

Gravitational Separation in Polar Firn

ble of learning." Our results (2) and those of Silva *et al.* (1) do not suggest, as Deutsch implies, that there is a dissociation between LTP and learning, and that therefore these processes are not linked. The data (1–3) indicate that interference with LTP can impair spatial learning. We believe it is naive to think that deficits in LTP in the CA1 region of the hippocampus will eliminate spatial learning in an all-or-none fashion, because even rodents with hippocampal lesions or with a complete pharmacological blockade of LTP can demonstrate some spatial learning, and in both the *fyn*[−] and α -CaMKII mutant mice, LTP in the CA1 region is impaired but not completely abolished.

We would simply emphasize that our initial behavioral studies of transgenic mice bearing specifically engineered mutations were not meant to be a definitive description of the behavioral repertoire of these animals. Instead, they represent the first steps toward exploiting the power of target gene disruption in a combined molecular, physiological, and behavioral study of learning and memory. We believe that our studies (2), as well as those of Silva *et al.* (1), demonstrate the usefulness of gene targeting techniques for investigating the molecular components of the signaling pathways responsible for long-term potentiation as well as providing a new approach to the study of behavior.

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D. Raynaud *et al.* (1) describe the processes affecting the composition of trapped air in polar ice. They state (1, p. 927)

It was recently shown that the composition of the air column sampled at different depth levels in the open porosity of the firn, before its enclosure as air bubbles in ice, essentially reflects diffusive and gravitational equilibrium with the atmosphere at the surface of the ice sheet. . . .

In figure 2 of their article (1, p. 927), Raynaud *et al.* state that

the air column tends to reach a state of diffusive equilibrium, in which the heaviest components become enriched as a result of gravitation at the bottom of the air column. . . .

Raynaud *et al.* refer to a paper by Schwander *et al.* (2, p. 2836) as the authority for their position. I pointed out in the paper with the original theory and data for the effects of gravitational separation in polar firn (3), that an attribution such as that in (1, 2) of the heavy isotope enrichments in firn columns is premature. From observations, one cannot distinguish enrichments by gravitational settling from the effects of effusion through partially sintered micropores. That is, the enrichment of a heavy species (*i*) relative to a lighter component is proportional to $(M_i - M)$, the atomic mass difference between the components, multiplied by gZ/RT , where g is the gravitational acceleration, Z is the depth in a firn layer, R is the gas constant, and T is the absolute temperature; while in effusion through porous barriers, the heavy component enrichment is proportional (for small enrichments) to $[(M_i - M)/2M_i]F$, where F is the fraction of gas lost in the actual fractionating process. The observed isotopic enrichments in ¹⁵N and ¹⁸O at the base of a 75-m column of firn are consistent with either gravitational separation or with an effusive loss of approximately 2% of the gas (3). For large mass differences, the expected enrichments diverge for the two processes, but for isotopic species the enrichment factors are indistinguishable for these processes (3).

Raynaud *et al.* (1) and Schwander *et al.* (2) base their attribution of the enrichment process on their analyses of gases within the firn column above the nascent ice (2, p. 2836), in which ¹⁵N/¹⁴N, ¹⁸O/¹⁶O, and O₂/N₂ enrichments were measured in two sets of samples from five depths, and the measured ratio enrichments were compared with those predicted by gravitational settling. However, good agreement was found with only one set of N isotope results. The second set of N data, and both sets of O isotope data, were systematically more enriched at all depths than the predicted

values: O₂/N₂ ratios (predicted to be enriched by 0 to 1.4 per mil from the surface to 75 m) actually clustered at "−6 per mil" in one set and ranged from 0 to 4 per mil, below 60 m, in the second set. If one assumes that the fractional loss of gas by effusion varies from 0 to 2% down the depth of the firn (a reasonable postulate given that air is actually removed from the firn), then gravitational or effusional fractionation equally predict the isotopic N and O enrichments.

