incubation-derived indices of C_s decomposition rates will probably differ from those developed in the field, relative differences among sites are presumably real[17,18,21,26].

We used single-pool exponential decay models to estimate C_s turnover time in method 1 and method 2 studies. Single-pool models are widely used to describe C_s turnover, but they may over-estimate rates because the approach assumes that all C_s will behave as did the C_s released during the study[30]. It is unlikely, however, that our single-pool approach masked a relationship between the turnover of a large, temperature-sensitive C_s pool and temperature. In method 1 studies, we would suspect masking if C_s mass loss per year increased with temperature early in the decomposition sequence. However, for sites with <11 yr since conversion, C_s mass loss per year was higher for cool sites (9.5% yr^{-1}) than for warm (4.5% yr^{-1}) climate soils ($P < 0.01$). In method 2 studies, we would suspect masking if the total quantity of C_s released per gram of soil increased with temperature because the release of this C_s is independent of total C_s pool size. However, C_s released per kilogram of soil in one year declined with increasing incubation temperature ($R^2 = 0.11$, $P = 0.04$). Further, for masking to have occurred, the proportion of total C_s that is temperature sensitive or fast-cycling must decline steeply with increasing temperature. Using the best techniques available, Trumbore *et al.*[2] found no relationship between the proportion of fast-cycling C_s (from 50% to 80% of total C_s) and MAT. Nonetheless, we tested the potential for masking by assuming that all C_s released in method 2 studies was fast cycling and that 50%, 65% and 80% of total C_s in tropical, temperate and subalpine soils, respectively, was fast cycling. We then recalculated turnover times for fast-cycling C_s alone. Overall, patterns of C_s decomposition were unchanged.

1. Schimel, D. S. *et al.* Climatic, edaphic, and biotic controls over storage and turnover of carbon in soils. *Glob. Biogeochem. Cycles* **8**, 279–293 (1994).
2. Trumbore, S. E., Chadwick, O. & Amundson, A. Rapid exchange between soil carbon and atmospheric carbon dioxide driven by temperature change. *Science* **272**, 393–396 (1996).
3. Kirschbaum, M. U. F. The temperature dependence of soil organic matter decomposition, and the effect of global warming on soil organic C storage. *Soil Biol. Biochem.* **27**, 753–760 (1995).
4. VEMAP members. Vegetation/ecosystem modeling and analysis project: Comparing biogeography and biogeochemistry models in a continental-scale study of terrestrial ecosystem response to climate change and CO_2 doubling. *Glob. Biogeochem. Cycles* **9**, 407–437 (1995).
5. Cao, M. & Woodward, F. I. Dynamic responses of terrestrial ecosystem carbon cycling to global climate change. *Nature* **393**, 249–252 (1998).
6. Jenkinson, D. S., Adams, D. E. & Wild, A. Model estimates of CO_2 emissions from soil in response to global warming. *Nature* **351**, 304–306 (1991).
7. Nadelhoffer, K. J., Giblin, A. E., Shaver, G. R. & Laundre, J. A. Effects of temperature and substrate quality on element mineralization in six arctic soils. *Ecology* **72**, 242–253 (1991).
8. Peterjohn, W. T., Melillo, J. M., Bowles, F. P. & Steudler, P. A. Soil warming and trace gas fluxes: experimental design and preliminary flux results. *Oecologia* **93**, 18–24 (1993).
9. Townsend, A. R., Vitousek, P. M., Desmarais, D. J. & Tharpe, A. Soil carbon pool structure and temperature sensitivity inferred using CO_2 and $^{13}CO_2$ incubation fluxes from five Hawaiian soils. *Biogeochemistry* **38**, 1–17 (1997).
10. Winkler, J. P., Cherry, R. S. & Schlesinger, W. H. The Q_{10} relationship of microbial respiration in a temperate forest soil. *Soil Biol. Biochem.* **28**, 1067–1072 (1996).
11. Updegraff, K., Pastor, J., Bridgham, S. D. & Johnston, C. A. Environmental and substrate controls over carbon and nitrogen mineralization in northern wetlands. *Ecol. Applic.* **5**, 151–163 (1995).
12. Holland, E. A., Townsend, A. R. & Vitousek, P. M. Variability in temperature regulation of CO_2 fluxes and N mineralization from five Hawaiian soils: implications for a changing climate. *Glob. Change Biol.* **1**, 115–123 (1995).
13. Liski, J., Livesniemi, H., Maketa, A. & Westman, C. CO_2 emissions from soil in response to climate warming are over-estimated—The decomposition of old soil organic matter is tolerant of temperature. *Ambio* **28**, 171–174 (1999).
14. Feller, C. & Beare, M. H. Physical control of soil organic matter dynamics in the tropics. *Geoderma* **79**, 69–116 (1997).
15. Gregorich, E. G., Ellert, B. H. & Monreal, C. M. Turnover of soil organic matter and storage of corn residue C estimated from C-13 abundance. *Can. J. Soil Sci.* **75**, 161–167 (1995).
16. Bashkin, M. & Binkley, D. Changes in soil carbon following afforestation in Hawaii. *Ecology* **79**, 828–833 (1998).
17. Motavalli, P. P. *et al.* Comparison of laboratory and modeling simulation methods for estimating soil carbon pools in tropical forest soils. *Soil Biol. Biochem.* **26**, 935–944 (1994).
18. Hart, S. C., Nason, G. E., Myrold, D. D. & Perry, D. A. Dynamics of gross nitrogen transformations in an old-growth forest: the carbon connection. *Ecology* **75**, 880–891 (1994).
19. Trumbore, S. E. *et al.* Belowground cycling of carbon in forests and pastures of Eastern Amazonia. *Glob. Biogeochem. Cycles* **9**, 515–528 (1995).
20. Balesdent, J., Mariotti, A. & Guillet, B. Natural ^{13}C abundance as a tracer for studies of soil organic matter dynamics. *Soil Biol. Biochem.* **19**, 25–30 (1987).
21. Paul, E. & Clark, F. *Soil Microbiology and Biochemistry* (Academic, New York, 1996).
22. Binkley, D. & Resh, S. C. Rapid changes in soils following *Eucalyptus* afforestation in Hawaii. *Soil Sci. Soc. Am. J.* **63**, 222–225 (1999).
23. Veldkamp, E. Organic carbon turnover in three tropical soils under pasture after deforestation. *Soil Sci. Soc. Am. J.* **58**, 175–180 (1994).
24. Cheng, W. *et al.* Is available carbon limiting microbial respiration in the rhizosphere? *Soil Biol. Biochem.* **28**, 1283–1288 (1996).
25. Bonde, T., Christensen, B. T. & Cerri, C. C. Dynamics of organic matter as reflected by natural ^{13}C abundance in the particle size fractions of forested and cultivated Oxisols. *Soil Biol. Biochem.* **24**, 275–277 (1992).
26. Sørenson, L. H. Carbon-nitrogen relationships during the humification of cellulose in soils containing different amounts of clay. *Soil Biol. Biochem.* **13**, 313–321 (1981).
27. Mahieu, N., Powlson, D. H. & Randall, W. Statistical analysis of published carbon-13 CPMAS spectra of soil organic matter. *Soil Sci. Soc. Am. J.* **63**, 307–319 (1999).
28. Post, W. M., Emanuel, W. R., Zinke, P. J. & Stangenberger, A. G. Soil carbon pools and world life zones. *Nature* **298**, 156–159 (1982).
29. Goulden, M. L. *et al.* Sensitivity of boreal forest carbon balance to soil thaw. *Science* **279**, 214–217 (1998).
30. Townsend, A. R., Vitousek, P. M. & Trumbore, S. E. Soil organic matter dynamics along gradients in temperature and land use on the Island of Hawaii. *Ecology* **76**, 721–733 (1995).

