Implementation of such a neural network–based system will require additional studies to determine the most efficient neural network architecture and the best training set to obtain a system with good discrimination capabilities while maintaining tolerance toward experimental variations.

The powerful recognition capabilities of artificial neural networks reported here suggest that neural networks are adaptable to other spectroscopic techniques in addition to NMR spectroscopy. We have already extended this approach to the identification of mass spectra (*8*). Neural networks have a great advantage over conventional spectroscopic library searches in that neural networks do not require definition of rules by scientists but rather extract the characteristic differences between the spectra during the training process. Furthermore, the retrieval of information from a neural network system is significantly faster than conventional library searches, which take many seconds up to minutes to retrieve the information. The response time of our neural networks is less than 0.1 s and is virtually independent of the number of spectra that are contained in its knowledge set. Other pattern recognition techniques that have been applied to the NMR spectra of carbohydrates have not been able to fully recognize all members of a family of molecules and required a complete assignment of the spectra before they could be used in the pattern recognition (*9*).

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# Rapid Changes in the Range Limits of Scots Pine 4000 Years Ago

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**Paleoecological data provide estimates of response rates to past climate changes. Fossil *Pinus sylvestris* stumps in far northern Scotland demonstrate former presence of pine trees where conventional pollen evidence of pine forests is lacking. Radiocarbon, dendrochronological, and fine temporal-resolution palynological data show that pine forests were present for about four centuries some 4000 years ago; the forests expanded and then retreated rapidly some 70 to 80 kilometers. Despite the rapidity of this response to climate change, it occurred at rates slower by an order of magnitude than those necessary to maintain equilibrium with forecast climate changes attributed to the greenhouse effect.**

MUCH CONCERN IS FOCUSED upon the responses of organisms and ecosystems to global climate change (*1*). The paleoecological record provides evidence of both past distributions (*2–4*) and migration rates in response to past climate changes (*3, 4*). For example, subfossil stumps demonstrate that trees were formerly present in areas that are today treeless. Scots pine (*Pinus sylvestris* L.) stumps are recorded from peat deposits across northern Europe (*5–11*). Most occur where pollen analyses have recorded regional pine forests (*5–7, 11*). Far northern Scotland, however, is exceptional. Although stumps are present (*5*), conventional palynological studies have not provided evidence of pine forests (*12*). Two hypotheses have been advanced. First, pine trees were sparse for several millennia, growing only in particularly favorable sites and perhaps producing little pollen because of harsh climatic conditions; the stumps represent trees on mire surfaces during periods favorable for preservation (*5, 13*). Second, regional pine forests developed for an interval brief enough to be overlooked by conventional pollen studies. We have tested these hypotheses by making a regional survey of the distribution of stumps in conjunction with radiocarbon and dendrochronological analyses and a detailed palynological study.

The systematic mapping of subfossil pine stumps preserved in blanket peats in far northern Scotland showed that pine was formerly present throughout most of the region; only in a small area of the extreme northwest and a somewhat larger area of the northeast have pine stumps not been located (Fig. 1). Mapping involved systematic searches for stumps exposed in peat faces and ditches. The mapping was greatly facilitated by widespread afforestation and associated road building and drainage operations. Radiocarbon dating of 22 samples of subfossil pinewood from 11 localities (Fig. 1) gave ages ranging between 4405 and 3815 years B.P. (before present) (Table 1), a time span of 590 ± 71 years. Time spans are shorter at individual sites, ranging up to only 350 ± 85 years. A $^{14}C$ measurement on subfossil pinecones from blanket peat in 10-km National Grid square 29/84 gave an age comparable to those for nearby pine stumps (SRR-3563 4450 ± 65 years B.P. (Table 1). These ages are comparable with previously published ages for stumps from the region, which range between 4393 and 3976 years B.P. (*5*). They contrast, however, with the age of 6980 ± 100 years B.P. (Q-887) for a stump from Coire Bog (National Grid Reference 28/582857; 57°50′10″N 4°23′50″W) in the extreme south of the region studied (Fig. 1); the age of this stump is comparable with ages determined from many localities in the region of the Highlands that lies to the south of our study area (*5, 6*). High pine-pollen values are also recorded at Coire Bog between ~7000 and 5000 years B.P. (*6*), as at many palynologically studied sites throughout the Highlands. In addition, some of the most northerly of the relict stands of native pine forest are found today at scattered localities near Coire Bog (Fig. 1).