Raynaud *et al.* (1) follow Schwander *et al.* (2, p. 2832), who write the equation for their model of the flux of air out of the firn column to the atmosphere as the sum of chemical and gravitational free energy contributions (after J. Willard Gibbs); however, there is an advective loss of air upward through the firn (3) as a result of its compaction with depth and its decreasing porosity. Thus it is a priori possible that effusion through the compacting firn is the process that is responsible for the isotopic enrichments observed (1, 2, 3). The negative O₂/N₂ ratio enrichments (2) are another matter: they cannot be explained by either process because both gravitational and effusional enrichments favor the heavier species. It has been shown (3) that these negative enrichments are a result of differential capillary flow during gas loss from firn either in situ or from stored samples, a process that is dependent on molecular volumes for fractionation of chemical species, but not isotopes. Indeed, the relative losses of O₂, Ar, and N₂ based on experimental calibration, are observed (3, 4) to be in the expected order (5) and are almost exactly the negative values measured in (3). Therefore the O₂/N₂ ratios used by Raynaud *et al.* cannot be used to support the gravitational theory. As noted above, the isotopic data are not sufficient to distinguish two physically plausible (though perhaps not equally aesthetic) physical processes.

The only discriminant for these two processes is the use of two species of the quasi-isotopic inert gases with a large mass difference. This has now been done by measurement of ⁸⁴Kr/³⁶Ar ratios, species that differ in atomic weight by fully 48 atomic mass units. For this large mass difference, the predicted enrichments in Greenland ice are 12 per mil for gravity, but only 6 per mil for effusion. The first data (6) for ice at 70 to 150 m have a mean value of 13.4 per mil, with a standard deviation of 3 per mil ($n = 5$). This is the only set of measurements that support the postulate that gravity is responsible for the isotopic enrichments observed in recent ice cores (3).

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3. H. Craig, Y. Horibe, T. Sowers, *Science* **242**, 1675 (1988); carrier diffusion [H. Craig, *ibid.* **159**, 93 (1968)] is another process that may be responsible for fractionation effects.
4. T. Sowers, M. Bender, D. Raynaud, *J. Geophys. Res.* **94**, 5137 (1989).
5. Note however, that the elemental enrichment order deduced by Sowers *et al.* from their data [(4), p. 5147] is that air gases are lost in the order Ar, O₂, N₂, which is stated to be that predicted from molecular diameters, following (3). This is an error: their data actually show that the order of gas loss in their samples is O₂, Ar, N₂, as predicted and observed (3).
6. H. Craig, *Eos* **69**, 1211 (1988); _____, D. Burtner, R. C. Wiens, *ibid.* **70**, 1151 (1989).

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Response: Craig discusses the O₂/N₂ ratios shown by Schwander *et al.* (1), but it was not stated in that paper that these ratios illustrated gravitational fractionation. Furthermore, in our *Science* article (2), we discussed exclusively the ice record of greenhouse gases (especially CO₂ and CH₄); our reference to Schwander *et al.* (1) concerned the CO₂ and CH₄ results of that paper.

Gases will be gravitationally fractionated only if the ratio of the diffusivity (*D*) to the convection velocity (*w*) is larger than

the firn thickness; indeed they must then be fractionated. This condition is satisfied, at least for the Greenland site of Summit (1), and so gases in the firn are in fact enriched in heavier elements and isotopes because of gravitation. This argument was first made by Craig *et al.* [note 14 in (3)], who pointed out that the assumption was first made that "gases . . . continuously readjust to the time-independent equilibrium state . . . is approximately true." The dominance of the diffusivity is also clearly indicated by the ⁸⁵Kr, CO₂, and CH₄ data measured in the firn at Summit (1). These results could not be explained if the diffusive equilibrium were not closely fulfilled; effusion at Summit obviously plays a minor role, but additional effects on gas fractionation are not ruled out.

Craig predicts that firn air enrichments in ¹⁸O will differ by up to 0.15 per mil depending on whether fractionation in the firn results from effusion or gravitational fractionation. Analytical precision allows one to look at such a difference. Craig *et al.* (3), for example, noted that the maximum δ¹⁵N and δ¹⁸O enrichments for the D57 ice core are predicted exactly from the firn depths and temperatures for gravitational equilibrium. We note that the δ¹⁸O values would need to be shifted by 0.1 per mil to be explained by effusion, when the experimental accuracy is 0.04 per mil.

On the basis of such observations, Craig *et al.* wrote (3, p. 1678)

Thus, 60 years after publication of the canonical theorem of Gibbs, a fluid system at the earth's surface—atmospheric gases in the firn layers of

polar ice caps—has provided experimental verification [italics ours] of this effect . . .

namely, gravitational fractionation.

Finally, Craig's ⁸⁴Kr/³⁶Ar measurements appear to confirm the role of gravitational fractionation.

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4. We thank M. Bender for useful discussions.

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