··

Respiration as the main determinant of carbon balance in European forests

R. Valentini[1], G. Matteucci[1], A. J. Dolman[2], E.-D. Schulze[3,4], C. Rebmann[3,4], E. J. Moors[2], A. Granier[5], P. Gross[5], N. O. Jensen[6], K. Pilegaard[6], A. Lindroth[7], A. Grelle[8], C. Bernhofer[9], T. Grünwald[9], M. Aubinet[10], R. Ceulemans[11], A. S. Kowalski[11], T. Vesala[12], Ü. Rannik[12], P. Berbigier[13], D. Loustau[14], J. Guðmundsson[15], H. Thorgeirsson[15], A. Ibrom[16], K. Morgenstern[16], R. Clement[17], J. Moncrieff[17], L. Montagnani[18], S. Minerbi[19] & P. G. Jarvis[17]

··

Carbon exchange between the terrestrial biosphere and the atmosphere is one of the key processes that need to be assessed in the context of the Kyoto Protocol[1]. Several studies suggest that the terrestrial biosphere is gaining carbon[2-8], but these estimates are obtained primarily by indirect methods, and the factors that control terrestrial carbon exchange, its magnitude and primary locations, are under debate. Here we present data of net ecosystem carbon exchange, collected between 1996 and 1998 from 15 European forests, which confirm that many European forest ecosystems act as carbon sinks. The annual carbon balances range from an uptake of 6.6 tonnes of carbon per hectare per year to a release of nearly 1 t C ha^{-1} yr^{-1}, with a large variability between forests. The data show a significant increase of carbon uptake with decreasing latitude, whereas the gross primary production seems to be largely independent of latitude. Our observations indicate that, in general, ecosystem respiration determines net ecosystem carbon exchange. Also, for an accurate assessment of the carbon balance in a particular forest ecosystem, remote sensing of the normalized difference vegetation index or estimates based on forest inventories may not be sufficient.

