

## CHAPTER 21

# *Change of the Origin of Calcium in Forest Ecosystems in the Twentieth Century Highlighted by Natural Sr Isotopes*

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## I. INTRODUCTION

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Acidification of forest soils by atmospheric deposition involving depletion of alkaline earth cations is still an active subject of research. Factors implicated in this process are numerous and strongly interconnected so that a lot of questions still remains unresolved today. However, the understanding

of the soil acidification process is essential to maintain the environment quality and to guarantee forest sustainability for commercial forestry.

Works undertaken in Western Europe and North America reported increasing depletion of exchangeable base cations (mainly Ca and Mg) in sensitive soils (i.e., poor base status), caused by inorganic acid inputs (Falkengren-Grerup *et al.* 1987, Thimonier *et al.* 2000) that can cause tree nutritional deficiencies. Excess of anion deposition affects the ecosystem balance by depleting the pool of cation buffers more rapidly than the buffers that can be replaced, leading to an aluminization of the exchange complex, which interferes with the uptake of calcium by trees. In soils with a low weatherable mineral reserve, weathering inputs may not be sufficient to replace the accelerated losses of basic cations associated with disturbances such as acidic deposition or intensive forest harvest.

In order to counteract this effect, international environmental regulations were carried out and have led to widespread decline in the rate of acidic deposition across large areas of Europe and North America (Hedin *et al.* 1994). This change was mainly due to reduction in SO<sub>2</sub> emissions through the installation of filter systems in power plants and industry. However, the decline in ecosystem inputs of the acid anion SO<sub>4</sub> is accompanied by the reduced deposition of base cations so that changes in net acidity may be small (Hedin *et al.* 1994). As a consequence, the base cation status of the soils would not be expected to improve and soil acidification could actually continue.

Only few methods are able to reconstruct accurately the steps of the acidification mechanism in soils and its impact on the tree mineral nutrition. Decrease of soil base saturation (BS) during different periods of the last century has been highlighted by several methods, for example soil resampling (Falkengren-Grerup *et al.* 1987) and long-term site observation (Blake *et al.* 1999).

The depletion of Ca is a reliable indicator of overall cation depletion in an ecosystem because of its relative prevalence in the vegetation and its status as a major base cation on the soil exchange complex. Indeed, calcium plays a key role in these ecosystems, both as plant nutrient and in soils as buffer of acidic inputs. Therefore, the determination of the sources of Ca into the soil–vegetation–atmosphere system allows to estimate the real danger of soil impoverishment process on the mineral nutrition of forest stands. The two main sources of calcium in forest ecosystems are soil mineral weathering and the atmospheric inputs through dissolved cations in rainwater and dust fall. Our approach was to use strontium (Sr) as tracer of calcium. Strontium acts as an analogue for Ca because both are alkaline earth elements with similar ionic radius and the same valence. Because of their similar chemical structure, Ca<sup>2+</sup> and Sr<sup>2+</sup> behave similarly in the soil–plant system (Drouet 2005), although some fractionation of Sr/Ca ratio may occur once elements have passes through some plant compartments (Poszwa *et al.* 2000).

Stable Sr isotopes offer a powerful tool to discriminate atmospherically derived Ca from Ca originating from minerals. Isotope techniques do not require to determine element fluxes (extensive variables), instead using intensive-type variables (isotopic ratios) which do not impose the knowledge of structure or boundaries of the system studied. Strontium 86 is nonradiogenic whereas <sup>87</sup>Sr is produced by the radioactive β<sup>-</sup> decay of <sup>87</sup>Rb (half-life ~48.8 × 10<sup>9</sup> year; decay constant λ = 1.42 × 10<sup>-11</sup> year<sup>-1</sup>) so that their proportions vary between different natural materials. The principle of this isotopic method is to measure the natural variation of the Sr isotopic composition, expressed by the <sup>87</sup>Sr/<sup>86</sup>Sr ratio, as tracer of the sources of Ca in forest ecosystems. Because of the slight mass ratio between Sr isotopes, biological and chemical processes cause neglected isotopic fractionation compared to low-mass isotopic systems such as O, C, N, and S. Variations in the Sr isotopic composition in the different components of the forest ecosystem are therefore caused entirely by the mixing of Sr derived from sources with specific <sup>87</sup>Sr/<sup>86</sup>Sr ratio. For this reason, the <sup>87</sup>Sr/<sup>86</sup>Sr ratio can be used to identify and quantify the contribution of different Sr (and Ca) sources to the forest vegetation.

