Anisotropy of iron in the Earth's inner core

Seismological studies[1–3] suggest that there is 3–4% anisotropy of P-waves in the Earth's inner core. Hexagonal closed-packed solid iron has been proposed to be the major constituent of the inner core[4], but a lack of knowledge about the elastic properties of this phase at inner-core pressures (330 to 360 GPa) and temperatures (4,000 to 8,000 K) prevents a conclusive interpretation of the seismic results in terms of the inner-core composition. The elastic properties of hexagonal closed-packed iron have been computed from first principles using a theoretical method[4] and Mao *et al.*[5] have recently measured them by using X-ray diffraction and ultrasound techniques at pressures of up to 211 GPa. Despite these exciting technological achievements, we believe that the new results may be misleading.

Although the theoretical and experimental results both indicate similar aggregate P-wave and S-wave velocities as a function of pressure[5], there is an inconsistency in the elastic constants that Mao *et al.*[5] have attempted to resolve by multiplying the P-wave velocities at 16 and 211 GPa by 1.08. However, this treatment results in a 15–40% change in elastic parameters at 211 GPa and is accompanied by a 7–30% decrease in the S-wave velocity (Fig. 1). The authors assume that the values at 39 GPa are correct, but even at that pressure some of the elastic parameters have changed by up to 15% (Fig. 1). Furthermore, in their correction, Mao *et al.*[5] obtain a value for the elastic constant C_{33} of 491 GPa, which is 63% less than the value of 802 GPa obtained at 39 GPa pressure[4]. Such a low value for C_{33} yields a very low Poisson's ratio (0.04) along the symmetry axes. Mao *et al.*'s[5] value for C_{44} is 38% higher than that obtained at 211 GPa pressure[4].

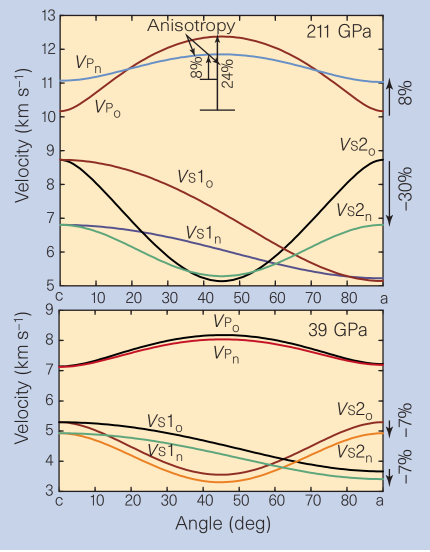

Figure 1 P-wave and S-wave velocities (V_P and V_s, respectively) as a function of the propagation direction relative to the *c*-axis of the hexagonal close-packed iron crystal for the original and corrected tables of Mao *et al.*[5]. The subscript 'o' denotes values derived from the original table and 'n' denotes those from their amended table. The percentage increase or decrease in velocity from the original values is indicated. The difference between the two results is significant: the P-wave anisotropy has decreased from 24% to 8%.

Our analysis suggests that the uncertainty in the individual elastic constants is much greater than in parameters based on a combination of them, such as the P-wave velocity. Given the large uncertainties and the physical implications of the elastic parameters, the results of Mao *et al.*[5] must be interpreted with caution.

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Nitrogen deposition and carbon sequestration

Nadelhoffer *et al.*[1] use ^{15}N-tracer studies in nine northern forests to argue that increasing inputs of combined nitrogen from the atmosphere are unlikely to cause the increase in forest growth that has been postulated as the 'missing sink' for atmospheric CO$_2$. Only about 20% of the tracer ended up in the trees and about 70% remained in the organic and mineral layers of the soil. If only 20% of the nitrogen input from the atmosphere were available for tree growth, then not enough combined nitrogen would be coming into the northern forests each year to explain the missing carbon sink.