[1] University of Tuscia, Department of Forest Environment and Resources, I-01100 Viterbo, Italy. [2] Alterra, PO Box 47, 6700 AA Wageningen, The Netherlands. [3] Max-Planck-Institut für Biogeochemie, D-07745 Jena, Germany. [4] Former address: Lehrstuhl für Pflanzenökologie, Universität Bayreuth, D-95440 Bayreuth, Germany. [5] Centre de Recherches de Nancy, Unité d'Ecophysiologie Forestière, Equipe de Bioclimatologie, F-54280 Champenoux, France. [6] Risoe National Labouratory, DK-4000 Roskilde, Denmark. [7] Lund University, Department of Physical Geography, Box 118, SE-221 00 Lund, Sweden. [8] SLU, Department for Production Ecology, Faculty of Forestry, PO Box 7042, S-7042 Uppsala, Sweden. [9] TU Dresden, Institut für Hydrologie und Meteorologie, D-01737 Tharandt, Germany. [10] Unité de Physique, Faculté Universitaire des Sciences Agronomiques de Gembloux, B-5030 Gembloux, Belgium. [11] Department of Biology, University of Antwerpen, Universiteitsplein 1, B-2610 Wilrijk, Belgium. [12] Department of Physics, PO Box 9, FIN-00014, University of Helsinki, Finland. [13] Unité de Bioclimatologie, INRA Bourdeaux, BP 81, F33883 Villenave d'Ornon Cedex, France. [14] Unité de Recherches Forestières, INRA Bourdeaux, BP 45, F33611 Gazinet, France. [15] Agricultural Research Institute, Department of Environmental Research, Keldnaholti, 112, Reykjavik, Iceland. [16] Georg-August Universität, Institut für Bioklimatologie, Büsgenweg 2, D-37077-Göttingen, Germany. [17] University of Edinburgh, Institute of Ecology and Resource Management, Edinburgh EH9 3JU, UK. [18] University of Padova, Department of Land and Agro-Forestry Systems, Agripolis, I-35020 Legnaro, Padova, Italy. [19] Autonomous Province of Bolzano, Forest Services, I-39100 Bolzano, Italy.

The terrestrial sink for carbon is estimated to be of the order of 2 $\pm$ 1 Gt C yr^{-1} (ref. 1). In the Northern Hemisphere, the terrestrial biosphere is currently absorbing carbon according to several studies[2–8]. These studies use different techniques dependent on indirect estimates of the carbon fluxes, like isotopic analysis and inversion methods from CO_2 concentration measurements[5–7], remote sensing[8], growth trend analysis[2–4] and modelling. All these methods provide the necessary global and continental scale perspective for carbon balance calculations. However, these studies suffer from uncertainties in the assumptions used. For instance, in the inverse modelling studies the anthropogenic sources and sinks are frequently prescribed a priori and they lack adequate representation of the carbon balance at local scales. Their use in addressing small temporal and spatial changes in the carbon balance is therefore rather limited.

The net carbon exchange of terrestrial ecosystems is the result of a delicate balance between uptake (photosynthesis) and loss (respiration), and shows a strong diurnal, seasonal and annual variability. Under favourable conditions, the net ecosystem flux is dominated by photosynthesis during daytime, and by respiration at night and for deciduous ecosystems in leafless periods. The influence of climate and growing-season length can in some cases shift a terrestrial ecosystem from a sink to a source of carbon[9–11].

Global- and continental-scale techniques are of limited use in addressing one of the key questions raised by the Kyoto Protocol, namely how to calculate the changes in "carbon stocks" associated with land use changes and forestry activities during the commitment period. Indeed, one of the major effects of land-use changes, including the afforestation, reforestation and deforestation of land, is to change soil organic matter (SOM), by both build up and decomposition[12]. For most ecosystems, the changes in stocks of soil carbon in a 4–5 year period are unfortunately within the errors of the survey techniques used. Remote sensing approaches also appear inadequate for such purposes, because they have limited capability for estimating below canopy processes such as soil respiration.

In this context, the direct, long-term measurement of carbon fluxes by the eddy covariance technique[13] offers the possibility of assessing on a local scale the carbon sequestration rates of forests and of different land-uses. The technique can also provide a better understanding of the vulnerability of the carbon balance of ecosystems to climate variability, and can be used to validate ecosystem models and to provide data for land surface exchange schemes in global models[14].

Automated eddy covariance measurements of CO_2 fluxes have been made routinely over 15 forests in Europe since 1996 within the EUROFLUX network[15]. In 1998, the network approach was expanded in the US (AMERIFLUX) and plans exist to implement similar networks in Brazil (the Large Scale Biosphere Atmosphere