At one site with stumps in northern Scotland, Lochstrathy (National Grid Reference 29/796491; 58°24′51″N 4°3′40″W), dendrochronological data were also collected. Ring widths were measured on 42 stumps, and the transformed sequences were cross matched by minimizing the multiple proba-

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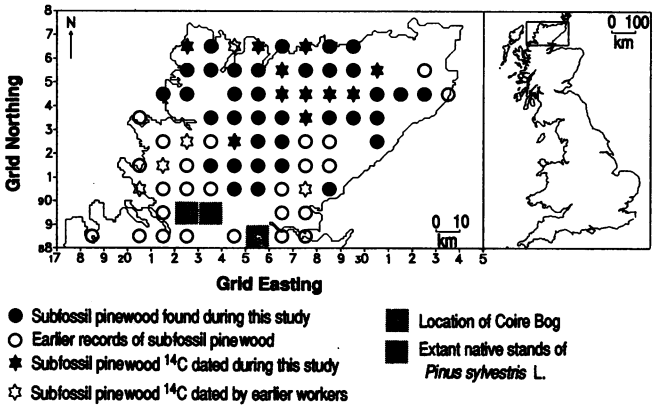

**Fig. 1.** Ten-kilometer grid square distribution map of subfossil pine stumps and of the distribution of relict native pine woodlands (*22*) in far northern Scotland. Earlier (*5, 6, 21*) as well as our $^{14}C$ determinations give ages of between 4405 and 3815 years B.P. for stumps from this region (Table 1). The references to National Grid squares are given as easting followed by northing; the smaller digits on the map relate to the 100-km squares, the larger to the 10-km squares, thus Coire Bog lies in 10-km square 58 of 100-km square 28, that is 28/58. We did not confirm earlier workers' records of subfossil pinewood.

**Table 1.** Carbon-14 age determinations of pine stumps from far northern Scotland: $^{14}C$ ages are in uncalibrated radiocarbon years before present (years B.P.). Present is taken as A.D. 1950 and the Libby half-life of 5568 ± 30 years for $^{14}C$ is used to calculate the ages. SRR laboratory numbers relate to samples dated in this study. See Fig. 1 for grid notation.

| Grid | Ages (with laboratory numbers) |
|---|---|
| 29/00 | 4420 ± 102 (NPL-13) |
| | 4220 ± 105 (NPL-14) |
| 29/11 | 4674 ± 60 (Q-1031) |
| 29/22 | 4163 ± 80 (Q-1155) |
| 29/26 | 4275 ± 50 (SRR-3568) |
| 29/42 | 4395 ± 50 (SRR-3573) |
| 29/46 | 4393 ± 50 (Q-1121) |
| 29/56 | 3825 ± 50 (SRR-3555) |
| | 4045 ± 65 (SRR-3556) |
| 29/64 | 4390 ± 65 (SRR-3559) |
| | 4220 ± 65 (SRR-3560) |
| 29/65 | 4295 ± 65 (SRR-3557) |
| | 3945 ± 55 (SRR-3558) |
| 29/70 | 3976 ± 100 (Q-1156) |
| 29/73 | 4405 ± 50 (SRR-3566) |
| | 4370 ± 50 (SRR-3567) |
| 29/74 | 4385 ± 50 (SRR-3574) |
| | 4255 ± 50 (SRR-3575) |
| | 4360 ± 50 (SRR-3577) |
| | 4300 ± 65 (SRR-3578) |
| | 4155 ± 50 (SRR-3576) |
| | 4225 ± 60 (SRR-3501) |
| 29/76 | 4050 ± 60 (SRR-3569) |
| 29/84 | 3955 ± 55 (SRR-3561) |
| | 4335 ± 50 (SRR-3562) |
| 29/94 | 3985 ± 50 (SRR-3564) |
| | 3815 ± 50 (SRR-3565) |
| 39/05 | 3865 ± 50 (SRR-3571) |