The determination of the origin of Ca in the vegetation is based on the measurement of the <sup>87</sup>Sr/<sup>86</sup>Sr ratio in the vegetation and the supplying sources, providing sufficient contrast in isotopic composition between the two sources. Strontium released by weathering of ancient geological substrates is characterized by a high isotopic ratio (rich in radiogenic <sup>87</sup>Sr). By contrast, atmospherically derived Sr has a

low isotopic ratio, generally closed to that of seawater, which is constant through the timescale studied. Vegetation has an intermediate  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio between the end-members so that the relative contributions to the binary mixing can be calculated. Atmospheric signature can be estimated by direct measurement on bulk precipitation samples. Sea-salt aerosols, which have constant marine  $^{87}\text{Sr}/^{86}\text{Sr}$  ( $\sim 0.709$ ), dominate the sites studied, but continental dust sources may impart spatial and temporal variations on this value in other locations (Nakano and Tanaka 1997). Whereas the isotopic signature of the atmospheric inputs and the plant materials are relatively easy to determine, the estimation of the weathering end-member remains more problematic. Weathering involves combination of different minerals, each with a particular weathering rate and isotopic signature. The minerals  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios depend on the Rb/Sr ratio and the age of the parent material because  $^{87}\text{Sr}$  is produced by the decay of  $^{87}\text{Rb}$ . Therefore, bulk soil  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio cannot be used as weathering signature in old substrates because individual minerals of the parent material have different weathering rates, and their  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios have diverged over geologic timescale. Some studies estimated this weathering end-member on the basis of the seasonal variation of chemistry and  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of stream waters (Clow *et al.* 1997, Kennedy *et al.* 2002). Natural weathering can also be simulated by extraction of soil samples with acidic solutions (Blum *et al.* 2002, Drouet *et al.* 2005a). The soil exchangeable fraction, which corresponds to the plant-available pool, can be leached from the soil by salt solution as ammonium acetate.

## II. THE USE OF STRONTIUM ISOTOPE TECHNIQUE

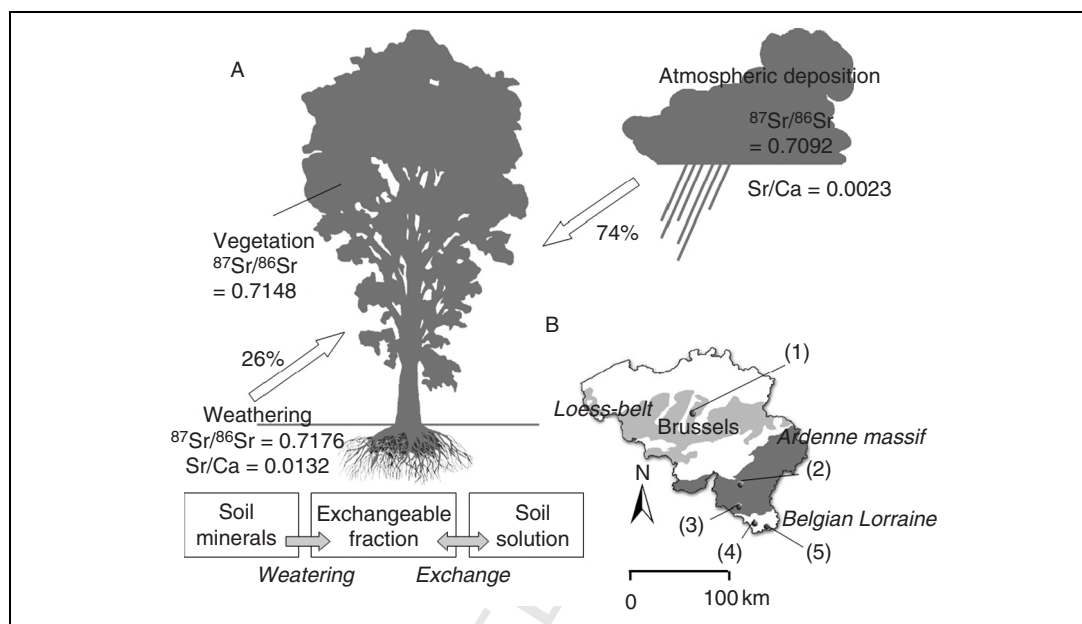
Sr isotopic ratios were measured in several ecosystem compartments: plant material, precipitation, exchangeable, and acid extractable fractions (Figure 21.1). Chemical separation of Sr from these samples was carried out by cation exchange chromatography. Sr isotopic compositions were measured on a VG Sector 54 thermal ionization mass spectrometer with solid source, housed at the Laboratoire de Géochimie isotopique, Université Libre de Bruxelles. Samples were analyzed in static multicollector mode, with 100 repeated measurements per sample. The measured  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios were normalized to  $^{86}\text{Sr}/^{88}\text{Sr} = 0.1194$  in order to correct for the effects of any fractionation of Sr isotopes that occurs during thermal ionization over the course of analysis in the mass spectrometer. The NBS-987 Sr standard, measured to determine instrument bias, yielded on average an  $^{87}\text{Sr}/^{86}\text{Sr}$  value of  $0.710270 \pm 0.000009$  ( $2\sigma$ ,  $n = 25$ ). The proportions of Sr in a mixture (in this case, vegetation) derived from two sources (atmosphere and soil weathering) are calculated using a mixing equation (Capo *et al.* 1998):

