justifications for the two types of equation are related but somewhat different. However, the important point is that in crystal structures many different structural variables can be highly correlated, with none that by itself describes all magnetic interactions. More work on a wider range of compositions, and particularly single-crystal ^{29}Si NMR studies, is needed to understand such models completely.

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Arctic Lakes and Streams as Gas Conduits to the Atmosphere: Implications for Tundra Carbon Budgets

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Arctic tundra has large amounts of stored carbon and is thought to be a sink for atmospheric carbon dioxide (CO_2) (0.1 to 0.3 petagram of carbon per year) (1 petagram = 10^{15} grams). But this estimate of carbon balance is only for terrestrial ecosystems. Measurements of the partial pressure of CO_2 in 29 aquatic ecosystems across arctic Alaska showed that in most cases (27 of 29) CO_2 was released to the atmosphere. This CO_2 probably originates in terrestrial environments; erosion of particulate carbon plus ground-water transport of dissolved carbon from tundra contribute to the CO_2 flux from surface waters to the atmosphere. If this mechanism is typical of that of other tundra areas, then current estimates of the arctic terrestrial sink for atmospheric CO_2 may be 20 percent too high.

Arctic ecosystems are expected to be strongly affected by future climatic change (*1–3*), and, if these ecosystems either accumulate additional C or lose C to the atmosphere, they will be important to the global C budget (*4–8*). At present, tundra ecosystems appear to be small sinks for C; that is, the amount of C extracted from the atmosphere during photosynthesis is slightly more than that respired by plants and soils and lost to the atmosphere (*7, 9*). But there is evidence that additional C loss to and from aquatic ecosystems may also be significant. One type of loss, by erosion of peat into lakes and rivers, can be a substantial part of the long-term accumulation rate of terrestrial C (*10, 11*). There is also some indication that terrestrial C washed into lakes is respired and lost to the atmosphere as CO_2 (*10, 12*). It is not known how widespread these CO_2 losses from surface waters are, and thus to what extent tundra C budgets are affected. In this report, we describe measurements of CO_2 concentration and flux from 25 lakes and 4 rivers on the North Slope of Alaska. Our results suggest that the transport of dissolved C from terrestrial to aquatic environments is significant.

We sampled locations on the North Slope of arctic Alaska within several kilometers of the oil pipeline and between the foothills of the Brooks Range and Prudhoe Bay on the Arctic Ocean (Table 1). Partial pressures of CO_2 (P_{CO_2}) were obtained by direct measurement or by calculation from data on pH, temperature, and concentrations of alkalinity or dissolved inorganic C (DIC) (*13*). The CO_2 flux was calculated from partial pressure differences between air and water and an estimated gas transfer coefficient, or measured directly at one site with a floating chamber (*14*). We used a gas transfer coefficient of 2.1 cm hour^{-1} for all sites; this value could be too small (*15*), and therefore our calculated CO_2 fluxes may well underestimate actual fluxes.

Although these lakes and rivers lie in varied terrain, we observed no systematic patterns of CO_2 flux with site location, lake area, or maximum depth. The average P_{CO_2} value for surface waters of all lakes was 1162 ± 134 parts per million by volume (ppmv) (±1 SE), which is supersaturated by more than three times with respect to the atmosphere (Table 1). The flux of CO_2 from water to the atmosphere ranged from −5.5 to 59.8 mmol m^{-2} day^{-1} and averaged 20.9 ± 3.3 mmol m^{-2} day^{-1} in the lakes and 7.1 ± 3.0 mmol m^{-2} day^{-1} in the rivers.

Annual variations in CO_2 flux are small for lakes with a long run of data (Table 1). Multiyear trends in flux are absent, and much of the interannual variation is probably a result of the fact that sampling was done at different times of the year. In Toolik Lake, the highest CO_2 evasion rates occurred early in the season in most of the 9 years studied (Fig. 1). These high, early-

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season fluxes suggest that a substantial buildup of CO_2 occurs under ice during winter. For example, P_{CO_2} values under ice in several lakes were higher than maximum values recorded during the open-water season (*16*). Similar increases in P_{CO_2} under ice have been documented in lakes on the arctic coastal plain (*12*). Thus, there must be a large evasion of CO_2 from these lakes during ice-out and lake turnover in early June that was missed by our sampling.