bility for Fisher's *z* (*14*). The sequences could be cross matched into a single set with significant multiple probabilities and an overall time span of 344 years (Fig. 2). Subsamples containing 37 to 81 rings from five of the stumps used for dendrochronological measurements were $^{14}C$ dated (Fig. 2); the ages obtained spanned 230 ± 71 years. When allowance was made for the numbers of rings in both the dated and undated parts, an overall estimate of ~350 years was obtained for the period spanned by these five stumps. This estimate corresponds well to the estimate provided by the dendrochronological data.

The widespread stumps, the radiocarbon determinations on the wood samples, and the dendrochronological evidence all support the hypothesis that a brief period of regional pine growth has been overlooked by conventional palynological studies in which the average sampling interval was one sample per every 200 to 400 years represented in a section. This hypothesis was further tested at Lochstrathy by means of a fine-resolution pollen stratigraphic study of a peat exposure containing an interstratified subfossil pine stump. Pollen samples were taken from a peat monolith by means of a microtome (*15*), which allowed consecutive 1-mm-thick peat samples to be analyzed. Although the record is discontinuous because some samples were extremely humified and did not contain pollen, a total of 101 samples was analyzed spanning 123 mm (Fig. 3). The most important finding was that pine-pollen values sufficient to indicate the local presence of trees (>30% of the terrestrial pollen sum) were restricted to only 68 mm of peat; furthermore, the highest values formed two distinct peaks spanning only 7 and 15 mm of peat, respectively. Age determinations ($^{14}C$) on the peat yielded an estimate of 325 ± 85 years for the duration of the whole phase of higher pine-pollen values. This age span is in close agreement with the independent estimates made from $^{14}C$ and dendrochronological measurements upon wood from this site (*16*).

Stratigraphic charcoal analyses of the samples used for the pollen analyses, along with changes in relative abundance of other major pollen and spore taxa, show that substantial changes in mire surface wetness and the associated likelihood of fire occurred before, during, and after the period of pine growth on the mire surface. The most probable explanation for such changes lies in variations in regional climate. The extent, some 70 to 80 km, and virtual synchroneity, to within one to two centuries, of the range expansion and of its subsequent retreat require that any explanation invoke causal factors operating at a regional scale. In addition, the ages ($^{14}C$) of subfossil stumps elsewhere in northern Europe show that pine suffered marked and widespread reductions in both altitudinal and latitudinal range about 4000 years ago (*5–7, 9, 10*). The southward shift of the range margin in Finnish Lapland at about this time has been estimated at 70 km (*10*), almost exactly the same as we have recorded in far northern Scotland. The geographical extent of observed impacts on pine at this time suggests that the regional climate changes resulted from a change in broad-scale atmospheric circulation. We hypothesize that expansion of pine in far northern Scotland ~4400