Table 1 Main characteristics of the EUROFLUX and associated sites

Site*	Latitude	Species†	Ecosystem type‡	Elevation (m.a.s.l.)	T (°C)	P (mm)	Age (yr)	LAI§ (m^2 m^{-2})	Period of observation‖	NEE¶ (t C ha^{-1} yr^{-1})	RE# (t C ha^{-1} yr^{-1})
1 Italy 2	41° 45′	M, BE	N	3	15.3	770	50	3.5	1997	−6.6	
2 Italy 1	41° 52′	BD	NM	1,560	6.2	1,180	105	5.5	28/06/96–27/06/97	−6.6	6.4
3 France 2	44° 05′	C	PNM	60	13.7	936	29	2.8	13/07/96–12/07/97	−4.3	8.0
4 Italy ext.	46° 18′	M, C	NM	1,720	4.1	1,010	80	4	1998	−4.5	4.45
5 France 1	48° 40′	BD	NM	300	8.5	672	30	5.7	01/05/96–30/04/97	−2.2	7.9
6					9.8	871		5.6	1997	−2.6	9.9
7 Germany 1	50° 09′	C	NM	780	5.8	885	45	6.7	01/05/97–30/04/98	−0.77	13
8 Belgium 1	50° 18′	M, BD+C	PNM	450	7.5	792	75	5.1	Aug 96–Jul 97	−4.3	10.1
9 Germany 2	50° 58′	C	NM	380	8.3	724	105	4.8	1996	−3.3	8.3
10									1997	−4.8	9.5
11									1998	−5.4	9.7
12 Belgium 2	51° 18′	M, C+BD	PNM	10	10.4	662	70	3	1997	−1.57	
13 Germany ext.	51° 46′	C	PNM	505	6.6	1,045	110	7	1996	−3.1	8.3
14									1997	−4.9	9.6
15 Netherland 1	52° 10′	C	PNM	25	9.8	786	80	3	1997	−2.1	13.4
16 Denmark 1	55° 29′	BD	NM	40	8.5	510	80	4.7	1997	−0.9	10.6
17					7.5	441			01/06/96–31/05/97	−1.7	9.7
18					8.8	621			01/06/97–31/05/98	−1.3	11.1
19 Unit. King. 1	56° 37′	C	IMP	340	7.9	1,200	17	7.0	1997	−6.7	13.2
20					7.8	1,100	18	7.5	1998	−5.7	13.5
21	60° 05′	M, C	PNM	45	6.8	437	80	4	1995	0.9	13.4
22					6.1	393			1996	−0.05	12.4
23					6.9	580			1997	0.8	14
24 Finland 1	61° 51′	C	PNM	170	4.2	669	30	4	1997	−2.45	7.6
25 Iceland 1	63° 50′	BD	IMP	78	4.6	1,168	7	2	1997	−1	6.1
26 Sweden 2	64° 07′	C	PNM	225	4.4	480	37	2.4	1997	−1.9	10.65
2a Italy 1	41° 52′	BD	PNM	1560	6.2	1,180	100	4.5	1993–94	−4.7	5.4

* The site number refers to the data labels in figures. Sites are nominated as in the EUROFLUX project.
† M, mixed; BE, broad-leaved evergreen; BD, broad-leaved deciduous; C, coniferous.
‡ NM, natural origin and managed; PNM, planted stand with traditional forest management; IMP, intensively managed plantation.
§ Leaf area index, projected basis.
‖ Period for the flux data presented; all the sites are currently measuring fluxes.
¶ Net ecosystem exchange (see Methods).
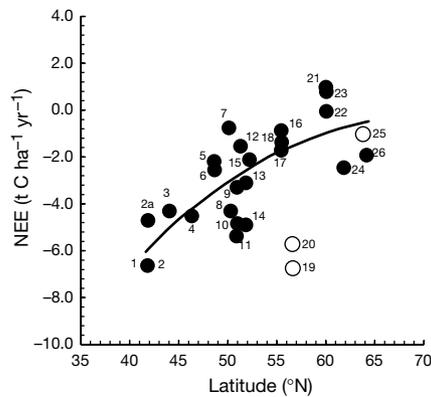# Total ecosystem respiration (see Methods).

Figure 1 Net ecosystem exchange (NEE) of the EUROFLUX sites plotted against latitude. Closed symbols, forest of natural origin and planted stands with traditional forest management; open symbols, intensively managed plantations. According to the eddy covariance theory, a negative sign indicates that carbon is absorbed by the forest, while a positive sign indicates that carbon is released by the forest to the atmosphere.

Experiment in Amazonia), South East Asia (the GEWEX Asian Monsoon Experiment) and Siberia. These tower sites are now forming a global network, FLUXNET[16], with standard measurement protocols, data quality control and storage systems[15]. The flux stations measure the net flux of carbon entering or leaving the ecosystem. This is the flux which provides a measure of net ecosystem exchange (NEE), and, if summed annually, provides a direct estimate of the annual ecosystem carbon balance (excluding disturbances by harvest and fire which give rise to net biome productivity)[17]. In several studies the accuracy of annual sums has been estimated to be about 5%, or typically 0.3 t C ha^{-1} yr^{-1} (refs 18, 19), with the error influence decreasing with increasing size of the flux data set[20].