The results of two ecosystem-level experiments were used to determine the effects of algal uptake on the CO_2 flux. From 1985 to 1989, Lake N2 was divided into two sections by a plastic curtain and one half of the lake was fertilized with both P and N (*17*). A lack of strong seasonal trends in CO_2 flux was observed on the control side of the lake for each year and for the combined data from all 5 years (Fig. 2). On the fertilized side of the lake, however, the onset of nutrient enrichment increased chlorophyll a concentrations, algae reduced the pool of $CO_2(aq)$, and CO_2 evasion decreased. After mid-July, the flux of CO_2 reversed in the fertilized side and there was net invasion of CO_2 into the lake (*18*). This response of decreased CO_2 evasion with increased phytoplankton growth contrasts with a similar fertilization experiment in the Kuparuk River. Since 1983 the Kuparuk has been fertilized with P or both P and N, and an upstream reach was maintained as a control (*19*). In 1985 and again in 1988 and 1989, we found no significant differences in CO_2 flux between fertilized and control reaches (*20*). This contrast in the response of the lake and the river is most likely because the renewal time of water in the river was much faster than in the lake, and thus the mass of CO_2 passing through the fertilized reach during summer was too great to be changed significantly by algal uptake.

In typical temperate lakes of low to moderate alkalinity, CO_2 invades from the atmosphere to support net algal production (*21*). This invasion is in direct contrast to the response of these arctic lakes, where CO_2 was continually released to the atmosphere. To support this CO_2 release, there must be a net influx of C to the lake or a critical change in sediment conditions such that old particulate organic C (POC) previously accumulated in the sediment is respired. Most likely, bottom mud was not being depleted in organic C to provide the CO_2 lost from these systems. Rates of net benthic respiration, which include respiration of terrestrial detritus washed into the lake, are about 5 mmol of CO_2 per square meter per day in the control side of Lake N2 and Toolik Lake, or only one-half to one-eighth of the average summer flux of CO_2 to the atmosphere in these two lakes (Table 1).

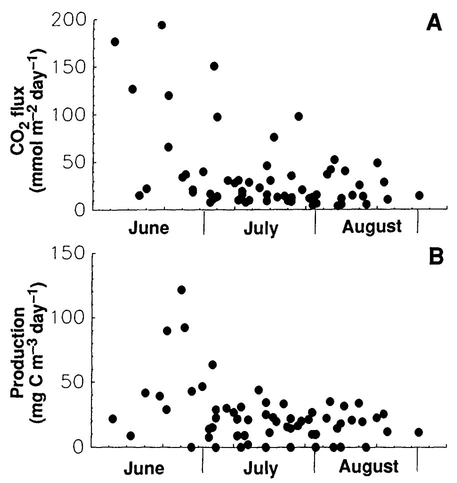

Fig. 1. Seasonal variation in weekly measurements of (**A**) CO_2 flux and (**B**) primary production of Toolik Lake during 1975 to 1980, 1983, 1984, and 1989. All values are for ice-free surface water. Scheffe's multiple comparison of means failed to detect differences in CO_2 flux between years at the 0.05 significance level.

Table 1. CO_2 flux data for arctic Alaskan lakes and rivers. Positive fluxes indicate evasion of CO_2 from water to atmosphere. Mean and grand mean values are given ±1 SE.

