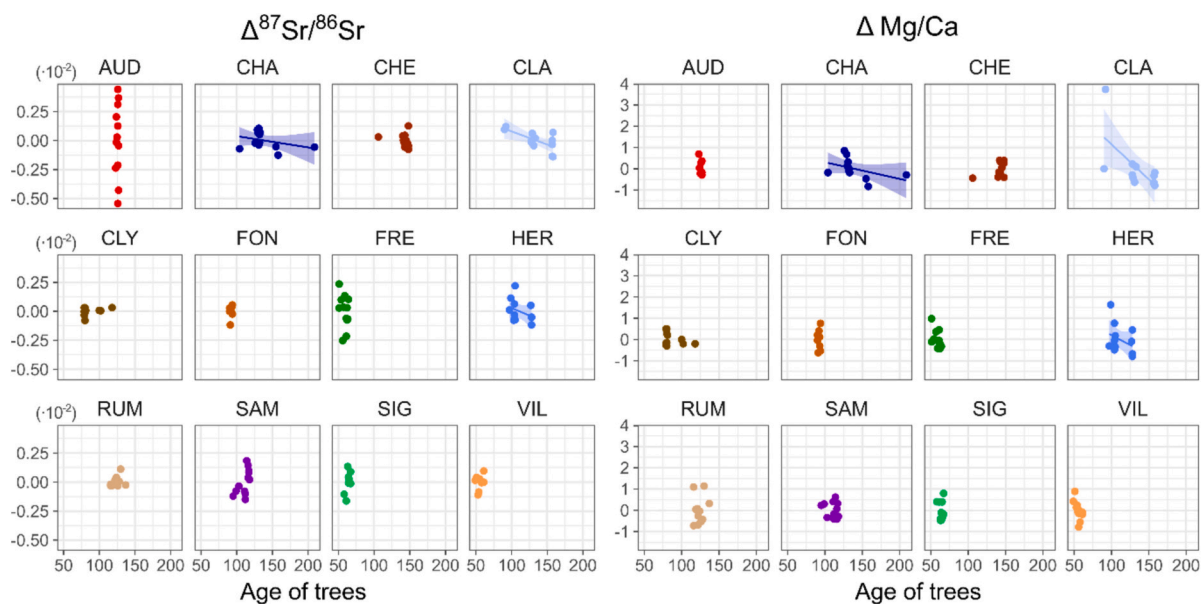


Fig. 4. Relationship between selected tracers, $^{87}\text{Sr}/^{86}\text{Sr}$ and Mg/Ca , and age of trees per site. Δ stands for the relative difference between each sample and the average site value, in proportion of the average site value. The linear regression is represented only for multi-generational stands. The color palette used here is introduced in Table 1.

species.

4. Discussion

4.1. Effect of normalization

The correctness of the site classification by the linear discrimination models 1, 2 and 3 (described in Section 3.1.3) was 94 %, 95 and 93 %, respectively, with absolute elemental concentrations, while the same models based on Ca-normalized concentrations achieved slightly lower correctness rate of 90, 93 and 93 %, respectively. One reason why our models with normalized concentrations had lower discrimination potential than those with elemental concentrations was that tree age might emphasize geochemical contrasts between sites. Although here the normalization did not enhance site discrimination, we decided to keep elemental ratios because they were reported to be less susceptible to age than absolute elemental concentrations (Bondietti et al., 1989; Kuang et al., 2008).

The different reference elements tested for normalization - Ca, Mn, Sr and K or the sum of measured elements - produced similar results, for example predicting, in all cases, the origin of around 90 % of trees with model 2 (elemental ratios and $^{87}\text{Sr}/^{86}\text{Sr}$, $n = 132$). On the basis of the semi-partial R^2 values for the site factor (Table A.4 in the appendix), normalization by Ca concentrations was the closest to normalization by the sum of all elements, which could be considered the most appropriate way of reducing the effect of physiological variations unrelated to site variations. The advantage of selecting a single element for normalization, contrary to the sum of the elements, is that it does not depend on the selection of measured elements, which varies among studies. We chose Ca because it is the most abundant element in wood and thus is highly correlated with the sum of all elements ($r = 0.93$). Moreover, Ca normalization is a standard method in dendrochemistry (Bondietti et al., 1989; Kuang et al., 2008), so its use facilitates comparison with previous studies. Finally, it is also adapted to carbonized wood analyses. The stability of Ca-normalized ratios with temperature in 200–800 °C range has been demonstrated in (Imbert Stulc et al., 2023). Therefore, the tracing system based on Ca-normalized elemental ratios and Sr and Nd isotope ratios was deemed as the most appropriate for provenance studies of charred archeological wood.