$$X(\text{Sr})_1 = \frac{(^{87}\text{Sr}/^{86}\text{Sr})_{\text{Mix}} - (^{87}\text{Sr}/^{86}\text{Sr})_2}{(^{87}\text{Sr}/^{86}\text{Sr})_1 - (^{87}\text{Sr}/^{86}\text{Sr})_2} \quad (21.1)$$

where  $X(\text{Sr})_1$  represents the mass fraction of Sr derived from source no. 1. Subscripts 1 and 2 refer to the two sources. The “Mix” subscript indicates the mixture component. The calculated percentage of atmospheric Sr in vegetation cannot be directly transposed to that of Ca because of the different proportion of Ca and Sr (Sr/Ca ratio) between the two sources in the ecosystems. The relative contribution of Ca from two sources to a mixing component is given by a two-component mixing equation (Capo *et al.* 1998):

$$X(\text{Ca})_1 = \frac{[(^{87}\text{Sr}/^{86}\text{Sr})_{\text{Mix}} - (^{87}\text{Sr}/^{86}\text{Sr})_2](\text{Sr}/\text{Ca})_2}{[(^{87}\text{Sr}/^{86}\text{Sr})_{\text{Mix}} - (^{87}\text{Sr}/^{86}\text{Sr})_2](\text{Sr}/\text{Ca})_2 + [(^{87}\text{Sr}/^{86}\text{Sr})_1 - (^{87}\text{Sr}/^{86}\text{Sr})_{\text{Mix}}](\text{Sr}/\text{Ca})_1}, \quad (21.2)$$

where  $X(\text{Ca})_1$  represents the mass fraction of Ca derived from the atmospheric source. Sr/Ca ratios are correcting factors used to take into account the different proportions of Ca and Sr between the two sources. The distinct isotopic signatures of Sr contained in atmospheric precipitations and of Sr derived



**FIGURE 21.1** (A) Schematic showing the different compartments and sources of Ca (mineral weathering and atmospheric deposition) of a forest ecosystem. Calculation of the relative contributions of these sources to vegetation is illustrated for a mature beech stand (*F. sylvatica*) in high Belgium. (B) Localization of the sites studied in Belgium. (1) Soignes Regional Forest (nine sites), (2) Herbeumont State Forest, (3) Smuid Wood, (4) Meix-devant-Virton Wood, and (5) Côte Wood (two sites).

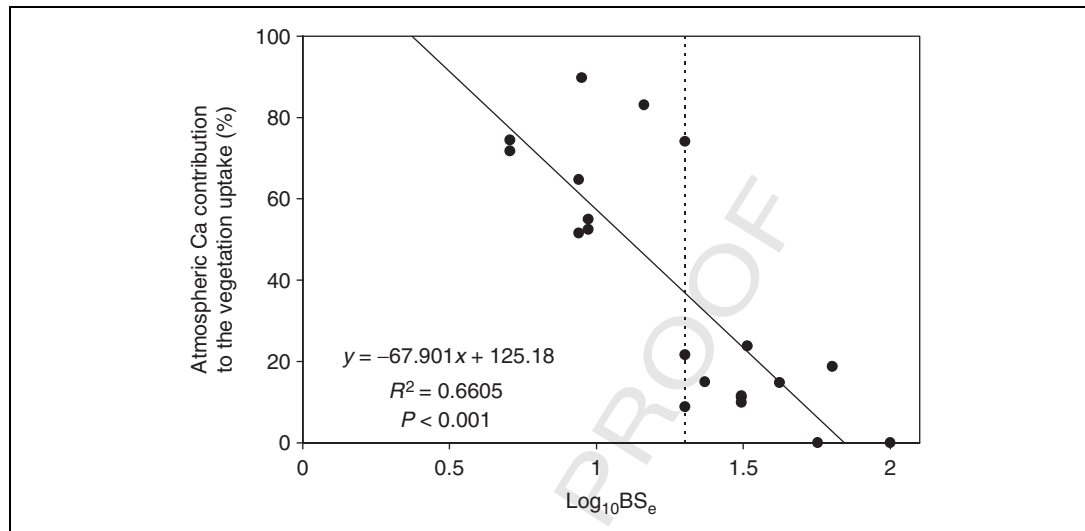
from mineral weathering allow to quantify the respective contributions of these two sources to the vegetation.