Lake or river	Location (°N, °W)	Date	*n*	P_{CO_2} (ppmv)	CO_2 flux (mmol m^{-2} day^{-1})
		Lakes			
E1	(68.38, 149.33)	Aug83 to Jul86	3	2758 ± 1215	59.8 ± 30.2
NE14	(68.41, 149.37)	Aug86 to Jun88	2	1954 ± 904	39.7 ± 21.3
Toolik	(68.38, 149.36)	Jun75 to Aug89	62	1847 ± 238	35.0 ± 5.3
N1	(68.38, 149.37)	Aug83 to Jul88	3	1170 ± 689	20.5 ± 16.4
Island	(68.32, 149.28)	Jul86 to Jul88	2	1040 ± 6	17.8 ± 0.3
N2	(68.38, 149.38)	Aug83 to Aug89	44	825 ± 89	12.5 ± 2.2
S6	(68.38, 149.39)	Jul86 to Jul88	2	628 ± 303	7.8 ± 7.6
I8	(68.37, 149.35)	22July86	1	2155	45.5
NE2	(68.38, 149.37)	22July86	1	1972	41.5
Windy	(69.58, 148.44)	8July88	1	1836	40.1
Dam	(68.38, 149.36)	4July85	1	1591	30.9
Silhouette	(70.05, 148.32)	8July88	1	1552	32.4
Galbraith	(68.28, 149.30)	6July88	1	1477	29.1
Carolyn	(70.21, 148.35)	9July88	1	1333	26.1
S3	(68.38, 149.38)	22July86	1	1194	22.1
NE12	(68.39, 149.37)	29June88	1	925	15.3
Africa	(70.20, 148.48)	9July88	1	919	15.1
Charles	(69.11, 148.51)	8July88	1	818	13.0
Colleen	(70.13, 148.28)	10July88	1	761	11.0
Maxine	(70.22, 148.30)	9July88	1	584	6.2
William	(69.35, 148.38)	11July88	1	504	4.5
Bern	(70.17, 148.18)	10July88	1	459	3.0
George	(68.44, 148.58)	7July88	1	359	1.1
Anne	(68.44, 148.56)	7July88	1	291	−0.7
Camp	(68.38, 149.36)	13July88	1	93	−5.5
		Grand mean		=1162 ± 134	20.9 ± 3.3
		Rivers			
Kuparuk	(68.38, 149.24)	Aug83 to Aug89	21	812 ± 177	11.9 ± 1.5
Hershey	(68.37, 149.25)	Aug85 to Jul88	3	845 ± 182	12.8 ± 4.3
Mt. Roche	(68.23, 149.19)	6July88	1	369	1.4
Oksrukuyik	(68.43, 149.01)	7July88	1	418	2.3
		Grand mean		= 611 ± 126	7.1 ± 3.0

We propose that much of the CO_2 released from these lakes and rivers originated in the terrestrial environment. Thermokarst and fluvial processes cause great erosion of peat and release of dissolved organic carbon (DOC) into lakes and rivers (*10, 11, 22*), and this C may be respired to CO_2 (*12, 16*). There is also direct evidence that dissolved inorganic C in ground water is moving from land to lakes and rivers. For example, P_{CO_2} values from 11 soil lysimeters near the Kuparuk River averaged 8315 ± 2191 ppmv (±1 SE; n = 16) (*23*). Movement of CO_2-charged ground waters into the Kuparuk River can easily account for the high P_{CO_2} observed in the river (mean, 812 ± 177 ppmv). To test whether dissolved CO_2 in the Kuparuk originated from the atmosphere, from radiocarbon-rich surface plants, or from radiocarbon-poor peat, we measured the ^{14}C activity of the attached river algae. The ^{14}C activity of algae from fertilized and control reaches was 103 and 109% modern, respectively (*24*). Because the ^{14}C activity of atmospheric CO_2 is curently about 118% modern, whereas peat from 10 to 20 cm depth near the Kuparuk is about 70% modern (*11*), the river CO_2 must be derived from a mixture of older peat and new plant material or atmospheric CO_2.

An independent estimate of the importance of CO_2 transport from land to water comes from balancing the inputs and out-

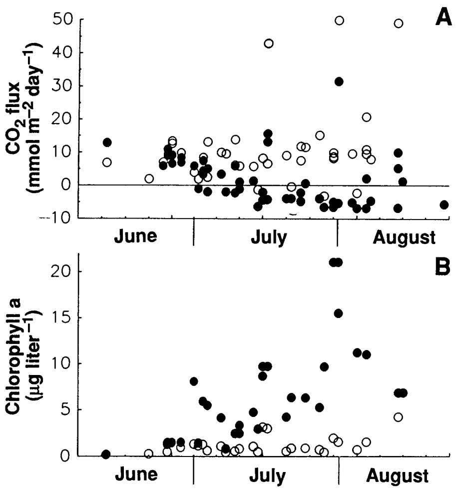

Fig. 2. Seasonal variation in weekly measurements of (**A**) CO_2 flux and (**B**) chlorophyll a for Lake N2 during 1985 to 1989. All values are for ice-free surface water. Open circles indicate the control side of the lake and closed circles indicate the fertilized side of the lake.