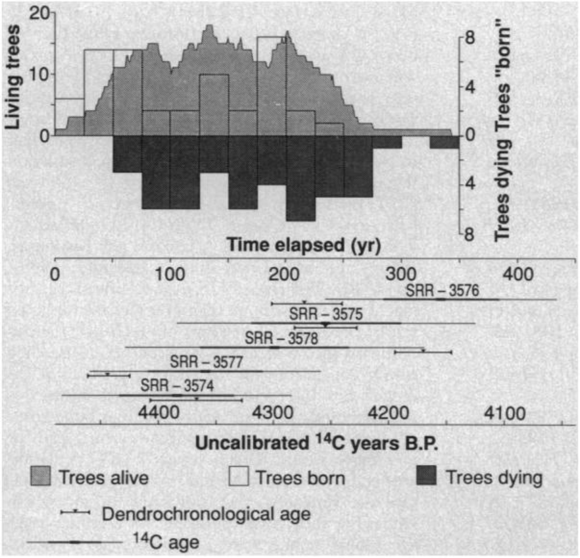

**Fig. 2.** Dynamics and duration of the pine population at Lochstrathy as deduced from dendrochronological analysis of 42 stumps. The number of living trees out of the total of 42 is shown for each year, along with the numbers of recruits to (trees born) and losses from (trees dying) the population for 25-year intervals. The relative dendrochronological ages and $^{14}C$ ages for five dated stumps are also shown; the dendrochronological sequence has been fixed with the $^{14}C$ age determination for the stump with the longest ring sequence (SRR-3575). The bars show limits of 1 and 2 SD around each $^{14}C$ age and the span of rings upon which the $^{14}C$ measurements were made.

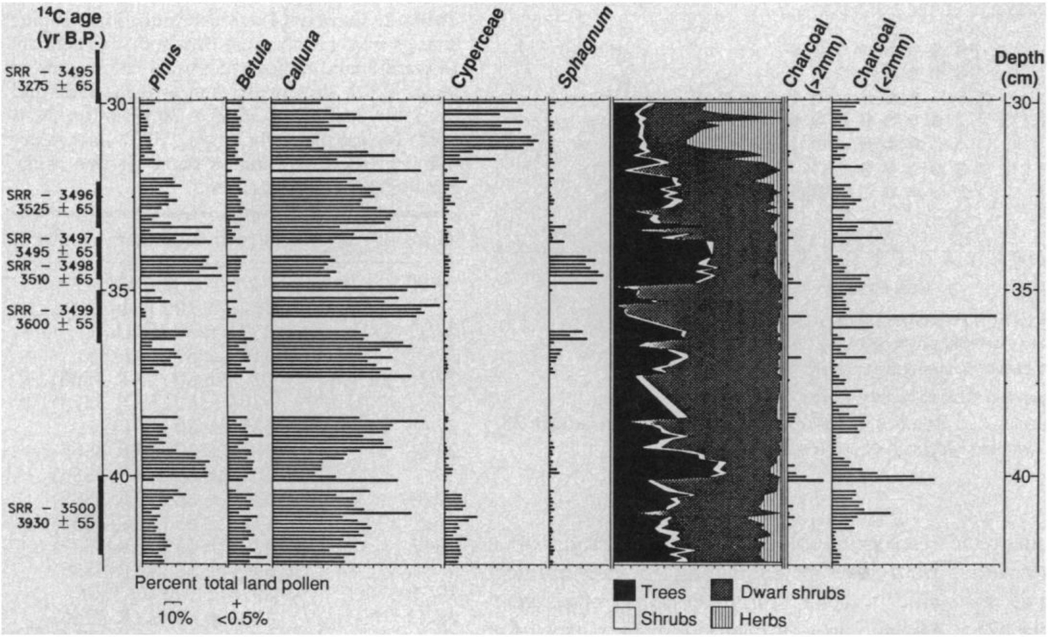

**Fig. 3.** Fine-resolution pollen and charcoal diagram from blanket peat at Lochstrathy. Only selected pollen taxa are shown. Pollen and charcoal analyses were carried out by A.J.G. A $^{14}$C determination made on part of a pine stump interstratified adjacent to the monolith from which the diagram was prepared gave an age of 4225 ± 60 years B.P. (SRR-3501). This is comparable with other age determinations from the region made upon stumps, but shows a systematic bias of ~700 years with respect to age determinations upon the surrounding peat (*16*).

years ago was the result of drying of blanket mire surfaces and that the more northerly range margin in Fennoscandia subsequently was the result of warmer summers. These climate changes are consistent with a northeastward expansion or northward shift of the Azores high in summer and a consequent northward shift of the jet stream that would reduce rainfall in northern Britain and increase summer temperatures in Fennoscandia. Subsequently, ~4000 years ago, a reversal of these circulation trends led to southward shift of the pine treeline in Fennoscandia and extinction of pine on blanket mires in Britain.