### III. SEPARATION OF ATMOSPHERIC AND WEATHERING SOURCES OF CALCIUM IN FOREST ECOSYSTEMS

The isotopic approach was first applied on two temperate forest ecosystems (Drouet *et al.* 2005a). In this preliminary study we shown that, unexpectedly, some beech forests in Belgium were supplied by more than 70% of Ca from atmospheric origin (Figure 21.1A). This illustrated the low amount of Ca released by weathering. Moreover, low annual inputs of Ca by atmospheric precipitation ( $<10 \text{ kg Ca ha}^{-1} \text{ year}^{-1}$ ) relative to tree growth requirements may cause nutritional deficiencies enhanced by intensive logging and acid deposition. These first results emphasize the importance of the atmospherically derived Ca for tree mineral nutrition in the stands studied, suggesting that these ecosystems on acid soils are sensitive to changes in the atmospheric chemistry, for example, acid deposition associated with decreasing input of atmospheric cations. This fundamental finding has important implications regarding forest stand management.

Second, the calculation of the contributions of the two above-mentioned sources was extended to 14 forest ecosystems in central and high Belgium (Figure 21.1B) growing in soils displaying a wide range of Ca reserves (Drouet 2005). All study sites were located on broad upland topography (mainly plateaus) and supported mature beech trees as dominant species.

Criteria for site selection were: (1) Sr isotopic composition of the parent material sufficiently different from that of the atmospheric source, (2) beech (*Fagus sylvatica* L.) as a dominant species



**FIGURE 21.2** Relationship between the percentage of atmospherically derived Ca in the vegetation and the log value of the mean effective BS<sub>e</sub> of the soil in the first meter depth. Decreasing BS<sub>e</sub> is associated with concomitant decrease of Ca concentrations in foliage. Vertical dotted line indicates the 20% BS beneath which exchange complex and soil solution are dominated by cationic Al (Reuss 1983).

of the forest stand, and (3) for all the sites, a large range of soil exchangeable Ca concentration. The majority of the sites were situated in central Belgium and have developed a Dystric Podzoluvisol (FAO classification) on Pleistocene loess. A carbonated horizon appears at different depth (from 180 to 400-cm depth) related to the sites, delimiting a soil sequence of contrasting Ca reserve. Other sites were chosen in central and high Belgium on soils with large range of Ca content, from Ca poor Orthic Podzol (FAO classification) on Tertiary sands (400-kg exchangeable Ca ha<sup>-1</sup> 0.5 m<sup>-1</sup>) to Ca saturated Mollic Leptosol on outcropping of Jurassic limestone (>4 × 10<sup>6</sup> kg exchangeable Ca ha<sup>-1</sup> 0.5 m<sup>-1</sup>). This large-scale investigation showed that Ca supply of the trees was very variable, from stands getting their nutrients mainly from mineral weathering to stands principally supplied by the atmospheric source. Data from this study pointed out a general inverse relationship between the percentage of atmospheric Ca in the vegetation and the soil reserves in exchangeable Ca or BS rate (Figure 21.2). The close connection between the proportions of the two sources on the soil exchange complex and in the vegetation was also confirmed.

#### IV. EXCHANGE PROCESSES IN THE SOIL

Measurement of the Sr isotopic composition in precipitation, the vegetation and the exchangeable fraction and soil solution in different soil horizons allow to gain insight into the exchanges of Ca between the compartments of the soil. Reserves of bioavailable cations in the soil are mainly in exchangeable form, adsorbed on the mineral and organic matter surface (exchange complex). The advantage of the use of the Sr isotope technique is that, although concentrations in major elements released by weathering can be modified by the formation of secondary minerals or exchange processes on the adsorbing complex, soil <sup>87</sup>Sr/<sup>86</sup>Sr remains a robust signature.