puts of CO_2(aq) in the Kuparuk River basin. On the basis of CO_2(aq) concentrations in rainwater and ground water in the upper Kuparuk basin, we calculate that the input to the basin each year is 295 × 10^5 mol of CO_2(aq) (*25*). Losses from the aquatic system include a river output of 182 × 10^5 mol of C per year, a CO_2 flux to the atmosphere of 1.4 × 10^5 mol $year^{-1}$ (Table 1, *25*), and consumption by net primary production of 1.3 × 10^5 mol of CO_2(aq) per year (*11*); the excess input from the terrestrial system is therefore 110 × 10^5 mol of C per year. There is little respiration of peat to CO_2 in the river (*11*), and therefore the excess CO_2 must originate from soil respiration and transport by ground water. By comparison, in lakes the ground-water input of dissolved CO_2 is supplemented by in-lake respiration of DOC and POC washed in from the land.

On the basis of experimental measures of photosynthesis and respiration, the current estimated C accumulation rate for the Alaskan arctic is 40 to 120 g m^{-2} $year^{-1}$ (*7, 9, 26*). Taking even the lowest rate implies that all the soil C stored above permafrost accumulated during only several hundred years (*9*). This scenario is inconsistent with data from ^{14}C-dated peat cores from the Arctic, however, which suggest that the soil C is much older and that the accumulation rate is only 13 g m^{-2} $year^{-1}$ (*10*). The ^{14}C method measures the long-term net accumulation and would account for C losses from land to aquatic systems that the experimental methods would miss. Our results show that at least 24 g of C per square meter are lost to the atmosphere from lakes and ponds on the North Slope each year (100 active days per year). This loss through aquatic systems would equal the terrestrial C accumulation rate in areas where 40 to 80% of the surface area near the coast is water or marsh (*22*). Thus, accounting for this C loss partially reconciles the difference between high and low accumulation rates. Although lake density decreases away from the coast, water coverage on the entire North Slope above 69.5°N is still about 14% of the total surface area (*22*). On this basis the global loss of C from tundra lakes and rivers is 0.02 Pg $year^{-1}$, which is 7 to 20% of the current estimated C sink of 0.1 to 0.3 Pg $year^{-1}$ for arctic tundra (*6*). This aquatic loss term is probably conservative because DOC and POC exported from tundra rivers to the sea can be respired and lost to the atmosphere.

Results from global climate models imply that, for a doubling of greenhouse gases, northern latitudes will experience the largest temperature changes (4° to 12°C) under a scenario of future global warming (*1–3*). Accumulation or loss of arctic C stocks depends on the balance between primary production and decomposition, although at present the effect of possible warming and the associated buildup of greenhouse gases on C cycling in the Arctic is uncertain. Nonetheless, it is known that primary production in aquatic and terrestrial arctic ecosystems is most severely limited by nutrients rather than by temperature (*7, 27*). Temperature, however, is most limiting to decomposition or respiration rates and thus to the release of CO_2 (*28*). Because of these relations, recent projections hold that large releases of C gases to the atmosphere will occur given a 5°C increase in average annual temperature (*6*).

These C releases would be augmented by CO_2 evasion from lakes and rivers. In addition, our data indicate that this model of CO_2 transport and loss to the atmosphere applies to methane as well (*29*). Accurate estimates of future aquatic gas fluxes are difficult because the response of land plants to global warming and the role of hydrology and nutrients are ill-defined. Hydrologic conditions may change the transport of C through the landscape (*1, 6*), and nutrient loss from the soil (*30*) may stimulate production in receiving water bodies. The CO_2 flux data from our experiments indicate that, for the case of high nutrient enrichment and a slow water renewal time, photosynthesis could slow the loss of CO_2 from surface waters; the critical studies in which both nutrients and temperature are varied have yet to be done.