4.2. Identifying the primary dendrochemical tracers of wood origin

Among the measured variables, the Sr isotope ratio was by far the most powerful geochemical indicator of origin. Models 2 and 3, which included $^{87}\text{Sr}/^{86}\text{Sr}$, achieved 93 % of correct prediction and $^{87}\text{Sr}/^{86}\text{Sr}$ on its own was successful at 55 %. Although the Sr isotope ratio has been demonstrated as an efficient tracer of the geographical origin of plants (Branch et al., 2003; Goitom Asfaha et al., 2011; Bong et al., 2012; Ariyama et al., 2012; Hajj et al., 2017; Fu et al., 2021), it does not feature in provenance studies as often as multi-elemental composition or other isotope systems, such as carbon, oxygen and nitrogen isotopes (Kelly et al., 2005; Drivelos and Georgiou, 2012; Li et al., 2016). The aforementioned isotope ratios are sensitive to climatic variations as well as physiological conditions and have been mostly used as tracers of wood origin within large geographic areas. Differences in climatic conditions at a more regional level are usually too small to generate local variations in isotope ratios of carbon, oxygen or nitrogen. For instance, relative variation in hydrogen and oxygen isotope ratios recorded in tap water within the Seine river catchment is on the order of 7 and 2 ‰, respectively (Daux et al., 2021), which would allow for distinction between the western coast and the eastern inland, but not for a more spatially resolved differentiation. Here we demonstrate that the Sr isotope ratio is able to differentiate sites within distance of 30 km *i.e.*, Fretoy and Hervaux, under the condition of contrasting geological parent materials.

In compliance with observations from our previous study (Imbert Stulc et al., 2023), Mn/Ca and Sr/Ca ratios (log-transformed) were

strongly related to the origin of wood.

The advantage of the multi-variable approach consisted in capturing complementary soil characteristics. For instance, the Mn/Ca ratio did not bring additional information compared to the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio, as both tracers were strongly related to acidity of geological parent material. The coupling of Sr/Ca with $^{87}\text{Sr}/^{86}\text{Sr}$ ratio was found to be considerably more relevant, in particular regarding forests growing on silty silicate sediments (brown color in Table 1). High Sr/Ca ratios were associated with low radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and the category of silt-based soils could be distinguished into two groups: 1) Fontainebleau, Villefermoy and Chêne à la Vierge, and 2) Claye-Souilly and Rumilly (Fig. 1). The former group had Sr isotope ratios consistent with moderately acid parent material, but the latter group including Claye-Souilly and Rumilly had $^{87}\text{Sr}/^{86}\text{Sr}$ values close to that typical of marine limestone (~ 0.710) or precipitation (~ 0.709).

The sensitivity of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio to differences between the categories of parent material (*i.e.*, limestone vs granite), but also within the categories (*i.e.*, silty silicate sediments) made it the most versatile tracer in this study. The relevancy of the Sr/Ca ratio was mostly based on the capacity of discriminating groups within the category of silty silicate sediments, such that this tracer would not necessarily be as powerful in other geo-pedological context. It is worth noting that we did not identify any tracer sensitive to differences in limestone-based soils among the measured variables. Thus, discrimination of sites on limestone - the most common type of parent material occupying approximately 60 % of surface of the study zone - was not fully reliable (correctness between 67 and 100 % depending on site according to the model with elemental and Sr isotope ratios).

4.3. Dendrochemical variation in the seine river catchment

The advantage of multi-variable approaches such as the one used in this study, consists in capturing diversity of soil characteristics. Our study sites were selected to represent the full range of contexts present in the Seine river catchment regarding soil pH, type of bedrock and age of bedrock (Section 2.1). These three criteria were in turn related to the bioavailability of some of the nutrients meaning that some of the primary dendrochemical tracers varied systematically between sites. For example, the Mn/Ca ratio of the wood was the highest at the low-pH site on granite (Au-Duc) and varied with the parent material acidity in compliance with the pH-dependent bioavailability of Mn (high at low pH) and Ca (low at low pH; Kuang et al., 2008; Hevia et al., 2019). The Mn/Ca ratio was in general consistent with soil pH except for the Rumilly forest. The soil at this site was characterized by a very low topsoil pH value around 4, which contrasted with a moderately acidic parent material (clay and silt) and intermediate Mn/Ca values. This discrepancy potentially pointed to waterlogging as another factor controlling soil pH. Indeed, soil pH can vary considerably over the year (Parent et al., 2008) as it tends to increase with rising water levels in winter- and spring, mainly due to carbonate and bicarbonate dissolution. The soil pH 4 at Rumilly was measured in soil sampled in October and might be reflective of conditions prevailing during the summer-autumn season.