To reduce the uncertainty associated with site-to-site variation in flux measurement methods and calculations and to make comparisons between sites, the EUROFLUX network was designed with the same hardware and software specifications at all sites[15]. The EURO-FLUX results for 1996−98 show a sink strength of up to 6.6−6.7 t C ha^{-1} yr^{-1} for two forests in Southern Europe and for a Sitka spruce plantation in Scotland, and indicate that European old boreal forests are close to equilibrium and may switch from being a carbon source one year to a carbon sink the next (Table 1). Within the same biome, younger stands still gain carbon, although at a lower rate than temperate forests, Mediterranean forests or fast-growing plantations. Despite the wide range of species composition, stand structure, soils, tree age, site disturbance history and year-to-year variability, a consistent latitudinal trend in NEE is found

(Fig. 1). Indeed a multivariate statistical analysis on the effect of the single factors (latitude, precipitation, ecosystem type, elevation, mean annual temperature, age, management type, leaf area index) on NEE, showed that latitude is the most significant single variable model ($r^2 = 0.55$, $P < 0.001$). Latitude is not a phenomenological driving variable *per se*, however it is a good proxy for the actions of a multiplicity of factors (for example, radiation balance, length of growing season, frost events, disturbance regime).

The trend indicates that high-latitude forests generally show lower and more variable carbon sequestration rates than low-latitude forests. The several forests growing within 50° and 52° N show a pronounced variability, with NEE ranging from an uptake of less than 1 t C ha^{-1} yr^{-1} (site Germany 1, point 7) to 5.4 t C ha^{-1} yr^{-1} (site Germany 2, point 11). In this latitudinal band, the variability can be related to stand, soil and climate characteristics, ranging from continental to maritime. With its maritime proximity, the intensively managed and fertilized fast-growing spruce plantation (site United Kingdom 1, points 19, 20) falls off the latitudinal trend, with a higher uptake of carbon than more continental stands located at similar latitude. Despite the large variation of NEE, gross primary production (GPP) is rather conservative across sites and latitude, indicating that other components of the carbon balance are responsible for the observed variation in NEE (Fig. 2). It is noteworthy that the young spruce plantation has the largest values of GPP, indicating strong stimulation of photosynthesis, while the young poplar plantation (point 25) growing in a cold climate at 64° N shows the smallest GPP.
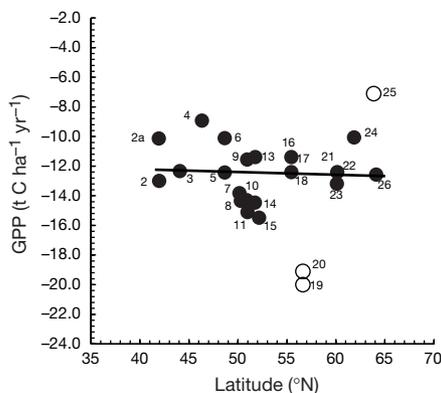

Figure 2 Gross primary production (GPP) of the EUROFLUX sites plotted against latitude. Closed symbols, forest of natural origin and planted stands with traditional forest management; open symbols, intensively managed plantations.
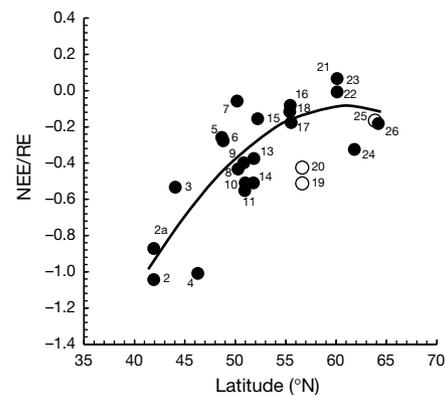

Figure 3 The ratio of net ecosystem exchange (NEE) and total ecosystem respiration (RE) plotted against latitude. Closed symbols, forest of natural origin and planted stands with traditional forest management; open symbols, intensively managed plantations.

The observed variation in NEE across sites can be explained by the relative importance of ecosystem respiration (RE) in relation to NEE. The ratio NEE/RE increases with latitude (Fig. 3) indicating that RE becomes more important for northern sites and can explain the decrease of NEE previously shown. Generally, while GPP tends to be constant across sites, annual ecosystem respiration increases with latitude, despite the general decrease of mean annual air temperature (Table 1). It is well known that temperature has a strong effect on soil and plant respiration. For single sites our data also show a significant relationship between temperature and ecosystem respiration for both short and annual timescales. However, when a plot of RE versus temperature is drawn across all sites the relationship is not significant, indicating that mean annual air temperature may not be an important contributing factor to forest ecosystem respiration on a broader scale.

In forests, total ecosystem respiration tends to be dominated by root and microbial soil respiration. Boreal soils contain a larger amount than temperate soils of soil organic matter (SOM) in a labile form[12,21-23] that is prone to rapid decomposition[21,22]. The effective temperature sensitivity (Q_{10}) of SOM decomposition is much higher in colder than in warmer climates and temperature increases in cold regions are likely to affect decomposition rates more than net primary productivity[23]. There is also evidence that northern latitudes have warmed by more than 4 °C, while southern latitudes have warmed less[24]. This may have resulted in non-steady state conditions for SOM which could explain relative enhancement of respiration in the north compared to the south.