We conclude, therefore, that changes in atmospheric circulation led, first, to northward expansion, by up to 80 km, of the range of pine in far northern Scotland after ~4400 years ago, and, subsequently, to a retreat to more or less its present, and earlier, limit by ~3800 years ago. This brief event is recorded by a legacy of numerous pine stumps in the blanket peats of the region but is easily overlooked by conventional palynological studies. The retreat of pine from far northern Scotland is contemporaneous with retreats in both its latitudinal and altitudinal range margins elsewhere across northern Europe and is evidence of a rapid and widespread climate change about 4000 years ago. Our data hence provide an indication of the rapidity with which a tree species may respond to climate change. We estimate that the rate of range boundary movement was 375 to 800 m $yr^{-1}$ (*17*); this rate is in remarkably close agreement with rates estimated from the palynological record for larger scale post-glacial migrations (*3, 4*). The consistent magnitude of migration rates estimated from paleoecological records (*3, 4, 17*) leads to the conclusion that these may represent the maximum rates attainable by such long-lived sessile organisms (*18*). If this is the case, then, spectacular though the short-lived expansion of *P. sylvestris* into far northern Scotland may have been, it occurred at rates more than an order of magnitude less than those required to maintain equilibrium with forecast anthropogenically induced climate changes of the near future (*19, 20*).

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displacement of range boundaries by >300 km. A temperature rise of this amount by 2050 gives a rate of movement of 5 km yr$^{-1}$. This must be regarded as a minimum rate, not only because few range limits are determined by absolute temperature alone—more often it is temperature sums that are important, and these are likely to show larger proportional increases—but also because Europe is likely to experience a greater degree of warming than the global average (*20*). Nonetheless, even this minimum rate is about 20 times faster than the post-glacial rate of expansion of many European trees (*3*).

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# Deuterium on Venus: Observations From Earth

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**Absorption lines of HDO and $H_2O$ have been detected in a 0.23–wave number resolution spectrum of the dark side of Venus in the interval 2.34 to 2.43 micrometers, where the atmosphere is sounded in the altitude range from 32 to 42 kilometers (8 to 3 bars). The resulting value of the deuterium-to-hydrogen ratio (D/H) is 120 ± 40 times the telluric ratio, providing unequivocal confirmation of in situ Pioneer Venus mass spectrometer measurements that were in apparent conflict with an upper limit set from International Ultraviolet Explorer spectra. The 100-fold enrichment of the D/H ratio on Venus compared to Earth is thus a fundamental constraint on models for its atmospheric evolution.**

THE DRYNESS OF THE ATMOSPHERE of Venus has been an intriguing puzzle for theorists and observers alike. Although the abundances of $CO_2$ and $N_2$ in the planet's atmosphere are similar to those outgassed over geologic time on Earth, water is deficient by four to five orders of magnitude. The two extreme explanations of this apparent anomaly are (i) that desiccation occurred before formation of the planet, as Venus formed from the high-temperature region of the solar nebula (*1*) and (ii) that formation with abundant water was followed by desiccation through atmospheric evolution, as $H_2O$ was photodissociated and hydrogen escaped (*2*). The assumption in the latter hypothesis is that Venus received most of its volatiles during accretion from late bombardment by comets and meteorites that formed in a cooler part of the nebula where water could condense (*3*). Because escape of hydrogen leads to relative enhancement of deuterium, the D/H ratio is an important constraint that must be accommodated by any theory for the history of water on Venus. The value of this ratio has been the subject of some dispute, however.