The discrimination potential of Sr/Ca has been reported by other studies on plant origin (Bong et al., 2012; Boeschoten et al., 2022), but the relation between Sr content in wood and soil characteristics has not been clarified. Boeschoten et al. (2022) found a weak, but positive correlation between Sr concentration in wood and the clay content in topsoil. Quantitative constraints on clay content were not available for the present dataset, but clay abundance can be estimated from soil type and on-site observations. The wood with the highest Sr content came from the Rumilly forest (4.4 $\mu\text{g/g}$ vs 1.6 $\mu\text{g/g}$ on average at other sites; Table A.3 in Appendix), which was indeed characterized by the presence of an argillaceous horizon at depth. However, the Sr concentration in wood did not differ between sites with clay-rich superficial horizons (on limestone *e.g.*, La Chaume) and sites with clay-poor superficial horizons

(on silty parent material e.g., Villefermoy). Thus, the clay content did not seem to control the bioavailability of Sr at sites analyzed in this study.

Another tracer whose variation can be predicted from the type and age of bedrock was the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio. In soil, this ratio depends primarily on the amount of parent radioisotope ^{87}Rb in the rock which is typically more abundant in K-bearing minerals than in Ca-bearing minerals. As a consequence, soils developed on silicate rocks should therefore have a higher $^{87}\text{Sr}/^{86}\text{Sr}$ ratio than soils on carbonated rocks and soils on felsic rocks should have a higher $^{87}\text{Sr}/^{86}\text{Sr}$ ratio than soils on mafic rocks. The content of radiogenic Sr in a given mineral also increases with the time elapsed since crystallization. In the Seine river catchment, only the Au-Duc site was located on old acidic magmatic rock rich in K-bearing minerals. Woods on this site were characterized by a notably more radiogenic Sr isotope ratio (0.72637) than the rest of the sites. In contrast with Au-Duc, trees growing on limestone soils (Hervaux, Clairvaux, La Chaume, Samoussy) had low Sr isotope ratio. This was expected, given that the main contribution of available Sr in these soils must come from its release following the weathering of calcite (Ca bearing mineral), the main mineral limestone with a signature close to that of the seawater in which it was formed.

Strontium isotopic compositions of trees underlain by siliceous detrital material (silt, sand) were between the values of trees growing on limestone and granite. As mentioned in Section 4.2, the sites in this last group can be divided in two sub-groups based on their Sr isotope ratio. Two of these sites display less radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ ratio (Rumilly and Claye-Souilly). At Claye-Souilly, Sr might be derived from colluvial deposits made of marl mapped in this area, even though they were not noticed during on-site prospection. As for Rumilly, the influence of waterlogging was suggested. The parent material at this site did not feature any calcareous material, such that the weakly radiogenic Sr isotopic signature might result from combined inputs of the parent material and groundwater.

Variations in the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in seawater are known for the period 0–509 Ma, which allows to date marine limestones, and thus can be used to distinguish marine carbonate rocks of different ages over this period. In our study, this discrimination criterion was assessed for four study sites on limestone by comparing their measured Sr isotopic signature with the theoretical values corresponding to their stratigraphic age (McArthur, 2001). The measured values showed a significant positive offset (-0.003) compared to the theoretical values and did not plot on the Sr marine curve. We concluded that sources other than the bedrock contributed substantially to the pool of bioavailable Sr at these sites (e.g., aeolian silt deposition during the Holocene), such that the age of the bedrock was an inefficient discrimination criterion in the Seine river catchment.