In this respect, land-use change and site history could also be important. For example, site Sweden 1 (points 21–23) is losing carbon as a result of past soil drainage, while the high respiration rates of the maritime spruce plantation may be linked to preparation of the site by ploughing, the favourable maritime climate and fertilization. Furthermore the relatively low rates of respiration of the southern sites may be the result of drought limitations to soil respiration[25-27].

The carbon balance is ultimately a delicate equilibrium between the two large fluxes of photosynthesis and respiration, and this appears to be particularly true for boreal European ecosystems, making them very vulnerable to disturbances in climate. Indeed, annual variability for these high latitude sites is very pronounced, as shown by the remarkable variation in NEE from year to year: warm winters tend to switch old boreal stands from a sink to a source of carbon by increasing the annual amount of respiration[9] (site Sweden 1; Table 1). In other boreal ecosystems, year-to-year changes in timing of the thawing of the soil in the spring are important for the carbon balance[10].

The direct flux estimates of carbon exchange provide a useful tool for understanding the overall carbon balance processes of terrestrial ecosystems. Indeed, partial accounting of carbon dynamics can easily lead to erroneous conclusions. For example, plant biomass is currently increasing in all the EUROFLUX sites, even though some of these sites have a carbon budget close to neutral and one is losing carbon on a yearly basis. Similarly, the increases in plant growth at northern latitudes estimated by remote sensing of the normalized difference vegetation index (NDVI) must be examined critically in the light of these results, confirming the need to consider ecosystem respiration[8]. Also forest inventory-based carbon balance estimates should be carefully examined in relation to comprehensive carbon budget accounting. Furthermore, flux tower networks can provide at local scale realistic constraints on the global carbon balance estimates. □

Methods

Instruments

In the EUROFLUX network, the same CO_2/H_2O infrared gas analyser (LI-6262, Licor Inc.) and sonic anemometer (Solent, Gill Inst.) are used. All the analysers are calibrated against the same CO_2 standard (NOAA Climatic Monitoring and Diagnostics Laboratory, Boulder, Colorado). The software for eddy covariance data acquisition and calculation have been extensively tested and compared against reference data sets, resulting in a maximum variation of calculated fluxes of less than 1% (ref. 15).

Data treatment

The collected data are quality controlled, corrected for frequency losses and sensor separation and, when needed, corrected for night-time fluxes under stable conditions with low wind speed or friction velocity typically less than $0.2\ ms^{-1}$ (refs 14, 15).

NEE values for the entire year are obtained by summation of fluxes measured on a 30-min time step. The average coverage of directly measured data for all of the sites was more than 70% of the annual half-hour periods (60–95%). Fluxes in stable conditions and data gaps have been filled through site-based functional relationships using meteorological variables, such as radiation during the day and temperature during the night. Small gaps (a few half-hours) during single days were filled by simple interpolation. For data gap filling procedure see Supplementary Information.

GPP values have been obtained by summing annual NEE and ecosystem respiration (RE). RE comes from the summation of night-time fluxes (all sites), whole-day fluxes for leafless periods (deciduous forests) and of the day-time respiration.

Night-time and leafless-period fluxes are obtained by summation of the fluxes measured by eddy covariance on a 30-min time step, including the CO_2 storage component. Daytime respiration has been obtained by extrapolating the night-time fluxes to the rest of the day, using functional relationships with soil or air temperature.

A multivariate statistical analysis, based on different procedures, namely the forward and stepwise selections and the maximum R-square improvement, was used to test the controlling factors on NEE[28].