The study of a large number of forest stands suggests that the soil exchange complex does not always reflect an equilibrium between the present mineral weathering and the atmospheric inputs. In some

**TABLE 21.1** Sr Isotopic Signature of the Exchangeable Fraction (CH<sub>3</sub>COONH<sub>4</sub> extract) and 0.1-N HCl Extracts (After the Exchangeable Cation Removed) of Soils

Site	Soil horizon	Depth (cm)	Soil type	<sup>87</sup> Sr/ <sup>86</sup> Sr exchangeable fraction	<sup>87</sup> Sr/ <sup>86</sup> Sr HCl extract	Clay (%)	Free Fe <sup>d</sup> (%)
MES	B2t	55–75	Dystric Podzoluvisol	0.715291 <sup>a</sup>	0.712067	19.1	0.81
	B3t	175–200		0.712234 <sup>b</sup>	0.713571	16.5	–
	C	230–240		0.710707 <sup>b</sup>	–	15.0	–
MLN	B2t	55–75	Dystric Podzoluvisol	0.721618 <sup>a</sup>	0.71639	16.2	–
DIEP	B2tg	55–75	Stagnic Podzoluvisol	0.71816 <sup>a</sup>	0.713607	37.7	2.19
COT II	B2t	55–65	Eutric Luvisol	0.710056 <sup>c</sup>	0.712396	65.9	11.8
LND	E	5–25	Orthic Podzol	0.714254	0.720862	0.2	0.05
	C	80–100		0.721445	11.8	1.11	

<sup>a</sup> Soil horizons influenced by highly radiogenic Sr from ancient sources.

<sup>b</sup> Soil horizons influenced by a removed carbonated fraction still present at 250-cm depth (<sup>87</sup>Sr/<sup>86</sup>Sr = 0.708255).

<sup>c</sup> Isotopic value of the exchangeable fraction is assumed to be that of the vegetation; influence of the ancient carbonates still present at 200-cm depth (<sup>87</sup>Sr/<sup>86</sup>Sr = 0.708020).

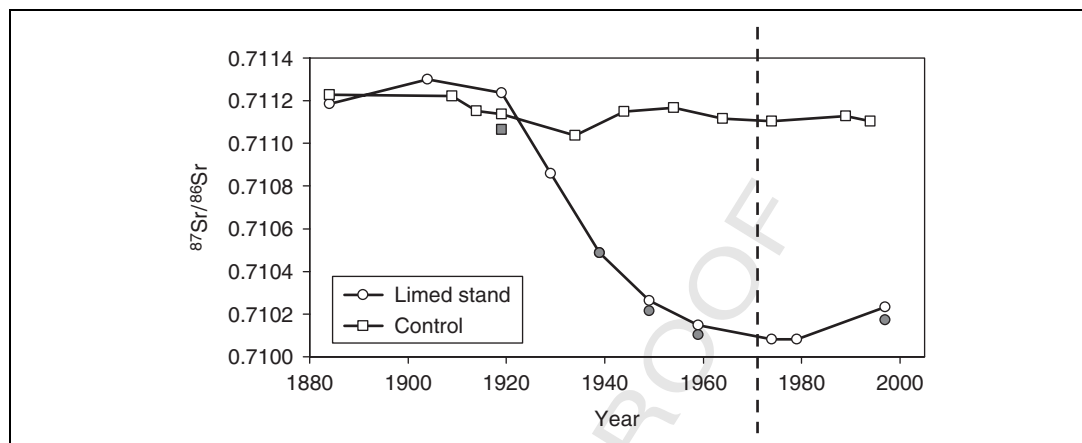
<sup>d</sup> Extracted with acid ammonium oxalate and Na dithionite at 60 °C.