We do not agree with this argument for several reasons. First, the ^{15}N-tracer was applied to the soil surface in all the experiments, minimizing the opportunity for assimilation by soil organisms living in the nitrogen-poor organic litter layer. But much of the combined nitrogen received by trees from the atmosphere will be taken up directly by leaves, without ever reaching the ground, irrespective of whether it arrives in rain, as an aerosol or in gaseous form[2,3]. The efficiency of use of the combined nitrogen received by forests will therefore be greater than the 20% used by Nadelhoffer *et al.* in their calculations.

A second problem arises in the interpretation of experiments using ^{15}N-labelled fertilizers. In unfertilized soil, assimilation of nitrogen by microorganisms that decompose nitrogen-poor plant debris is met from the unlabelled inorganic nitrogen pool. In fertilized soil, the same amount of assimilation occurs (assuming that assimilation is driven by microbial demand rather than the size of the pool), but some of this assimilated nitrogen is labelled. This means there is more unlabelled nitrogen and less labelled nitrogen left in the pool for the trees to take up, a process known as pool substitution. The net effect is that the percentage of ^{15}N taken up by the trees underestimates the true uptake. This underestimate is more serious[4] when the pool of unlabelled mineral nitrogen is small and when the soil contains much decomposing organic matter, as in most of the experiments of Nadelhoffer *et al.* A decline in the proportion of ^{15}N recovered by plants as fertilizer application decreases is an indication[5] that pool substitution has occurred (see their Fig. 1).

Nadelhoffer *et al.* may be right in saying that not enough combined nitrogen reaches the northern forests to explain the missing sink, but their analysis of ^{15}N-labelled-fertilizer data is not proof. They claim that a maximum of 20% of the combined nitrogen reaching the forest is absorbed by trees, but we think this is a minimum value.

Finally, Nadelhoffer *et al.* imply that retention of carbon in tree biomass leads to longer-term sequestration than retention in soil. But this depends on the fate of the trees, as part of the carbon from tree litter entering the soil is likely to be held in soil carbon fractions that have turnover times of several centuries[6].

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From their ^{15}N tracer results[1] and an estimated deposition rate to forests of 5.1×10^{12} g nitrogen per year[2,3], Nadelhoffer *et al.* conclude that about 0.25×10^{15} g carbon per year is sequestered by northern temperate forests. Their ^{15}N-tracer measurements are robust but there is a problem with their assumption that they have simulated atmospheric nitrogen deposition at forests by adding ^{15}N tracers systematically to forest

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floors “in all cases”. Atmospheric nitrogen deposition is actually intercepted by the forest canopy, particularly at the nine closed-canopy forests studied.

It is known that forest canopies chemically interact with HNO_3, NO_x and NH_3 gases (among others), as well as with the NO_3^- and NH_4^+ ions in particulate matter. The Integrated Forest Study[4], covering 13 sites with a wide range of North American and European forest types and atmospheric nitrogen deposition, varying from 5 to 30 kg per hectare per year, reported that “an average 40% of the incoming inorganic N is retained in or transformed at passage through the canopy; the net canopy exchange is greatest at those sites receiving the highest atmospheric N input.” At some sites in this study in the eastern United States, the canopy retention of atmospheric inorganic nitrogen deposition is very high: for example, at Howland Forest, Maine[5], nitrate canopy retention is about 90% and ammonium canopy retention is more than 80%. Retained nitrogen deposition can also be rapidly assimilated by canopy foliage[6].

The ^{15}N applied by Nadelhoffer *et al.*[1] to the forest floor would have bypassed the canopy retention and assimilation pathway. The nitrogen deposition allocated to the non-woody and woody biomass ecosystem pools (15 and 5%, respectively; Table 2 of ref. 1) may have been significantly increased if it had been possible to apply the labelled nitrogen to the forest canopy.

Doubling or tripling the percentage of nitrogen deposition allocated to woody biomass (10 or 15%, rather than the 5% used) would increase forest carbon uptake by 50–100% over that estimated by Nadelhoffer *et al.* The woody-biomass nitrogen allocation may be increased several-fold, and could be determined by using labelled nitrogen applied to the forest canopy.