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13. P_{CO_2} was measured on a gas chromatograph after equilibration of water samples with an air-filled headspace. Atmospheric concentrations of CO_2 were taken as 350 ppmv (*5*). Alkalinity was determined by Gran titration or by titration to a fixed end point previously determined by Gran titration. Water for DIC analysis was acidified with phosphoric acid and purged with nitrogen gas to extract total CO_2; CO_2 was collected by cryogenic distillation, and gas pressure was measured with an electronic manometric gauge (precision, ±5 μmol of CO_2 per liter). P_{CO_2} and the concentration of CO_2 in equilibrium with the atmosphere [CO_2(eq)] was calculated from Henry's law and the CO_2 fugacity-pressure relation presented in R. F. Weiss, *Mar. Chem.* **2**, 203 (1974).
14. The equation is

$$\text{flux} = (D/z)\,[CO_2(aq) - CO_2(eq)]$$

where D is the molecular diffusion of CO_2, z is the surface boundary layer thickness, CO_2(aq) is the concentration of CO_2 at the bottom of z, and CO_2(eq) is the concentration of CO_2 in water exposed to the atmosphere at the top of z. We tested this flux equation in one lake by measuring wind speed and by monitoring the flux of CO_2 into floating Plexiglas chambers. The calculated flux of 8.6 mmol m^{-2} day^{-1} [boundary layer of 400 μm (*15*)] compared well to a measured chamber flux of 6.7 mmol m^{-2} day^{-1}. Because the pH of natural waters studied was typically much less than 9.0, chemically enhanced CO_2 gas exchange was taken as negligible.
15. We used an empirical equation relating boundary-layer thickness to wind speed to derive gas-exchange coefficients [from R. Wanninkhof, J. R. Ledwell, W. S. Broecker, *Science* **227**, 1224 (1985)]. From 1988 to 1990 the mean wind speed in the ice-free months at two stations near Toolik Lake was 3.3 ± 0.2 m s^{-1} (±1 SE; 5-m height). On the coastal plain at Barrow the average wind speed is somewhat higher (June to September mean is 6.3 ± 0.2 m s^{-1}; 10-m height [J. E. Hobbie, Ed., *Limnology of Tundra Ponds* (Dowden, Hutchinson, and Ross, Stroudsburg, PA, 1980)].
16. Calculated P_{CO_2} values under ice (taken 10 to 11 May 1990) versus maximum concentrations in open-water samples (given in parentheses) are as follows: Lake N1, 4404 ppmv (2548); Lake S6, 6348 ppmv (930); Lake N2, 8866 ppmv (2916); and Toolik Lake, 3701 ppmv (1125).
17. Each year nutrients were added continuously starting on 1 July and ending on 15 August at loading rates of about 3 mmol of N and 0.25 mmol of P per square meter per day.

18. Maximum invasion rates during this time were similar to invasion rates in other softwater lakes [A. L. Herczeg, *Biogeochemistry* 4, 231 (1987)].
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23. High ground-water P_{CO_2} values were also measured in the Toolik Lake watershed in summer 1990 (up to 46,500 ppmv). Such high P_{CO_2} values are attributed in part to permafrost conditions; ground waters are usually confined by permafrost to shallow (50 cm) organic-rich soil layers, where they can accumulate CO_2 produced by plant and microbial respiration.
24. The ^{14}C activity of an A.D. 1950 sample is expressed as 100% modern. Dissolution of marine carbonate outcrops would tend to depress the ^{14}C activity of CO_2 in the river, but such rocks are scarce in the Kuparuk basin. Carbon-14 activities are from Beta Analytic (#31808 and #31809).
25. The basin area is 143 km^2, and the surface area of the river is 0.12 km^2 (*11*). Ground-water P_{CO_2} is taken as 8315 ppmv. We assumed that the river output had an average DIC concentration of 308 $\mu mol\ liter^{-1}$ (*11*). This value includes $CO_2(aq)$ plus bicarbonate and therefore is conservative with respect to the contribution of CO_2 from the terrestrial landscape.
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Putative Skeletal Neural Crest Cells in Early Late Ordovician Vertebrates from Colorado