cases, the exchange complex can conserve the isotopic signature of ancient weathering processes or a signature inherited from transfers of cations through the soil profile (Table 21.1). For example, in soils developed on loess, Ca and Sr derived from the dissolution of carbonate phase, present in the original loessic material but totally moved out now, were retained on the exchange complex of B<sub>3t</sub> and C horizons (MES site, Table 21.1 and Drouet *et al.* 2007). In another soil on Tertiary sandy-clayed substrate (DIEP site, Table 21.1), the exchange complex is constituted of Sr issued from the early weathering of glauconite, an <sup>87</sup>Sr-rich mineral, which is now strongly weathered and does not influence the weathering product (Drouet 2005). This phenomenon of exchange complex “memory” seems particularly active in soil horizons with large amounts of clay and/or Fe oxyhydroxide, the major part of the “free” Fe (Table 21.1). Such observations are in agreement with those reported in other studies (Blum and Erel 1997, Bullen *et al.* 1997). Soils without enriched clay horizon have lower exchangeable <sup>87</sup>Sr/<sup>86</sup>Sr ratio than that of the weathering source, and reflects the equilibrium between atmospheric and weathering sources of Sr (e.g., LND soil in Table 21.1).

## V. EVOLUTION OF THE Ca SOURCES THROUGH THE TIME HIGHLIGHTED BY TREE-RINGS RECORDS

Finally, Sr isotopes were associated to dendrochemistry, which uses archive properties of the tree growth rings. This technique allows a retrospective analysis of the origin of Ca in the tree nutrition (Åberg 1995, Poszwa *et al.* 2003, Drouet *et al.* 2005b). This last method is based on the hypothesis that the radial distribution of an element in the tree rings reflects the chemistry of the environment at the year of ring formation. Isotopic dendrochemistry can potentially give information on the evolution of Ca nutrition of trees on long periods of time (>100 years).

In this study (Drouet *et al.* 2005b), the validity of the tree-ring recorder was first evaluated on beech wood samples from a stand that experienced a large nutritional perturbation, namely a liming. The stand was limed in 1972 by means of 12 t of crushed limestone for soil status improvement. This liming material (CaCO<sub>3</sub>) has a Sr isotopic signature (very low <sup>87</sup>Sr/<sup>86</sup>Sr ratio: 0.707857) clearly distinct from

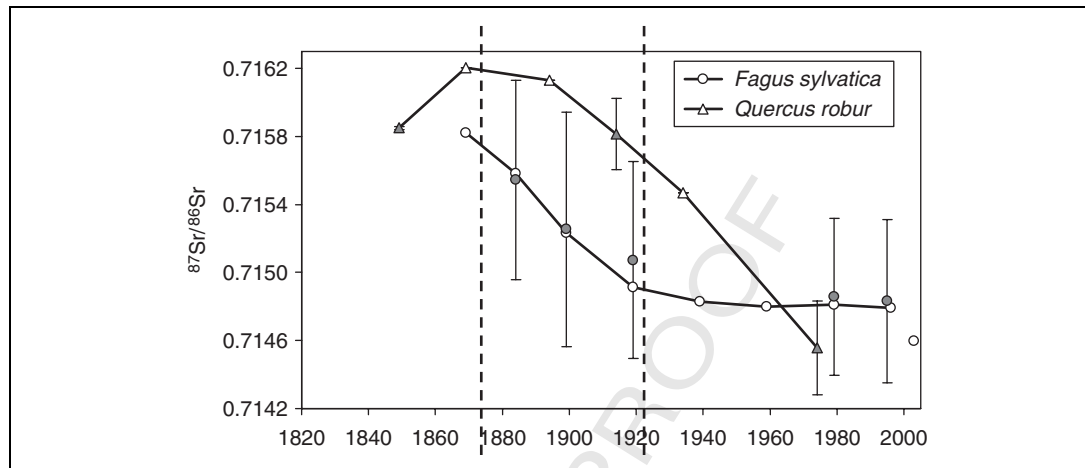


**FIGURE 21.3** Sr isotopic trend of a limed beech stand of central Belgium. Open circles indicate the limed stand chronology, solid squares show the  $^{87}\text{Sr}/^{86}\text{Sr}$  values of a control stand. The stand was limed by a blower with  $\sim 12 \text{ t ha}^{-1}$  of crushed Frasnian limestone ( $^{87}\text{Sr}/^{86}\text{Sr}$  ratio = 0.707857). The dotted line indicates the liming year (1972). Filled symbols show isotopic measurements on salt extractable Sr. [Redrawn from Drouet *et al.* (2005b) and from data on wood exchangeable forms ( $\text{CH}_3\text{COONH}_4$  extracts): Drouet, Herbauts, and Demaiiffe, unpublished data].