1. IGBP Terrestrial carbon working group. The terrestrial carbon cycle: implications for the Kyoto protocol. *Science* **280,** 1393–1394 (1998).
2. Dixon, R. K. *et al.* Carbon pools and flux of global forest ecosystems. *Science* **263,** 185–190 (1994).
3. Nabuurs, G. J., Pavinen, R., Sikkema, R. & Mohren, G. M. J. The role of European forests in the global carbon cycle – a review. *Biomass Bioenergy* **13,** 345–358 (1997).
4. Kauppi, P. E., Mielikäinen, K. & Kuusela, K. Biomass and carbon budget of European forests, 1971 to 1990. *Science* **256,** 70–74 (1992).
5. Ciais, P., Tans, P. P., Trolier, M., White, J. W. C. & Francey, R. J. A large northern hemisphere terrestrial CO_2 sink indicated by $^{13}C/^{12}C$ ratio of atmospheric CO_2. *Science* **269,** 1098–1102 (1995).
6. Denning, A. S., Fung, I. Y. & Randall, D. Latitudinal gradient of atmospheric CO_2 due to seasonal exchange with the land biota. *Nature* **376,** 240–243 (1995).
7. Fan, S. *et al.* A large terrestrial carbon sink in North America implied by atmospheric and oceanic carbon dioxide data and models. *Science* **282,** 442–446 (1998).
8. Myneni, R. B., Keeling, C. D., Tucker, C. J., Asrar, G. & Nemani, R. R. Increased plant growth in the northern high latitudes from 1981 to 1991. *Nature* **386,** 698–702 (1997).
9. Lindroth, A., Grelle, A. & Morén, A.-S. Long-term measurements of boreal forest carbon balance reveal large temperature sensitivity. *Glob. Change Biol.* **4,** 443–450 (1998).
10. Goulden, M. L. *et al.* Sensitivity of boreal forest carbon balance to soil thaw. *Science* **279,** 214–217 (1998).
11. Oechel, W. C. *et al.* Recent change of arctic tundra ecosystems from a net carbon dioxide sink to a source. *Nature* **361,** 520–523 (1993).
12. Schlesinger, W. H. in *Biogeochemistry: An Analysis of Global Change* 161–165 (Academic, San Diego, 1997).
13. Baldocchi, D. D., Hicks, B. B. & Meyers, T. P. Measuring biosphere-atmosphere exchanges of biologically related gases with micrometeorological methods. *Ecology* **69,** 1331–1340 (1988).
14. Baldocchi, D. D., Valentini, R., Running, S., Oechel, W. C. & Dahlman, R. Strategies for measuring and modelling carbon dioxide and water vapour fluxes over terrestrial ecosystems. *Glob. Change Biol.* **2,** 159–167 (1996).
15. Aubinet, M. *et al.* Estimates of the annual net carbon and water exchange of forests: the EUROFLUX methodology. *Adv. Ecol. Res.* **30,** 113–175 (2000).
16. Running, S. A blueprint for improved global change monitoring of the terrestrial biosphere. *Earth Obs.* **10,** 8–12 (1998).
17. Schulze, E. D. & Heimann, M. in *Asian Change in the Context of Global Change* (eds Galloway, J. & Melillo, J.) 145–161 (Cambridge Univ. Press, 1998).
18. Goulden, M. L., Munger, J. W., Fan, S.-M., Daube, B. C. & Wofsy, W. C. Measurements of carbon sequestration by long-term eddy covariance: methods and critical evaluation of accuracy. *Glob. Change Biol.* **2,** 169–181 (1996).
19. Chen, W. J. *et al.* Effects of climatic variability on the annual carbon sequestration by a boreal aspen forest. *Glob. Change Biol.* **1,** 41–53 (1999).
20. Moncrieff, J. B., Malhi, Y. & Leuning, R. The propagation of errors in long-term measurements of land atmosphere fluxes of carbon and water. *Glob. Change Biol* **2,** 231–240 (1996).
21. Anderson, J. M. Responses of soils to climate change. *Adv. Ecol. Res.* **22,** 163–210 (1992).
22. Vogt, K. A. in *Soil Management and Greenhouse Effect* (eds Lal, R., Kimble, J., Levine, E. & Stewart, B. A.) 159–178 (CRC Press, Boca Raton, 1995)
23. Kirschbaum, M. U. The temperature dependence of soil organic matter decomposition, and the effect of global warming on soil organic C storage. *Soil Biol. Biochem.* **6,** 753–760 (1995).
24. Chapman, W. L. & Walsh, J. E. Recent variations of sea ice and air temperatures in high latitudes. *Bull. Am. Meteorol. Soc.* **74,** 33–47 (1993).
25. Schlenter, R. E. & Van Cleve, K. Relationship between CO_2 evolution from soil, substrate temperature, and substrate moisture in four mature forest types in interior Alaska. *Can. J. Forest Res.* **15,** 97–106 (1985).
26. Hanson, P. J., Wullschleger, S. D., Bohlmann, S. A. & Todd, D. E. Seasonal and topographic patterns of forest floor CO_2 efflux from an upland oak forest. *Tree Physiol.* **13,** 1–15 (1993).
27. Burton, A. J., Pregitzer, K. S., Zogg, G. P., & Zak, D. R. Drought reduces root respiration in sugar maple forests. *Ecol. Applic.* **8,** 771–778 (1998).

28. SAS/STAT® User's Guide Version 6, 4th edn, Vol. 2, (SAS Institute Inc., Cary, North Carolina, 1989).

....

Determination of relative growth rates of natural quartz crystals

Phillip D. Ihinger & Stephen I. Zink

Department of Geology and Geophysics, Yale University, New Haven, Connecticut 06520-8109, USA

....

Although the theory describing crystal growth in the geological environment is well established[1–3], there are few quantitative studies that delimit the absolute time involved in the growth of natural crystals[4–6]. The actual mechanisms responsible for the variation in size and shape of individual crystal faces are, in fact, not well understood. Here we describe a micro-infrared spectroscopic study of a single, gem-quality quartz crystal that allows us to measure the size, shape and relative growth rate of each of the crystal faces that are active throughout its growth history. We demonstrate that the abundances of hydrogen-bearing impurities can serve as 'speedometers' to monitor the growth rate of advancing crystal faces. Our technique can be applied to crystals from a variety of geological environments to determine their growth histories. Within the electronics industry, the technique might facilitate the production of defect-free synthetic crystals required for high-quality resonators and, ultimately, might allow determination of the absolute time involved in geological processes such as the crystallization of magmas, fluid flow in metamorphism and the sealing of open cracks in earthquake rupture zones.