The range of ϵNd values in wood (-10.53 ; -5.40) corresponded to the Nd isotopic signature of continental rocks with the most radiogenic ϵNd value (-5.40) recorded at La Chaume. This site is underlain by compact limestone which is typically more radiogenic in Nd isotopes than the associated silicates (Lü et al., 2023). However, interpreting the ϵNd of non-silicate rock components is not trivial, because the quantity of Nd they contain is negligible and can be easily exceeded by Nd from sources other than bedrock, such as dust deposition. Sites developed on silicate-rich parent material (Villefermoy, Fontainebleau, Rumilly) showed a similar Nd isotopic signature (ϵNd values between -10.09 and -10.49) indicating a probable common source of detrital particles.

4.4. Inter-species difference

Even though the effect of species was significant for most of the tracers, differences between *Q. petraea* and *Q. robur* were so limited compared to those between sites, that they were considered negligible. However, several elemental ratios - above all P/Ca and Mg/Ca - displayed a systematic and positive offset in *Q. robur* compared to *Q. petraea*. Regarding the effect of species, Ca-normalized concentrations of P, Mg, S, Cu, Nd, Al and Sr were higher in *Q. robur*, while Ca-

normalized concentrations of Fe, K, Mn, Rb and Zn were equivalent between the two species. In terms of absolute elemental concentrations (log-transformed), which are easier to interpret, the content of 1) P, Mg and S was higher in *Q. robur*, 2) Mn, Ca, Rb and K was higher in *Q. petraea* and 3) that of other elements (Al, Cu, Fe, Nd, Sr and Zn) was equivalent between the two species.

A potential explanation might be related to the different ecological niches of the two oak species. At the level of the forest stand, *Q. petraea* are more frequently found on hilltops and *Q. robur* at the bottom of slopes (Lévy et al., 1992). Base cations Mg^{2+} and Sr^{2+} leached from the soil layers are transported by water flow downwards and can accumulate in depressions occupied by *Q. robur* (Johnson, 1992). This explanation based on the role of topography and hydrology was consistent with the spatial distribution of the two species at Fretoy, l'Abbaye and La Chaume where *Q. robur* at lower positions (difference of around ten to three tens of meters in altitude) had higher $\log(\text{Mg}/\text{Ca})$ and $\log(\text{Sr}/\text{Ca})$ ratios.

At Au-Duc, lower $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of *Q. robur* growing at the bottom of the slope can also be explained by differences in soil composition along slopes:

- Rainwater containing Sr with low radiogenic signature (0.710) can flow downwards the sandy soils of this site and accumulate at the slope toe, where Sr is absorbed onto fine soil mineral and organic particles also leached from the top down the slope.
- Evidence exists for more intense weathering processes on slopes, which have been observed to host traces of podzolisation. In this context, we propose that organic acids could lead to more rapid depletion of easily-weatherable minerals typically characterized by low $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and/or led to preferentially weathering of the more radiogenic minerals in soils upslope.

We thus suggest that ecological preferences of the two species led to different spatial distribution of oak populations, and that the inter-species difference in wood composition reflected the spatial soil heterogeneity.

However, dendrochemical variation between the two species existed even at the sites without topographic differences. A differential root system development between the two species could explain this variation. According to their resistance to drought and waterlogging, the two species develop distinct root profiles, with a differential access to nutrient reserves according to depths (Schmull and Thomas, 2000; Kuster et al., 2013). For example, Ca enrichment and P depletion are generally observed in the deep mineral horizons (Jobbágy and Jackson, 2001; He et al., 2023). *Q. petraea* typically has deeper roots and greater extraction depth than *Q. robur* (Bréda et al., 1993) which could explain the higher wood Ca content in the former and the higher wood P content in the latter.

4.5. Role of age and social status

Unlike for species, the selection of trees was not randomized regarding tree age and social status because the dataset was not primarily designed to study effects of the two variables. Sampling restricted to trees with diameter 35–50 cm limited our ability to detect the effects of social status. The size distribution of sampled trees was centered on the size distribution of dominant trees such that the sampled population was not fully representative of the integral population. This latter critique is to be nuanced as most of the stands were under the regime of high forest with even-aged population and as a result were relatively homogeneous in age and size. Although not exhaustive, the dataset allowed for a basic observation of trends in wood composition as a function of tree age and social status.