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Two vertebrates from the Colorado Formation are known to have acellular bone and dentine, tissues found in heterostracan fishes and proposed as the primitive exoskeleton. High-resolution optical microscopy and scanning electron microscopy indicate that a third vertebrate is represented by a quite distinct exoskeleton of denticles, with many cell and cell process spaces throughout, tissue that resembles that of osteostracans more than heterostracans. Cellular bone coexists with cellular dentine in this Ordovician vertebrate, demonstrating that these skeletal tissues are as old as acellular bone. Both are proposed to come from neural crest because denticles are considered homologous with teeth.

THE EARLIEST STRATIGRAPHIC OCCURRENCE of bone tissue of a type containing interconnected cells (osteocytes situated in lacunae) is central to any discussion of the evolution of bone with a role in mineral homeostasis (*1*), or in protection or insulation for sensory organs, or for mechanical support (*2*). It has also been proposed that the embryonic cell origin of the exoskeleton is from the neural crest and is a vertebrate innovation (*3–6*). Early vertebrate fossils with well-preserved histology are rare, but those from the Harding Sandstone in Colorado, dated as early Late Ordovician and known for almost 100 years, are the earliest of this kind (*7–13*). Two jawless fishes (agnathans) are recognized in these fossils (known only by their generic names, *Astraspis* and *Eriptychius*) based on differences in the shape and histology of their tubercles (odontodes fused to bony plates). However, it is accepted that the extensive exoskeleton in both consists of acellular bone (aspidin, with no evidence of cell lacunae), a feature of heterostracan fishes.

In contrast, uncertainty and controversy have accompanied the few descriptions of cellular bone in skeletal fragments of another vertebrate in this fauna (*10, 14–17*). With greater resolution of tissue microstructure, it can be seen that cell lacunae with interconnections are present in the skeletal remains of the undetermined third vertebrate (*10*). This exoskeleton is quite distinct in this character (the type of bone and dentine) from that of *Astraspis* and *Eriptychius*. Earlier reports (*14, 15, 18*) had suggested the presence of cellular bone but had either not illustrated it, or had not said to which part of the skeleton it belonged. However, it is emphasized here that the tissue with cell spaces is in the denticle of the exoskeleton. Such dermal denticles are considered to be homologous with teeth (*19*) and to share developmental origins. It is generally accepted that the mesenchymal component of the teeth (in gnathostomes) originates from neural crest cells (*20*) and that it produces the dentine and probably the bone of attachment. New information on these tissues in this early vertebrate will, therefore, contribute to understanding the role of neural crest in the evolution of bone and dentine.

The record of bone with cells now appears to be as old as that of bone without cells, 450 million years before the present (BP). In addition, the characteristic histology of dentine and bone could also indicate the presence of an osteostracan, making this their earliest recorded occurrence (*21*). Although the oldest vertebrates recorded are *Arandaspis* and *Porophoraspis*, in the Stairway Sandstone of central Australia (early Llanvirn, 470 $\times 10^6$ BP) (*12*), they are solely impressions in the sandstone, with no skeletal remains. Another older fossil, *Sacabambaspis* from the Anzaldo Formation, Bolivia (early Caradoc) (*22*), slightly younger than *Arandaspis*, retains skeletal material, but it has poorly preserved histology.

Newly prepared ground sections (60 to 80 μm) of bone-bed material from the Harding Sandstone Formation, near Canon City, Colorado, were examined with phase contrast and Nomarski optics. Consecutive, polished, etched section surfaces were examined in the scanning electron microscope. The formation has a high density of vertebrate skeletal remains, the dominant species are *Astraspis desiderata* Walcott and *Eriptychius americanus* Walcott (*7–11, 16*). However, there are also many examples in the sections of a denticulate exoskeleton with a histology, distinct from that of *Astraspis* and *Eriptychius*. This exoskeleton is characterized by two things: (i) the tissue of the denticles has many clearly defined lacunae (spaces for cell bodies), and interconnecting canaliculi (spaces for extensive cell processes) (Fig. 1,

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