that of the two other sources and produces a dramatic shift of the wood  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio. Surprisingly, the Sr isotopic mark of the  $\text{CaCO}_3$  appears about 50 years before the liming application date (Figure 21.3). This can be explained by the fact that tree rings remain active during several years after their formation. Therefore, the sap circulation through the living wood maintains the isotopic equilibrium between wood and the soil solution. This process has previously been found by other authors (Houle *et al.* 2002) and is called “lateral reequilibration.” The evaluation of this phenomenon is crucial for the interpretation of other dendrochemical profiles. Another explanation could be that Sr can migrate from a ring to another, for example, through parenchyma rays or by diffusion. Different wood fractions of cations with distinct mobility may be considered: water-soluble, salt-extractible, and residual (Herbauts *et al.* 2002). Most of the residual (not extractible with salt solution) calcium and strontium in wood tissues is probably occluded in pectic compounds of galacturonic acids cross-linked by Ca and Sr bridges (Buvat 1989). Following the hypothesis of element migration, residual fraction of Sr should be a more robust signature of the Sr fixed during the year of ring formation. By contrast, more labile fractions might display another isotopic signal. However, some exploratory Sr isotopic measurements on the mobile fraction of wood ( $\text{CH}_3\text{COONH}_4$  extracted) do not differ from that on the whole ring sample (Figure 21.3).

Second, Sr isotopic measurements were performed on tree rings of European beech and pedunculate oak from other forest stands of central and high Belgium (Figure 21.4). We measured a steep decrease of the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio in tree-rings dated from  $\sim 1870$  to  $\sim 1920$ , except for sites of central Belgium with higher soil Ca reserve. The modification of the isotopic signal occurs in a relatively short period (1870–1920). This clearly shows a decrease of the weathering contribution (high  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio) to the vegetation supply that benefits to the atmospheric source, which is characterized by a low  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio. Other tree-ring chronologies of sensitive stands (i.e., growing on base-poor soils) in Scandinavia (Åberg 1995) and United States (Bullen and Bailey 2005) display the same isotopic pattern and show the geographic extent of this perturbation. But foremost, the comparison between these dendrochemical studies enlightens a synchronic decrease of the Sr isotopic ratio in the growth rings of different tree species and arguably point out to a global environmental effect.

We can consider several mechanisms to explain this major change of Ca nutrition of forest sites with critical Ca-status. A modification of the weathering isotope signal by variation of the relative



**FIGURE 21.4** Sr isotopic chronology for beech (*F. sylvatica* L.) (circles) and oak trees (*Quercus robur* L.) (triangles) in a High Belgium site. Gray symbols indicate the mean  $\pm$  SE of four individual tree measurements. Open symbols indicate composite samples ( $n = 4$ ). Vertical dotted lines enclose the timescale of rapid evolution of the Sr isotopic ratio.

weathering contributions of individual minerals within a period of  $\sim 100$  years is very unlikely. An hypothetical effect of tree aging implying change in root prospecting layers (with different isotope compositions) or differences in organic acid production enhancing may also be rejected in view of the very similar isotope signature measured in plantlets, in young and mature trees of two different stands. Our study highlighted the striking parallelism between the beginning of the  $^{87}\text{Sr}/^{86}\text{Sr}$  decrease and the beginning of the increase of sulfur emission corresponding to the Industrial Revolution at the end of the nineteenth century. Time trends of these anthropic activities could be reconstructed by means of estimations of  $\text{SO}_4^{2-}$  deposition (Ulrich 1987) or by records of nonmarine  $\text{SO}_4^{2-}$  deposition in ice core from Greenland or Alpine glaciers (Mayewski *et al.* 1990, Schwikowski *et al.* 1999). Deposition of sulfates is known to increase the loss of basic cations from the rooting zone by leaching (Reuss 1983). Cations are displaced from the soil exchange complex at a rate faster than the replenishment of the cation pool by mineral weathering. As a result, the Sr isotope composition of the soil solution taken up by trees moves toward that of the atmospheric source. This explanation is also in agreement with the finding of a soil desaturation in base cation through the time in the same regions (Falkengren-Grerup *et al.* 1987, Thimonier *et al.* 2000). This suggests that forest ecosystems were affected by atmospheric inputs of strong acids earlier than previously thought.

As shown for trees of the limed stand, the Sr isotopic trend is influenced by a lateral reequilibration process in beech rings, which implies that ring activity can last about 50 years after the ring formation. So, this isotope recorder foredates the environmental signal. It may therefore be expected that the effect of acid deposition has not occurred gradually from 1870 to 1920, but more abruptly around the 1920s.