The effects were not significant, except for $\log(\text{Mg}/\text{Ca})$, ϵNd and $\log(\text{Cu}/\text{Ca})$ which were sensitive to age, and $\log(\text{Al}/\text{Ca})$, $\log(\text{K}/\text{Ca})$ and $\log(\text{Rb}/\text{Ca})$, which were sensitive to social status. The weak impact of age

and social status was rather surprising because both variables were supposed to have an influence on root development and consequently, on nutrient absorption. A change in rooting depth might lead to a change in dendrochemical composition if elemental or isotopic gradients in soil exist. The effect was expected to matter in particular for isotope ratios, which should not be affected by post-absorption translocation and should carry the signature of the source. The hypothesis was not confirmed for $^{87}\text{Sr}/^{86}\text{Sr}$ ratio as the two tree characteristics did not have any effect on it. The age variable had slightly significant effect on ϵNd explaining 10 % of its variation. The Clairvaux site with slightly decreasing $^{87}\text{Sr}/^{86}\text{Sr}$ and Mg/Ca ratios (Fig. 4) was characterized by shallow basic soil formed from compact limestone enriched in Ca at depth. The lower values of $^{87}\text{Sr}/^{86}\text{Sr}$ reported for old trees might be related to absorption of Sr from less radiogenic source in depth. A larger sample set based on trees representing a wider and continuous range of age from one or a few sites would be necessary to test this hypothesis more properly.

5. Conclusion

The aim of the present study was to evaluate the potential of multi-elemental and multi-isotopic tracing system as a provenance tool for oak wood from the Seine river catchment. The proposed system consisted of compositional data measured for 13 elements and two isotope ratios ($^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$) in 140 trees from 12 forests. Using the dendrochemical approach, we were able to determine the origin of >90 % of trees correctly. A confusion was observed between three geographically close (30–70 km) forests characterized by similar geological parent material (compact limestone). Therefore, calcareous bedrock in close distance set a limit of the proposed tracing system in the context of the Seine river catchment.

The model based solely on elemental analysis achieved correctness rate (92 %), which was equivalent to that of model that included the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in addition to elemental analysis. Thus, the combination of 12 elemental ratios proved sufficient to attain high levels of discrimination. Considering the tracers individually, the Sr isotope ratio $^{87}\text{Sr}/^{86}\text{Sr}$ was the most performant local tracer, capable of determining origin 55 % of trees on its own. Single elemental tracers did not show as high discrimination potential, with the most effective among them being $\log(\text{Sr}/\text{Ca})$, which achieved a correctness rate of 39 %. The Nd isotope ratio $^{143}\text{Nd}/^{144}\text{Nd}$ significantly improved predictions when added to the previous predictor variables.

Although the normalization did not enhance the discrimination, we recommend replacing absolute elemental concentrations with normalized elemental concentrations for wood provenance studies. Effects of three selected tree characteristics – species, age and social status – on wood composition were qualified as weak compared to the role of site. The inter-species difference between *Q. petraea* and *Q. robur* seemed to indicate a higher nutrient status of the latter, but at a level that did not allow for discrimination of species. As for age of trees and their social status, the sample set was not fully representative of intra-site variation, and absent or weak trends might be attributed to sampling constraints. In this respect, homogenization of age and social status across sites by controlling diameter proved to be a valuable practice for tree selection. In view of the present experience, we do not consider a species-specific referential database necessary for dendrochemical tracing of wood within the European white oak species complex, although comparison between phylogenetically close specimens remains preferential. This result is favorable for tracing the origin of archeological wood, which is often oak and for which it is currently very difficult to identify the species precisely.

CRedit authorship contribution statement

Anna Imbert Štulc: Writing – original draft, Visualization, Software, Methodology, Investigation, Data curation, Conceptualization. **Anne**

Poszwa: Writing – review & editing, Methodology, Investigation, Funding acquisition, Conceptualization. **Stéphane Ponton:** Writing – review & editing, Methodology, Investigation, Conceptualization. **Jean-Luc Dupouey:** Writing – review & editing, Software, Methodology, Investigation, Data curation, Conceptualization. **Julien Bouchez:** Writing – review & editing, Methodology, Conceptualization. **Maximilien Beuret:** Investigation. **Dimitri Rigoussen:** Investigation. **Thierry Paul:** Investigation. **Michel Lemoine:** Investigation. **Sylvie Coubray:** Investigation. **Olivier Girardclos:** Investigation. **Christophe Gauthier:** Investigation. **Jérémie Bardin:** Formal analysis. **Thanh Thuy Nguyen Tu:** Methodology, Conceptualization. **Alexa Dufraisse:** Writing – original draft, Methodology, Investigation, Funding acquisition, Conceptualization.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2024.177640>.

Data availability

Data will be made available on Zenodo server at publication.

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