Using a figure of 5.1×10^{12} g per year as the global nitrogen deposition to forests may also lead to an underestimate. It is recognized that there is much uncertainty in the estimates of forest nitrogen deposition[2,3], particularly in the case of NH_x–N deposition, which may be substantially greater[7,8] than the 2×10^{12} g nitrogen per year considered in ref. 1. Total anthropogenic nitrogen deposition has been estimated to be as much as 18×10^{12} g per year to temperate and boreal forests[9], which is three or more times the value reported in ref. 1. These two points can provide an upper bound for estimates of forest carbon sequestration of $1–2 \times 10^{15}$ g carbon per year, with the range dependent on the still poorly known nitrogen deposition allocated to woody biomass.

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Nadelhoffer et al. *reply* — Jenkinson *et al.* and Sievering are justifiably concerned that our ^{15}N additions to forest floors do not account for the potential uptake of nitrogen input by forest canopies. We agree that canopies can remove nitrogen from the atmosphere, resulting in inputs to forest floors that are less than the total nitrogen deposition. A North American study[1] has suggested that canopies remove, on average, 16% of total (organic + inorganic) atmospheric nitrogen input to forests, and concluded that nitrogen uptake by the canopy is probably small relative to the nitrogen requirements of trees. Spraying ^{15}N-labelled ammonium and nitrate on the crowns of five-year-old Norway spruce indicated that foliar uptake in mature forests probably constitutes only a small percentage of annual nitrogen uptake[2].

Although canopies can remove nitrogen from bulk deposition, the extent to which this nitrogen is biologically available and stimulates wood growth is poorly understood. Throughfall nitrogen fluxes at our sites either exceed the measured bulk nitrogen deposition or closely agree with modelled total deposition[3–5], so their use as a proxy for nitrogen deposition is reasonable and does not compromise our conclusions.

We think it is unlikely that “pool substitution” of unlabelled inorganic nitrogen for ^{15}N tracers in soils biased our estimates of throughfall uptake by trees, as claimed by Jenkinson *et al.*, who found this mechanism operating in theoretical models[6] and in potted, but not in field-grown, plants[7]. Comparison of the amounts of our tracer additions to the amount of unlabelled inorganic nitrogen already present in our soils with those amounts in their theoretical analysis (see Fig. 1 of ref. 6) indicates that pool substitution is unimportant at the low ^{15}N enrichment used in our throughfall manipulations.

We agree that forest soils can serve as long-term carbon sinks and that carbon turnover times in soil pools are longer than in trees. Nevertheless, as nearly all carbon enters forests through trees, it is here that the influence of nitrogen inputs on carbon uptake is important. We point out, however, that our simple stoichiometric budget (Table 2 of ref. 8) actually factors in the role of soils, with soil storage calculated as the product of the C:N ratio and nitrogen immobilization in soils.

Finally, we recognize that there is a wide range of estimates for nitrogen deposition on temperate forests. This is because of uncertainties and likely but unknown biases in the atmospheric mixing models, emissions data and site-specific wet + dry nitrogen deposition data used to generate spatial predictions of nitrogen deposition on forests. Our temperate-forest deposition value of 5.1×10^{12} g nitrogen was derived from a comparison of modelled NO_y and NH_x deposition estimates[9]. If this value were to be in serious disagreement with estimates based on greatly improved monitoring and modelling efforts, then our assessment of the effects of nitrogen deposition on temperate-forest carbon uptake would need to be revised.

Future estimates of this effect must also consider spatially explicit patterns of nitrogen loss from forests in relation to nitrogen deposition and land use[10], the likelihood of narrowing C:N ratios under increased nitrogen input, and possible nutritional imbalance of tree tissue subjected to high nitrogen input. Meanwhile, our tracer experiments indicate that, although nitrogen deposition in forests accounts for some of the northern-temperate CO_2 sink, other factors must account for most of this sink.

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