An alternative hypothesis implicates the increase of alkaline earth content (low isotopic ratio) in the atmosphere to explain the drop of the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio growth rings. This change of the isotopic signature in wood would not be due to a rapid desaturation of the exchange complex—mainly supplied by radiogenic Sr from weathering—but to a replacement of the exchangeable cations by increasing atmospheric inputs with low Sr isotopic ratio. Indeed, besides its role in the acid deposition, Industrial Revolution was also at the origin of an increasing emission of Ca-bearing particles (coal burning, cement manufacturing and so on). However, this hypothesis cannot be confirmed because no precise time trends on total deposition of basic cations and the emission of fine air particulate (PM-10) are available for such early dates. Nevertheless, it must be kept in mind that the annual input of Ca from mineral weathering and the atmosphere are far lower compared to the soil bioavailable reserves. These calcium reserves induce therefore inertia of the system against change in the amount of atmospheric

Ca inputs. So, such a change would probably come into sight through a progressive modification of the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio in the tree rings and is not compatible with an abrupt change (if we take into account the lateral reequilibration process) reconstituted from the sensitive sites.

The lack of a decrease of the Sr isotopic ratio in tree rings of beech in the central Belgium sites was a very instructive case to complete the explanation of the above-discussed processes. For this stands, we could calculate that an increase of 3% and 9% of the Ca atmospheric contribution should be detectable at a significant to highly significant level, respectively (paired *t*-test). So, the change in the Ca source proportion of 20–30% that could be necessary for the isotopic shift in the High Belgium trees, following the second hypothesis, would have been also detectable in central Belgium. The stability of the Sr isotopic signature in the beech wood of central Belgium could rather be explained by a soil-effective base saturation ( $\text{BS}_e$ ), on average higher than the critical value of 20% in the upper meter. Above these values, the soil solution is considered to be buffered mainly by release of base cations from the exchange complex (Reuss 1983) with higher  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio. Beneath this value, neutralization of acidity is provided by Al and the soil solution could be dominated by atmospheric Sr (Figure 21.2).

## VI. PERSPECTIVES

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These different studies show that the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio is a useful tool as tracers of the origin of Ca in several levels of the forest ecosystem. Nevertheless, the measurement of the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio does not give information on the internal cycle of the Ca (OM mineralization, cycling through the vegetation, and so on). However, these internal fluxes are generally dominant in forest compared to weathering and atmospheric inputs. The use of other isotopes (Ca, Mg) could constitute a complementary tool to determine the effect of environmental changes on the nutrient cycle and the possibility of the ecosystem to recover from acidification. Despite some technical difficulties, Ca isotopes can be measured with precision today (DePaolo 2004). Several studies showed that biotic processes fractionate Ca isotopes (Schmitt and Stille 2005). In forest ecosystems, light Ca isotopes are privileged in the absorption by the vegetation. As a consequence, soil is enriched in heavy isotopes at each element cycling through the vegetation (Wiegand *et al.* 2005). Given the isotopic fractionation induced by each cycling of Ca through the biological material,  $^{44}\text{Ca}/^{40}\text{Ca}$  ratio could be used in the forest stands as a direct measurement of the recycling intensity of nutrients by the vegetation and offers new perspectives of research.

## VII. SUMMARY

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Calcium is essential in forest ecosystems, both as nutrient for trees and for its role in the neutralization of acid inputs. The decline in bioavailable Ca reserve in the soil, caused by acid deposition produced by industrial activity, was reported for a lot of forest sites in Europe and North America. The understanding of the causal mechanisms requires a precise knowledge of the supplying sources of Ca. Measurements of natural Sr isotopes can be used to determine accurately the origin of Ca in the vegetation. By means of this method, we highlighted the extreme dependence of some forest ecosystems to the Ca input by atmospheric precipitation. The use of this isotopic tracer permits also to characterize the Ca exchanges between the ecosystem components. Finally, the coupling of this method with dendrochemistry adds an important piece to the knowledge of the soil acidification story. Change of the Sr isotopic ratio in the tree rings of several Belgian sites, and the comparison with similar trends in other regions suggest that the soil acidification in industrial regions started in the beginning of the twentieth century, that is, earlier than it is generally admitted.

## VIII. ACKNOWLEDGMENTS

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This research was supported by the Fonds National de la Recherche Scientifique (FNRS, Belgium, convention no. 2.457002 F) and by student research grants from the FRIA for the first author.

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