Euhedral quartz crystals grown in hydrothermal metamorphic environments reveal classic trigonal structural form[7]. Crystals grow into fluid-filled cavities typically with six well-defined $\{10\bar{1}0\}$ 'm' prism faces, three prominent $\{01\bar{1}1\}$ 'r' faces, and three $\{10\bar{1}1\}$ 'z' faces (Fig. 1). Despite the limited number of observable active growth faces, every natural hydrothermal quartz crystal has a unique crystal morphology, analogous to human fingerprints and snowflakes. Unfortunately, the final morphology of the crystal cannot be inverted uniquely to determine the relative growth rates of each face during growth. If *a priori* knowledge of the sizes of individual growth faces throughout the crystal's growth history are known, relative growth rates of faces within single crystals can be constrained[8]. Such knowledge has been ascertained by examining 'ghost' features of transparent crystals and by cathodoluminescence analyses[9,10]. However, neither inter-crystalline comparisons nor quantitative constraints of absolute growth rates of common metamorphic minerals are, as yet, available.

Although quartz is one of the purest minerals known, no crystal is pure SiO_2. Conventional infrared studies have shown that many of the impurities in quartz crystals are hydrogen-bearing species that form point defects in the crystal lattice[11,12]. Individual cations bond to the oxygen atom of the hydroxyl group with variable strength, and the O–H stretching motion absorbs energy at wavelengths characteristic of the individual species resulting in a sharp absorbance peak in the region between 3,600 and 1,000 cm^{-1} (ref. 13). Three hydrous species are especially common in natural quartz crystals: (1) AlOH species that absorb energy at 3,380 cm^{-1}; (2) LiOH species that absorb energy at 3,480 cm^{-1}; and (3) HOH species that absorb a relatively broad band of energy centred at 3,400 cm^{-1}. Spectroscopic studies have demonstrated that AlOH defects are oriented in the crystal structure such that O–H bonds extend nearly horizontally into channels that run parallel to the *c*-axis[11,14]. Al^{3+} replaces Si^{4+} in the rigid silicate lattice, and the H^+ serves to charge-balance the substitution. In contrast, HOH and LiOH species are incorporated as neutrally charged molecules and are not integral to the crystal lattice. The HOH species probably exist as isolated molecules (but may exist within minute clusters that are too small to allow formation of an ice phase)[11,12,14]. The broad absorbance spectrum indicates that these species are hydrogen-bonded to varying degrees within the crystalline structure[13]. Because H-bearing defects are believed to alter strongly the rheological properties of nominally anhydrous minerals and thereby affect the rheology of the upper mantle and the lower crust, much experimental and theoretical work has investigated the nature of H-uptake in major anhydrous phases[15–19]. In addition, H-bearing impurities are known to affect crystal quality relevant to the development of high-frequency devices used in the electronics industry[20,21]. Although these studies have broadened our understanding of the crystallography associated with the uptake of H-bearing defects, none have accounted for the large range in impurity concentrations observed in single natural crystals or in crystals across the spectrum of geological environments.

The results of our spectroscopic measurements for each of the traverses taken across levels 3, 7 and 8 of the crystal are illustrated in maps A, B and C in Fig. 2a. Map A in Fig. 2a illustrates the variation
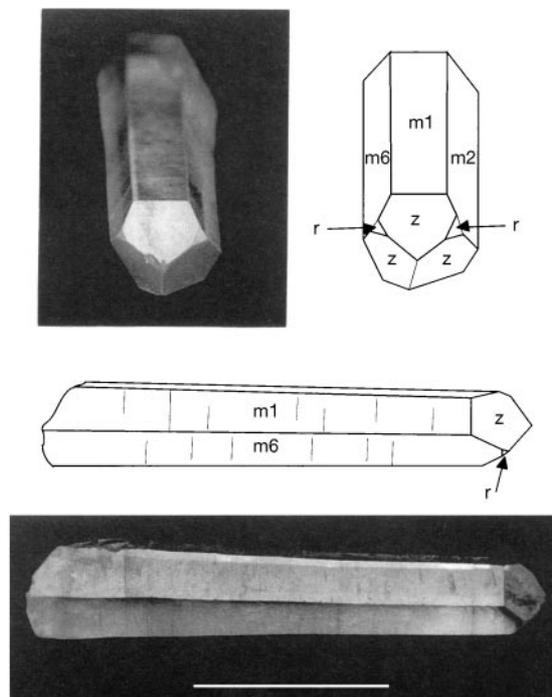

Figure 1 Photographs of the Brazilian quartz specimen analysed in this study, showing the specimen before sectioning. Diagrams next to the photographs show the three prominent 'z' and the three subordinate 'r' rhombohedral growth faces at the tip of the crystal, as well as the well-defined six 'm' prism faces. Scale bar, 1 cm.