McElroy *et al.* (*4*) were the first to suggest that the D/H ratio in Venus' atmosphere is much larger than on Earth. They proposed that the mass-2 ion detected by the ion mass spectrometer on the Pioneer Venus Orbiter was $D^+$, rather than $H_2^+$, as originally suggested by Taylor *et al.* (*5*). The corresponding D/H ratio is about $10^{-2}$, compared with the terrestrial value of $1.6 \times 10^{-4}$ (*6*). This interpretation was subsequently supported by more detailed analyses (*7*). Meanwhile, Donahue *et al.* (*8*) had published their investigation of a remarkable set of observations by the neutral mass spectrometer on the Pioneer Venus large entry probe. As the probe descended through the atmosphere, the inlets to the mass spectrometer became temporarily clogged, presumably by droplets of $H_2SO_4$ from the clouds on Venus. Mass spectra of the increased flux of $H_2O$ produced during this event revealed a value of the D/H ratio of $(1.6 \pm 0.2) \times 10^{-2}$. McElroy *et al.* (*4*) and Donahue *et al.* (*8*) interpreted their results to indicate that Venus once contained at least as much $H_2O$ as the equivalent of 0.3% of Earth's contemporary oceans.

In contrast to the good agreement between these two spacecraft measurements, Bertaux and Clarke (*9*) recently reported an upper limit of $(3.6 \pm 1.5) \times 10^{-3}$ for the D/H ratio from the absence of the D Ly$\alpha$ line in International Ultraviolet Explorer spectra of Venus. However, this upper limit is dependent on a model for the vertical distribution of molecular and atomic hydrogen in the planet's upper atmosphere, and difficulties in the analysis have led to the suggestion that more observations are needed (*10*).

In view of the significance of the D/H ratio and these discrepant results, a new measurement that is not affected by the complexities that plague the interpretation of upper atmosphere observations was clearly needed. We therefore decided to measure the D/H ratio in $H_2O$, the most abundant hydrogen-containing compound on Venus, far below the homopause using the same general approach that was successful on Mars (*11*). We used the Fourier Transform Spectrometer with the 3.6-m Canada-France-Hawaii Telescope on Mauna Kea to detect and measure lines of HDO and $H_2O$ in the spectrum of Venus.

We first tried to utilize the 3- to 4-$\mu$m region in spectra of the bright side of Venus, but this attempt was not fully satisfactory (*12*). We found that the detection of thermal emission from below the clouds on the dark side of Venus at 2.3 $\mu$m (*13*) provided a better opportunity to study both HDO and $H_2O$. We recorded the spectrum of the dark side of Venus in this region on 10 November 1989 at an unapodized resolution of 0.23 cm$^{-1}$ (*14*, *15*). The Doppler shift of Venusian lines was +0.19 cm$^{-1}$. The nightside spectrum was divided by a spectrum of the dayside recorded at a similar zenith angle to correct for telluric absorption and the filter response (Fig. 1).

A first analysis of this data set (*15*) has shown that a large number of molecular lines can be identified, including many absorptions of HDO and $H_2O$ between 4120 and 4275 cm$^{-1}$. In this region, CO is the dominant absorber; a few lines of HF are also present. Unlike the Venus $H_2O$ lines, which are difficult to distinguish in the raw spectra because they are blended with their telluric counterparts, most of the Venus HDO lines are easily discernible (Fig. 1). This difference alone indicates that the D/H ratio on Venus must be highly enriched compared to the terrestrial value (*15*).

To measure the $H_2O$ and HDO mixing ratios, we generated synthetic spectra of Venus from a radiative transfer program (*16*). In the spectral region where the $H_2O$ and HDO lines are present, thermal emission originates from altitude levels between 32 and 42 km, below the sulfuric acid cloud

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